



Spoon Feeding Redox Reactions



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.

CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

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 24th 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.

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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.

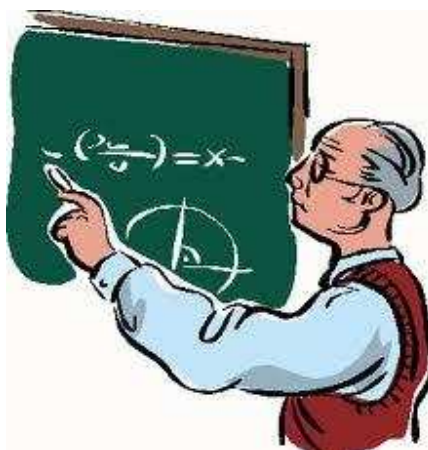
Printed books are not e-Books! Can’t be downloaded and kept in hard-disc for reading “later”
.....

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>

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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.

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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 (सल्लू से): मुझे
नई साड़ी ला दो प्लीज।
सल्लू :पर तुम्हारी
दो-दो अलमारियाँ साँ
डियों से ही तो भरी है।
पत्नी - वह सारी तो
पूरे मोहल्ले वालों ने
देख रखी है।
सल्लू - 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>

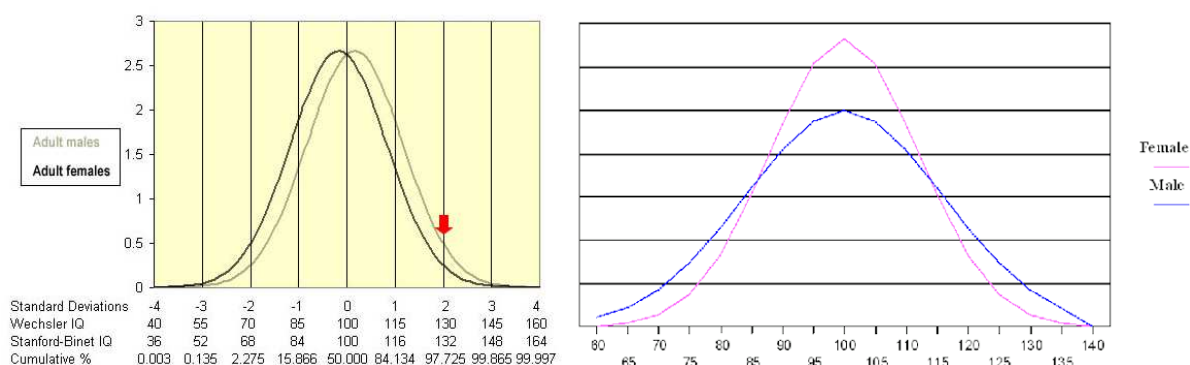
It was Boys and Men, who brought the girls / women home. The Laws are biased, completely favoring women. The men are paying for their own mistakes.

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.

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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

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.



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

Sometimes it hard to believe w From Alwayszturmtup

ALWAYZTURMTUP.ME



'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

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



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 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

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<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

Like Page

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

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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 offered Horst Hans Henkels at their...

NYPOST.COM

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

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.

DAILYMAIL

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..."

AMERICANNEWS.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

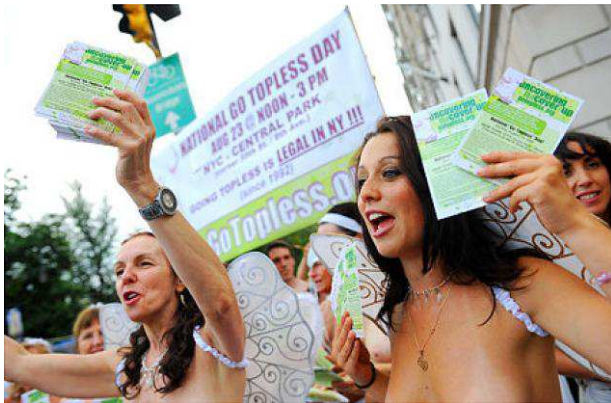
This is the type of women we have in this world. These kind of women were also someones daughter



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. He 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 DEFENSE¹
- ✗ DON'T SPEAK FOR WOMEN
- ✗ DON'T VALUE WOMEN'S FEELINGS
- ✗ DON'T PORTRAY WOMEN AS VICTIMS
- ✗ DON'T PROTECT WOMEN²

✓ **WITHOUT WHITE KNIGHTS FEMINISM WOULD END TODAY**

¹Don't even nawalt ("Not All Women Are Like That") ²for example from criticism or insults

How Society prioritize Men

High Priority

Low Priority

| | | |
|------------|--|---|
| 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. |

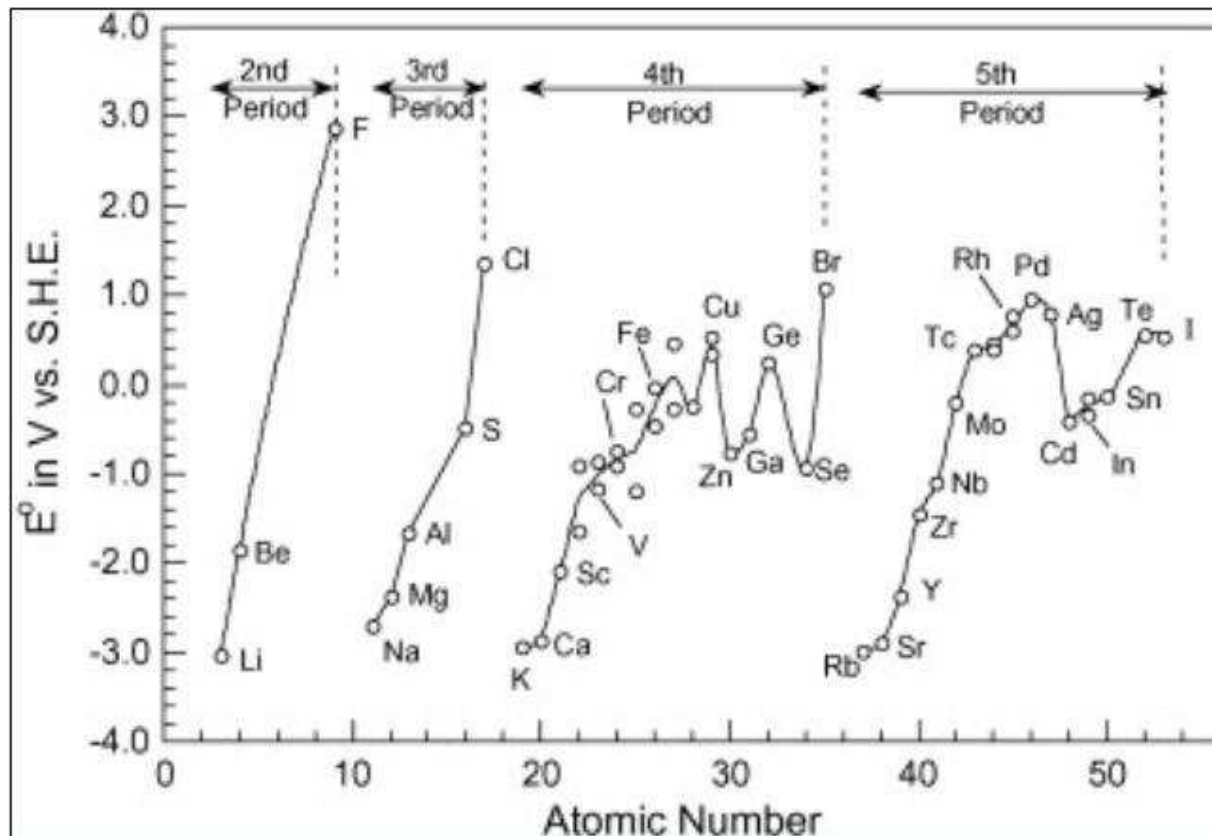
Who pays the most Taxes?
This is why MGTOW exist.

MGTOW

Professor Subhashish Chattopadhyay

Spoon Feeding Series - Redox Reactions

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



It is very strange, that so many Chemistry books exist 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

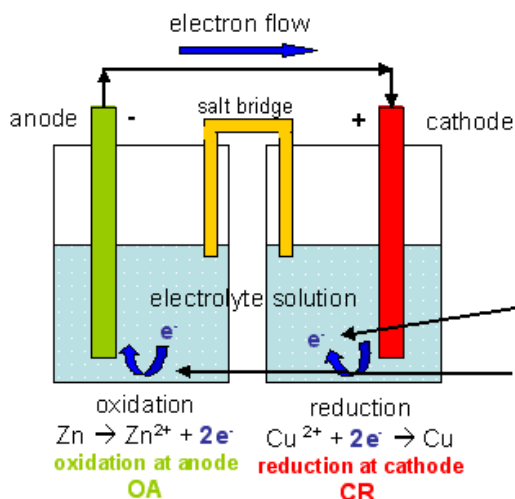
An electrochemical cell consists of two electrodes (metallic conductors) in contact with an electrolyte (an ionic conductor). An electrode and its electrolyte comprise an Electrode Compartment.

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.

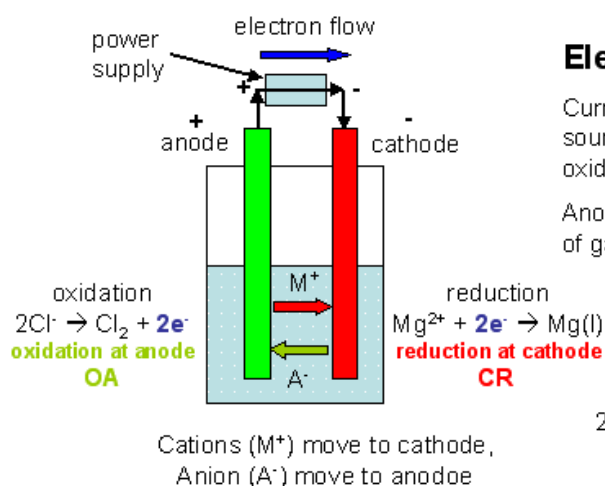
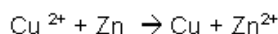
ELECTROCHEMICAL CELLS



Galvanic Cell

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

Example:

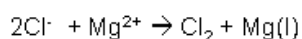


Electrolytic Cell

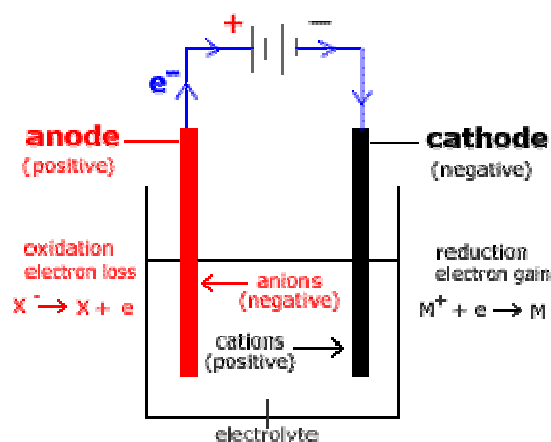
Current supplied by external source drive nonspontaneous oxidation/reduction reaction.

Anode + and cathode -, opposite of galvanic cell

Example:

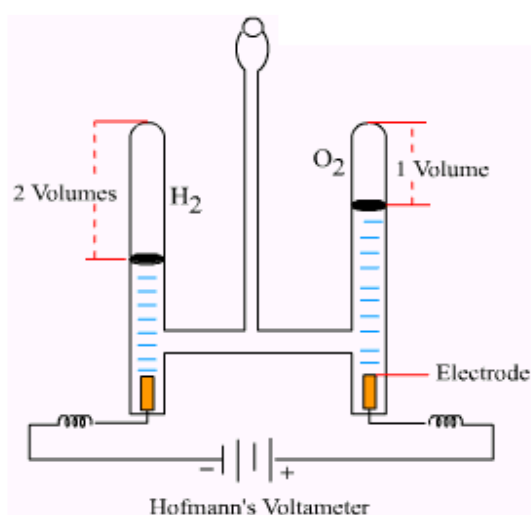
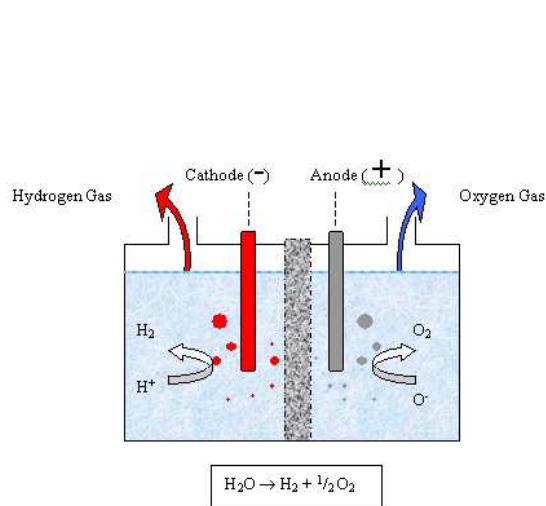


ELECTROLYSIS (Where a Positive current, of holes, is forced into the Anode. So electrons will come out of the Anode.)



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

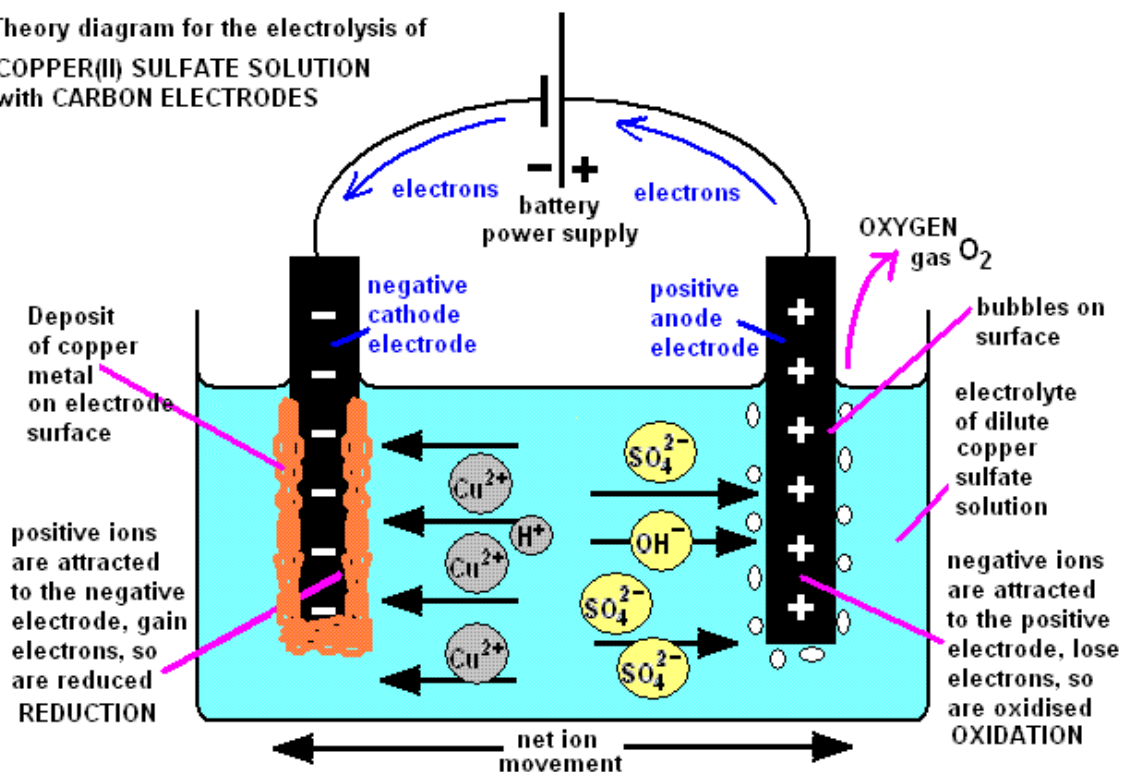
Electrodes are conductors through which electrons enter and leave the electrolyte.

- 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.)

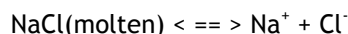
What happens during electrolysis?

- 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.

**Theory diagram for the electrolysis of
COPPER(II) SULFATE SOLUTION
with CARBON ELECTRODES**



ELECTROLYSIS OF MOLTEN SODIUM CHLORIDE



Reactions at anode (oxidation) $2 \text{Cl}^- \rightarrow \text{Cl}_2 (\text{gas}) + 2\text{e}^-$ Recall Losing electron is being oxidized

Reactions at cathode (reduction) $\text{Na}^+ + \text{e}^- = \text{Na}$

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

The attackable electrodes participate 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 are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remains the 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, $Q = I t$

\therefore

$w = Z I t$ 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.

\therefore 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 be predicted 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 oxidation potential (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 |
| $Sn^{4+}, Sn^{2+} Pt$ | $Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}$ | +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 |
| $Al^{3+} Al$ | $Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ | -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 referred 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

$$E_{RP} = E^\circ_{RP} - \frac{RT}{nF} \ln \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]}$$

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.

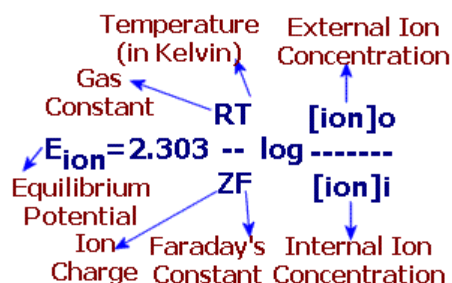
Note on Nernst Equation also uses Electrode potential

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

$$\text{At } 25^{\circ}\text{C}; E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \frac{M}{[M^{n+}]} \text{ or } \frac{1}{[M^{n+}]}$$

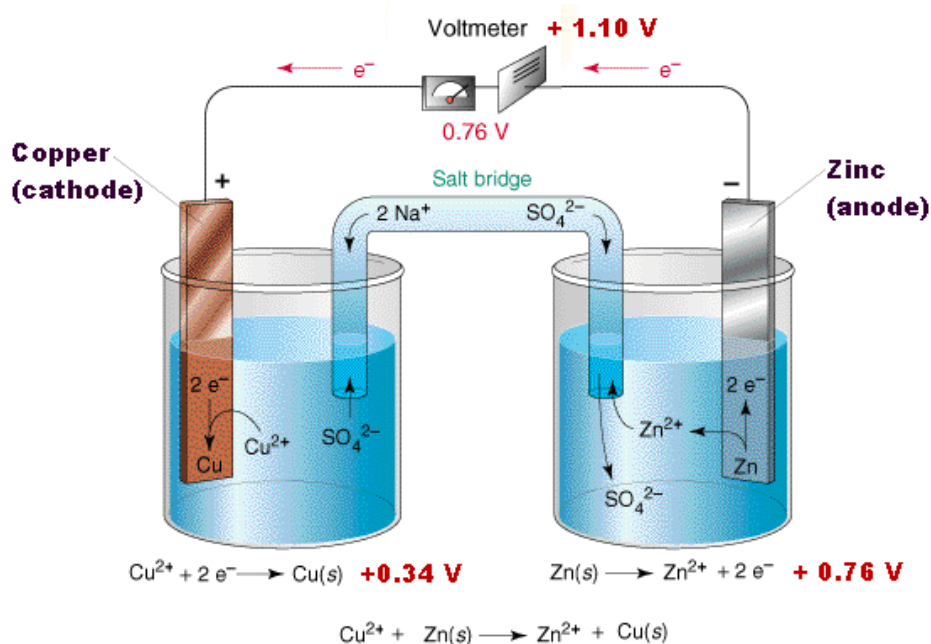
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log \left[\frac{\text{Products}}{\text{Reactants}} \right] \text{ or } Q.$$

$$E_{\text{cell}} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} - \frac{0.059}{n} \log \frac{[P]}{[R]}$$



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 $ZnSO_4$ behaves as anode and copper rod immersed in $CuSO_4$ 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 $Zn | Zn^{2+} || Ag^+ | Ag$ $E^{\circ}_{cell} = 1.562$ Volt

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

Solution : $E^{\circ}_{cell} = E_{Right} - E_{Left} = E_{Ag^+ | Ag} - E_{Zn^{2+} | Zn} = (E_{Reduction (Right)} - E_{Reduction (Left)})$

So $1.562 = E_{Ag^+ | Ag} - (-0.762) \Rightarrow E_{Ag^+ | Ag} = 0.8$ 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 Fe^{2+}/Fe is more negative than that for Cu^{2+}/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) |
|---|-------------|
| $F_2(g) + 2e^- \rightarrow 2F^-(aq)$ | +2.87 |
| $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ | +1.36 |
| $MnO_2(g) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$ | +1.23 |
| $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ | +0.96 |
| $Ag^+(aq) + e^- \rightarrow Ag(s)$ | +0.80 |
| $Fe^{3+}(g) + e^- \rightarrow Fe^{2+}(aq)$ | +0.77 |
| $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$ | +0.40 |
| $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ | +0.34 |
| $2H^+(aq) + 2e^- \rightarrow H_2(g)$ | 0.00 |
| $N_2(g) + 5H^+(aq) + 4e^- \rightarrow N_2H_5^+(aq)$ | -0.23 |
| $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ | -0.44 |
| $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ | -0.83 |
| $Na^+(aq) + e^- \rightarrow Na(s)$ | -2.71 |
| $Li^+(aq) + e^- \rightarrow Li(s)$ | -3.05 |

↑ strength of oxidizing agent

↓ strength of reducing agent

[A more detailed table](#)

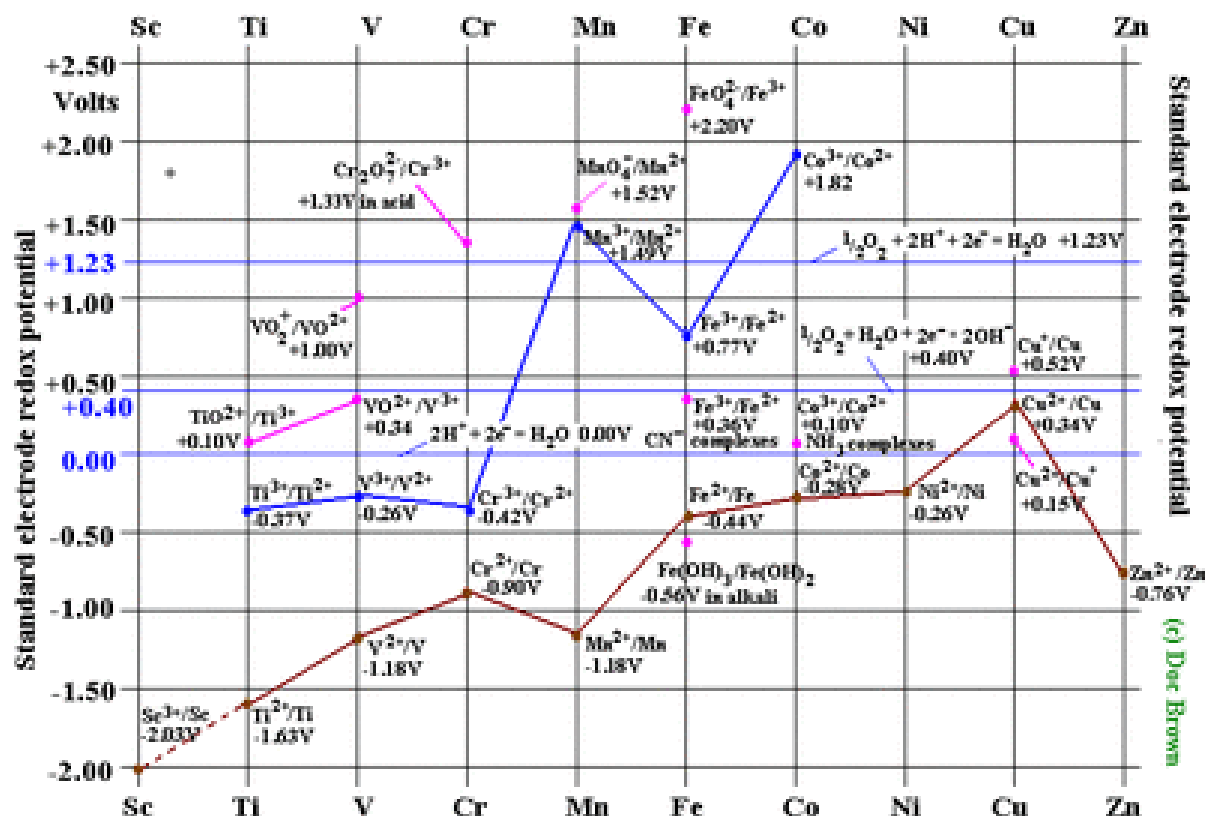
| Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions | | | |
|--|-----------------|--|-----------------|
| Half-Reaction | E° (V) | Half-Reaction | E° (V) |
| $F_2 + 2e^- \rightarrow 2F^-$ | 2.87 | $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | 0.40 |
| $Ag^{2+} + e^- \rightarrow Ag^+$ | 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 loses 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.



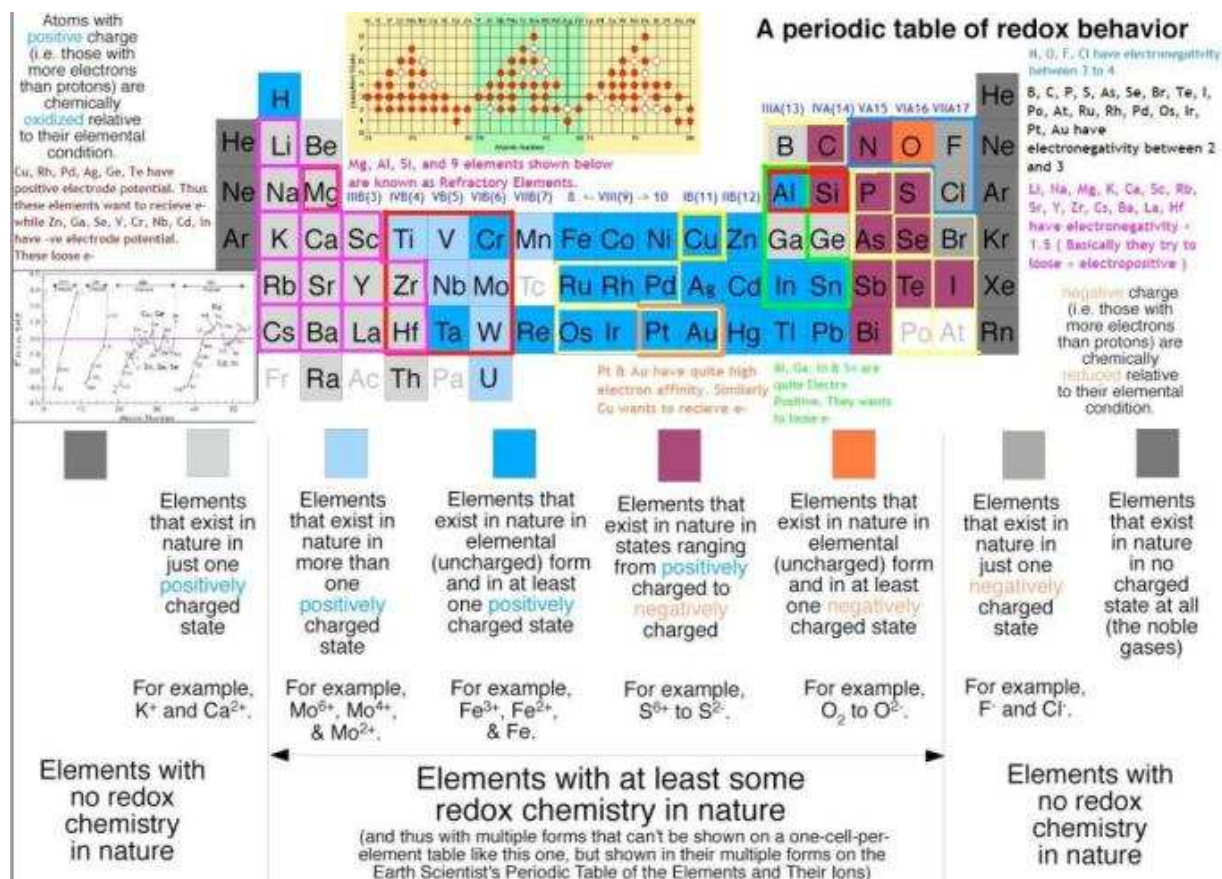
SALT BRIDGE

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.

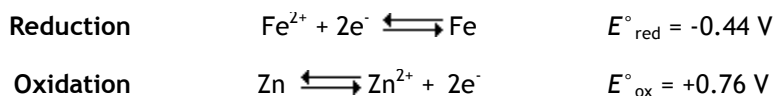
Representation of a cell (IUPAC conventions): Let us illustrate the convention taking the example of Daniel cell.

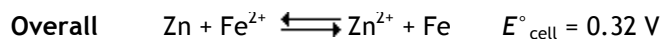
- (i) Anodic half cell is written on left and cathodic half cell on right hand side.
$$\text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \mid \text{Cu(s)}$$
- (ii) Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type 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.
$$\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$$

(Illustration of Phase boundary)
- (v) Inert electrodes are represented in the bracket
$$\text{Zn} \mid \text{ZnSO}_4 \parallel \text{H}^+ \mid \text{H}_2, \text{Pt}$$



Consider the following set of half-reactions





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 ($E_{\text{cell}} = 0 \text{ V}$). 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 be 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 $[\text{Fe}^{2+}] = 0.1 \text{ M}$ and $[\text{Zn}^{2+}] = 1.9 \text{ M}$

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

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

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:

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

Prediction and feasibility of spontaneity of a cell reaction.

Work done by the cell = nFE ;

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

Under standard state $\Delta G^{\circ} = -nFE^{\circ}$ (i)

- (i) From thermodynamics we know, $\Delta G = \text{negative}$ 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 $\Delta G = \text{positive}$, $E = \text{negative}$ 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 E° (i.e., standard reduction potential of cathode- standard reduction potential of anode) in eq. (i) we may get ΔG° .

THERMODYNAMIC TREATMENT OF NERNST EQUATION

Determination of equilibrium constant

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

: We know, that $E = \dots (1)$

At equilibrium, the cell potential is zero because cell reactions are balanced, i.e. $E = 0$
 \therefore From Eq. (i), we have

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

Or

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

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

$$-\Delta G = nFE \dots (i)$$

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

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

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

$$\Delta G = \Delta H - T\Delta S \dots (i)$$

where

ΔG = Free energy change ;

ΔH = Enthalpy change and

ΔS = entropy change.

According to Gibbs Helmholtz equation,

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

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

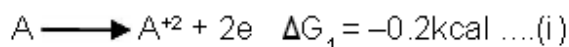
From Eqs. (i) and (ii), we have

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

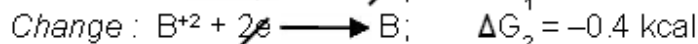
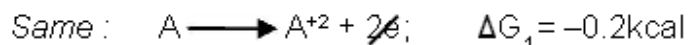
$$\text{or} \quad \Delta S = nF \left[\frac{\partial E}{\partial T} \right]_p$$

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

Spoon Feeding Rule of Electrochemistry



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.

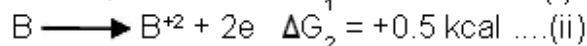


$$\Delta G_{\text{rxn}} = \Delta G_1 + \Delta G_2 = (-0.2 \text{ kcal}) + (-0.4 \text{ kcal}) = -0.6 \text{ kcal}$$

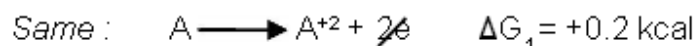
$$\text{Recall } \Delta G = -nFE \quad \text{or} \quad E = -\Delta G / nF$$

Spoon feeding Rule of Electrochemistry

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



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

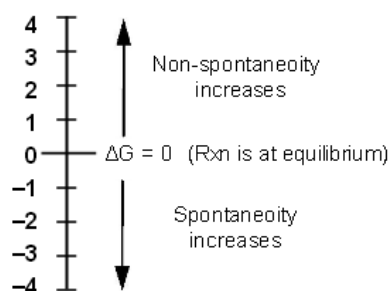


$$\Delta G_{\text{rxn}} = \Delta G_1 + \Delta G_2 = (-0.5) + (0.2) \text{ kcal} = -0.3 \text{ kcal}$$

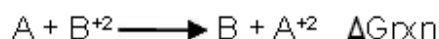
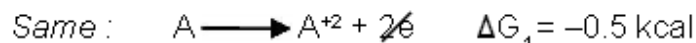
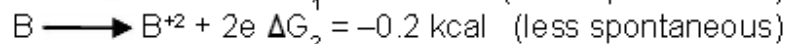
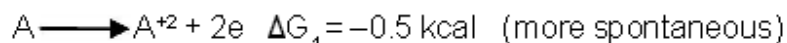
Recall Spontaneity of ΔG

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.



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

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



$$\Delta G = \Delta G^\circ + RT \ln Q$$

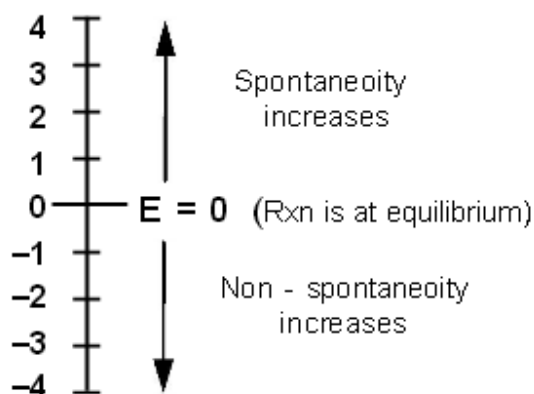
$$\text{If } Q = 1, \text{ then } \Delta G = \Delta G^\circ$$

$$\Delta G_1 = \Delta G_1^\circ + RT \ln [A^{+2}] \dots\dots(i)$$

$$\Delta G_2 = \Delta G_2^\circ + RT \ln [B^{+2}] \dots\dots(ii)$$

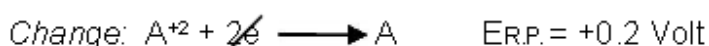
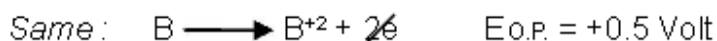
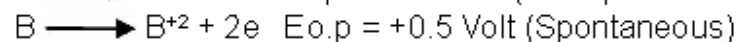
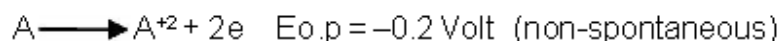
If emf of the half cell given in the problem then we predict the spontaneity of reaction by emf.
 $\Delta G = -nFE$

Spontaneity from E



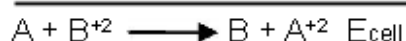
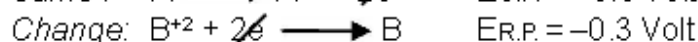
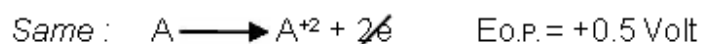
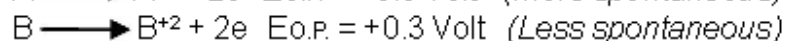
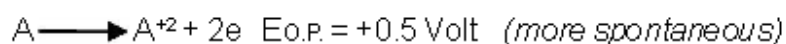
Greater the reduction potential greater will be ease of reduction. Greater the oxidation potential greater will be ease of oxidation.

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



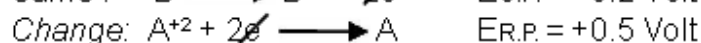
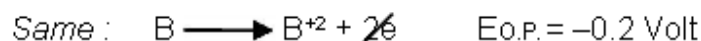
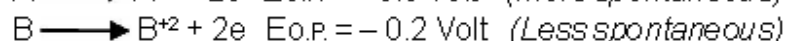
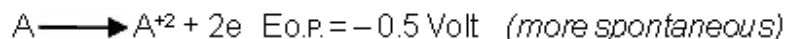
$$E_{cell} = E_{o.p.} + E_{r.p.} = 0.5 + 0.2 = 0.7 \text{ Volt}$$

Spoon Feeding



$$E_{cell} = E_{o.p.} + E_{r.p.} = +0.5 - 0.3 \text{ Volt} = +0.2 \text{ Volt}$$

Spoon Feeding



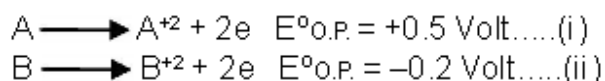
$$E_{cell} = E_{o.p.} + E_{r.p.} = -0.2 + 0.5 \text{ Volt} = +0.3 \text{ Volt}$$

Spoon Feeding

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

$$E_{o.p.} = E_{o.p.}^{\circ} - (0.0592/n) \log[A^{+2}]$$

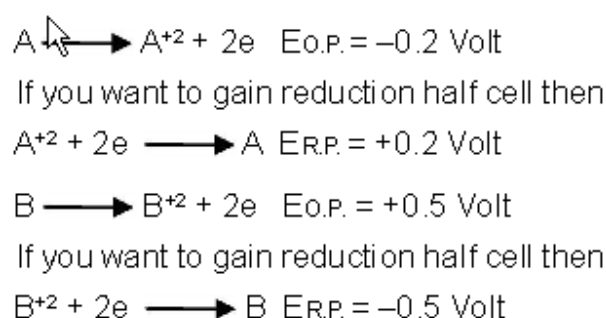
$$E_{o.p.} = E_{o.p.}^{\circ} - (0.0592/n) \log[B^{+2}]$$



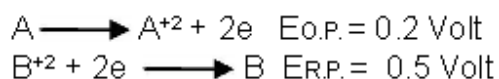
Greater the O.P. greater will be ease of oxidation.

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.

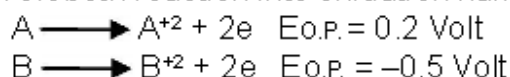


To calculate E_{cell} we convert all the half cell reactions are in same type (either oxidation half or reduction half)

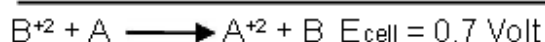
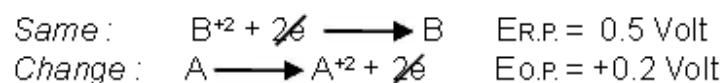


$E_{\text{cell}} = ?$

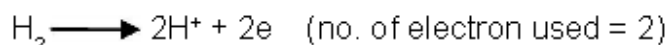
(i) Convert both reaction into oxidation half



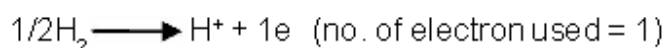
(ii) Convert both reaction into reduction half cell



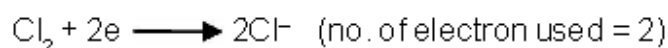
For following type half cell reaction hybrid reaction quotients (mixture of Q_p and Q_c) used in place of Q_c or Q_p



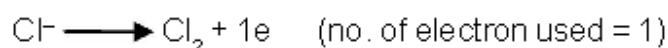
$$Q_{\text{Hybrid}} = \frac{[\text{H}^+]^2 \text{ mol / litre}}{(P_{\text{H}_2}) \text{ atm}}$$



$$Q_{\text{Hybrid}} = \frac{[\text{H}^+]}{(P_{\text{H}_2})^{1/2}}$$

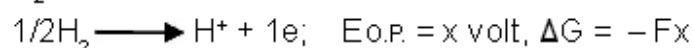
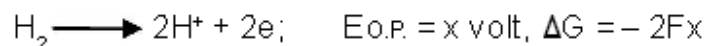


$$Q_{\text{Hybrid}} = \frac{[\text{Cl}^-]^2}{(P_{\text{Cl}_2})}$$

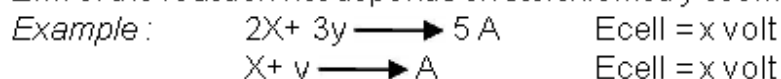


$$Q_{\text{Hybrid}} = \frac{(P_{\text{Cl}_2})^{1/2}}{[\text{Cl}^-]}$$

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

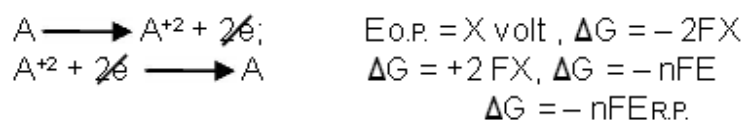


Emf of the reaction not depends on stoichiometry coeff.



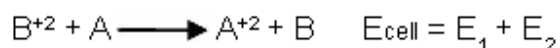
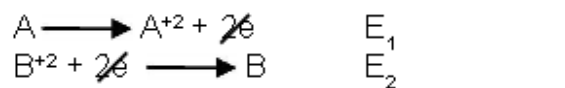
If reaction is spontaneous in forward direction then non-spontaneous in reverse direction and vice-versa.

Magnitude of Emf and ΔG are same but sign is reverse.

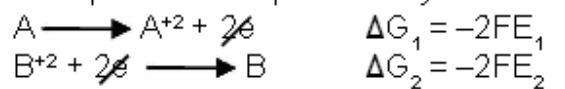


$$\text{E.R.P.} = \Delta G / -nF = 2FX / -2F = -X \text{ volt}$$

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



If we proceed this problem by ΔG then.

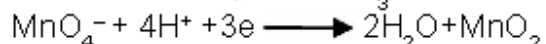
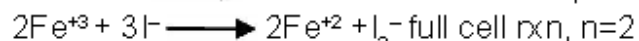
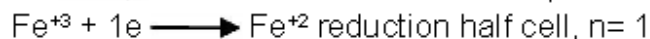
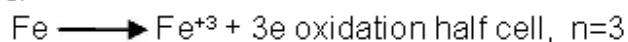


$$-2FE_{\text{cell}} = -2FE_1 - 2FE_2$$

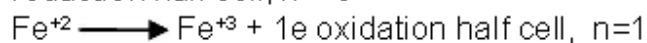
$$E_{\text{cell}} = E_1 + E_2$$

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:

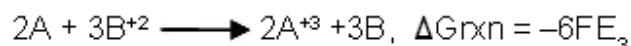
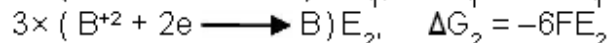
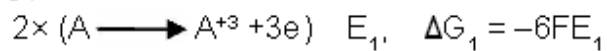


reduction half cell, $n = 3$



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

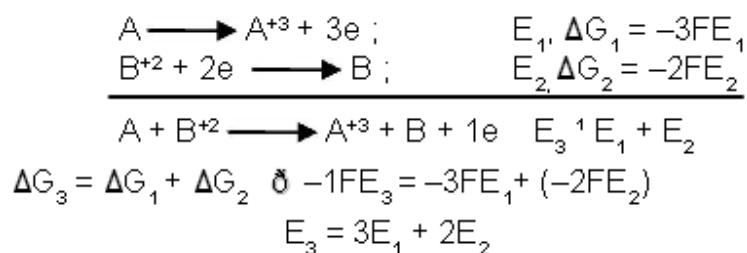
Example :



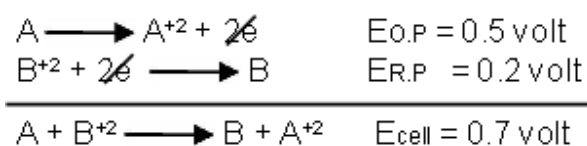
$$\Delta G_{\text{rxn}} = \Delta G_1 + \Delta G_2 = -6FE_1 - 6FE_2 = -6FE_3$$

$$E_3 = E_1 + E_2$$

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 ,



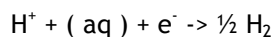
For writing shorthand notation or cell representation of electrochemical cell following conventions are used.



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.

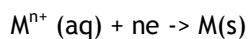


$$E_{H^+/H_2} = E^0_{H^+/H_2} - \frac{0.0591}{1} \log \frac{(pH_2)^{1/2}}{[H^+]}$$

So

(2) Metal-Metal Ion Half Cell:

This type of cell consist of a metal M in contact with a solution containing Mⁿ⁺ ions.



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

(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:

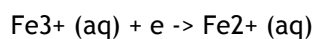
This half cell is represented as $\text{Cl}^-/\text{AgCl}/\text{Ag}$. The equilibrium reaction that occurs at the electrode is $\text{AgCl}(s) + e^- \rightarrow \text{Ag}(s) + \text{Cl}^-(aq)$

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

potential of such cells depends upon the concentration 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. $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ half cell.



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

CONCENTRATION CELL

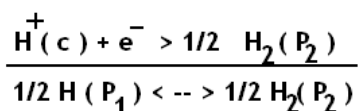
The cells in which electrical current is produced due to transport of a substance from higher to lower concentration. Concentration gradient may arise either in electrode material or in electrolyte. Thus there are two types of concentration cell.

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

Electrode Gas concentration cell :
 $\text{Pt}, \text{H}_2(\text{P}_1) | \text{H}^+(\text{C}) | \text{H}_2(\text{P}_2), \text{Pt}$

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

Cell Process : $\frac{1}{2} \text{H}_2(\text{P}_1) \rightarrow \text{H}^+(\text{c}) + e^-$ (Anode Process)

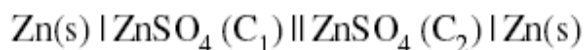


So $E = - \left[\frac{2.303RT}{F} \right] \log \left[\frac{\text{P}_2}{\text{P}_1} \right]^{\frac{1}{2}}$ Recall - $\log(a/b)$ is $\log(b/a)$

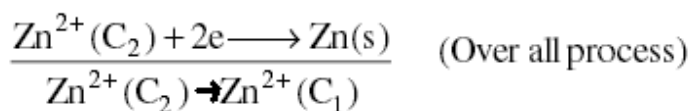
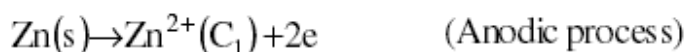
$$\text{Or } E = \left[\frac{2.303RT}{2F} \right] \log \left[\frac{P_1}{P_2} \right], \text{ At } 25^\circ\text{C}, E = \frac{0.059}{2F} \log \left[\frac{P_1}{P_2} \right]$$

For spontaneity of such cell reaction, $p_1 > p_2$

Electrolyte concentration cells:



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



∴ 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 spontaneity of such cell reaction, $C_2 > C_1$

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.

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

Specific resistance is the resistance of a conductor having lengths of 1 cm and cross sectional area of 1 cm².

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.

$$\frac{1}{R} = \frac{1}{\rho l} \quad \text{or} \quad C = \frac{KA}{L}$$

where C = conductance ohm⁻¹ ; K = specific conductance ohm⁻¹ cm⁻¹.

Mho and siemens are other units of conductance

$$\text{So } K = LC / A$$

Specific conductance = Cell constant \times 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 Λ .

$$\Lambda = K \times V$$

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

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

$$\text{Thus, } V = 1000 / C$$

$$\text{Also } \Lambda = K \times 1000 / C$$

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 Λ_m .

$$\Lambda_m = K \times V$$

Usually concentration of electrolyte solution is expressed as 'M' gm mole electrolyte per litre.

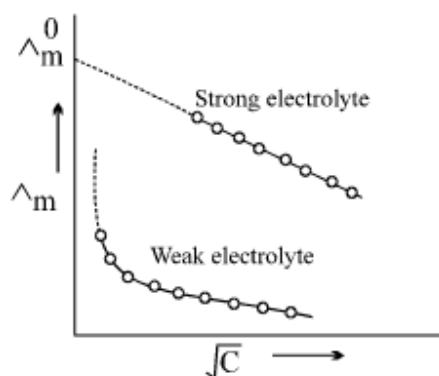
$$\text{Thus, } V = \frac{1000}{M}$$

$$\text{Hence, } \Lambda_m = K \times \frac{1000}{M}$$

$$\text{Relation between } \Lambda \text{ and } \Lambda_m : \Lambda_m = n \times \Lambda$$

Determination of Λ_m^0 OR Λ^0

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



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

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

Λ_m values are then plotted against \sqrt{C} when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects Λ_m axis is Λ_m^0 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 Λ_m axis. Hence extrapolation in this case is not possible. Thus, Λ_m^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 Λ_m^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 Λ_m^0 values in each case remains the same:

$$\Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{KF}) = \Lambda_m^0(\text{NaCl}) - \Lambda_m^0(\text{NaF})$$

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

$$\Lambda_m^0(\text{KF}) - \Lambda_m^0(\text{NaF}) = \Lambda_m^0(\text{KCl}) - \Lambda_m^0(\text{NaCl})$$

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,

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

Where λ_+^0 is the contribution of the cation and λ_-^0 is 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 Λ_m^0 of a weak electrolyte:

In order to calculate Λ_m^0 of a weak electrolyte say CH₃COOH, we determine experimentally Λ_m^0 values of the following three strong electrolytes:

- A strong electrolyte containing same cation as in the test electrolyte, say HCl
- A strong electrolyte containing same anion as in the test electrolyte, say CH₃COONa
- A strong electrolyte containing same anion of (a) and cation of (b) i.e. NaCl.

Λ_m^0 of CH₃COOH is then given as:

$$\Lambda_m^0(\text{CH}_3\text{COOH}) = \Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl})$$

Proof:

$$\Lambda_m^0(\text{HCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots(\text{i})$$

$$\Lambda_m^0(\text{CH}_3\text{COONa}) = \lambda_{\text{CH}_3\text{COO}^-}^0 + \lambda_{\text{Na}^+}^0 \quad \dots(\text{ii})$$

$$\Lambda_m^0(\text{NaCl}) = \lambda_{\text{Na}^+}^0 + \lambda_{\text{Cl}^-}^0 \quad \dots(\text{iii})$$

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

$$\Lambda_m^0(\text{HCl}) + \Lambda_m^0(\text{CH}_3\text{COONa}) - \Lambda_m^0(\text{NaCl}) = \lambda_{\text{H}^+}^0 + \lambda_{\text{CH}_3\text{COO}^-}^0 = \Lambda_m^0(\text{CH}_3\text{COOH})$$

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

$$\alpha = \frac{\text{No. of molecules ionised}}{\text{Total no. of molecules dissolved}} = \frac{\Lambda_m}{\Lambda_m^0}$$

(3) Determination of solubility of sparingly soluble Salt

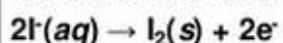
The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be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

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

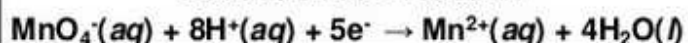
where C is the molarity of solution and hence the solubility.

A voltaic cell using inactive electrodes.

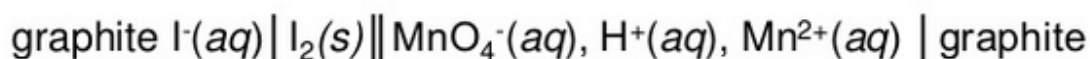
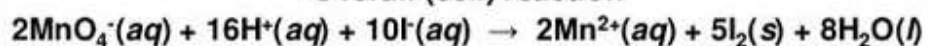
Oxidation half-reaction



Reduction half-reaction



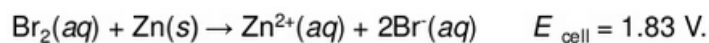
Overall (cell) reaction



↑
The inert electrode is specified.

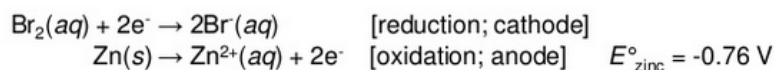
↑
A comma is used to show components that are in the same phase.

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



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

Solution :

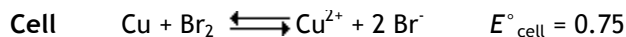
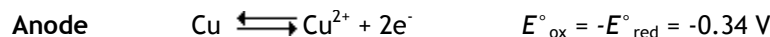
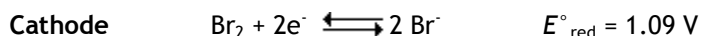


$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

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

$$1.83 - 0.76 = E_{\text{bromine}} \quad = 1.07 \text{ Volt}$$

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?



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

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

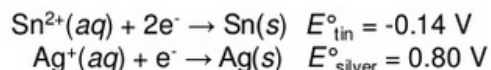
Let us always remember the basics. If something, say M, loses electrons, it is getting oxidized. Metals are basic. Metals lose electrons and get oxidized. The metals which lose electron very easily, get oxidized very easily. So these are better reducing agents.

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 losing 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 ?

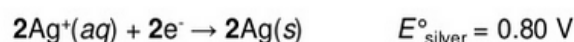
As my experience of teaching more than 25 years, almost every student understands these. Knowing this is essential but does not ensure success in chemistry. There are many kinds of details of oxidizing agent or Reducing agent that vary from reactions / situations.

Using half reactions write the spontaneous Redox reactions

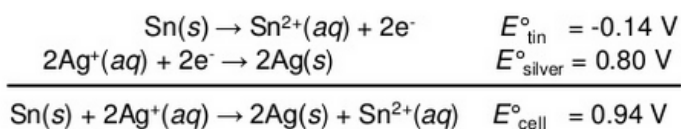


We have to multiply the Silver reaction with 2 to balance and match electrons

Note : This does not change the voltage obtained



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



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

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 loses 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.

The concept of electron transfer can easily explain the redox reaction in case of ionic substances. However, for covalent compounds oxidation and reduction or redox reactions are explained using oxidation number.

The term **oxidation** was first used to mean the addition of oxygen to an element or compound, or the removal of hydrogen from a compound. **Reduction** meant the addition of hydrogen to an element or compound, or the removal of oxygen from a compound. Such definitions have been extended and now many oxidation-reduction, or redox, reactions are best interpreted in terms of transfer of electrons.

- Oxidation is defined as the loss of electrons by a chemical species (atom, ion or molecule).
- Reduction is the gain of electrons by a chemical species (atom, ion or molecule).
- An oxidising agent that chemical species which takes electrons thus it is an electron acceptor.
- A reducing agent is the chemical species that gives electrons and thus acts as an electron donor.
- Redox reactions are those chemical reactions in which both oxidation as well as reduction occur simultaneously.
- The substance which undergo reduction is called oxidising agent while the substance which undergo oxidation is called reducing agent. One can say that the substance that causes the

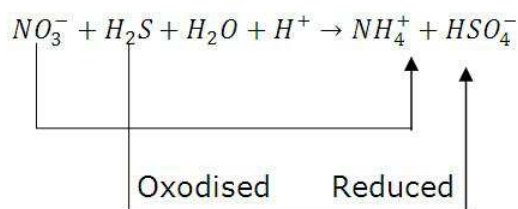
oxidation of any substance in reaction is called the oxidizing agent while the substance that causes the reduction is called the reducing agent.

- Neither reduction nor oxidation occurs alone. Both of them occur simultaneously. Since both these reactions must occur at the same time they are often termed as "redox reactions". The oxidation or reduction portion of a redox reaction, including the electrons gained or lost can be determined by means of a Half-Reaction

Two Types of Redox Reactions

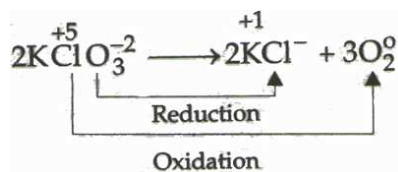
(i) Inter molecular Redox Reactions:

In these kinds of redox reactions, one molecule of reactant is oxidized whereas molecule of other reactant is reduced.



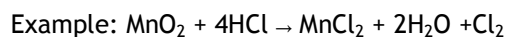
(ii) Intra molecular Redox Reactions:

One atom of a molecule is oxidized and other atom of same molecule is reduced then it is intra molecular redox reaction.



(1) Molecular Equations:

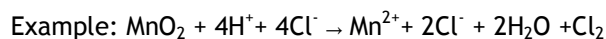
When the reactant and products involved in a chemical change are written in molecular form in a chemical equation, it is termed as molecular equation.



In above example the reactant and products have been written in molecular forms, thus it is a molecular equation.

(2) Ionic Equation:

When the reactant and products involved in a chemical change are ionic compounds, these will be present in the form of ions in the solution. The chemical change is written in ionic forms in the chemical equation, it is termed as ionic equation.



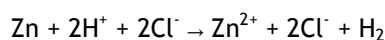
In the above example, the reactant and products have been written in ionic forms, thus the equation is termed as ionic equation.

The rules to be followed for writing ionic equations are:

- All soluble ionic compounds involved in a chemical changes are expressed in ionic symbols and covalent substances are written in molecular form. H_2O , NH_3 , NO_2 , NO , SO_2 , CO , CO_2 , etc., are expressed in molecular form.
- The ionic compound which is highly insoluble is expressed in molecular form.
- The ions which are common and equal in number on both sides, i.e., spectator ions, are cancelled.
- Besides the atoms, the ionic charges must also be balanced on both the sides.

(3) Spectator Ions:

Species that are present in the solution but not take part in the reaction and are also omitted while writing the net ionic equation are called spectator ions or bystander ions.



In this reaction, ions are omitted and are called as spectator ions and appear on the reactant as well as product side.

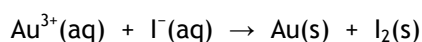
(4) Oxidising agent:

The substance (atom, ions or molecules) that gain electrons and is thereby reduced to a low valency state is called an oxidising agent.

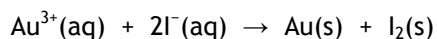
(5) Reducing agent:

The substance that loses electrons and its valency thereby oxidised to a higher valency state is called a reducing agent.

It is not always possible to balance redox equations using the simple “inspection” technique. The following unbalanced net ionic equation provides an example.

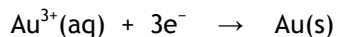
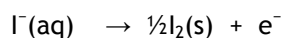


At first glance, it seems that this equation can be balanced by placing a 2 in front of the I^- .

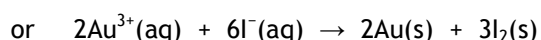
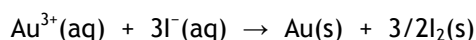


Note, however, that although the atoms are now balanced, the charge is not. The sum of the charges on the left is +1, and the sum of the charges on the right is zero, as if the products could somehow have one more electron than the reactants. To correctly balance this equation, it helps to look more closely at the oxidation and reduction that occur in the reaction. The iodine atoms are changing their oxidation number from -1 to 0 , so each iodide ion must be losing one electron. The Au^{3+} is changing to Au , so each gold(III) cation must be gaining three electrons.

The half-reactions are:



We know that in redox reactions, the number of electrons lost by the reducing agent must be equal to the number of electrons gained by the oxidizing agent; thus, for each Au^{3+} that gains three electrons, there must be three I^{-} ions that each lose one electron. If we place a 3 in front of the I^{-} and balance the iodine atoms with a 3/2 in front of the I_2 , both the atoms and the charge will be balanced.



Balancing Redox Equations Using the Oxidation Number Method

In most situations that call for balancing an equation, you are not told whether the reaction is redox or not. In these circumstances, you can use a procedure called the oxidation number method, which is outlined below. To balance an equation and if you are not told whether the reaction is a redox reaction or not, you can use the following procedure.

General Steps

Step 1: Try to balance the atoms in the equation by inspection, that is, by the standard technique for balancing non-redox equations. (Many equations for redox reactions can be easily balanced by inspection.) If you successfully balance the atoms, go to Step 2. If you are unable to balance the atoms, go to Step 3.

Step 2: Check to be sure that the net charge is the same on both sides of the equation. If it is, you can assume that the equation is correctly balanced. If the charge is not balanced, go to Step 3.

Step 3: If you have trouble balancing the atoms and the charge by inspection, determine the oxidation numbers for the atoms in the formula, and use them to decide whether the reaction is a redox reaction. If it is not redox, return to Step 1 and try again. If it is redox, go to Step 4.

Step 4: Determine the net increase in oxidation number for the element that is oxidized and the net decrease in oxidation number for the element that is reduced.

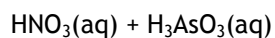
Step 5: Determine a ratio of oxidized to reduced atoms that would yield a net increase in oxidation number equal to the net decrease in oxidation number (a ratio that makes the number of electrons lost equal to the number of electrons gained).

Step 6: Add coefficients to the formulas so as to obtain the correct ratio of the atoms whose oxidation numbers are changing. (These coefficients are usually placed in front of the formulas on the reactant side of the arrow.)

Step 7: Balance the rest of the equation by inspection.

Balancing Redox Reactions Using the Oxidation Number Method

Balance the following redox equation using either the “inspection” technique or the “oxidation number” method. Be sure to check that the atoms and the charge are balanced.



Solution:

Step 1: Try to balance the atoms by inspection.

Step 2: The H and O atoms are difficult to balance in this equation. You might arrive at the correct balanced equation using a “trial and error” technique, but if you do not discover the correct coefficients fairly quickly, proceed to Step 3.

Step 3: Is the reaction redox?

The N atoms change from +5 to +2, so they are reduced. This information is enough to tell us that the reaction is redox. (The As atoms, which change from +3 to +5, are oxidized.)

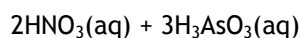
Step 4: Determine the net increase in oxidation number for the element that is oxidized and the net decrease in oxidation number for the element that is reduced.



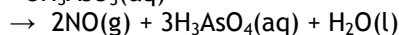
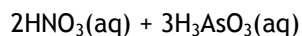
Step 5: Determine a ratio of oxidized to reduced atoms that would yield a net increase in oxidation number equal to the net decrease in oxidation number.

As atoms would yield a net increase in oxidation number of +6. (Six electrons would be lost by three arsenic atoms.) 2 N atoms would yield a net decrease of -6. (Two nitrogen atoms would gain six electrons.) Thus the ratio of As atoms to N atoms is 3:2.

Step 6: To get the ratio identified in Step 5, add coefficients to the formulas which contain the elements whose oxidation number is changing.

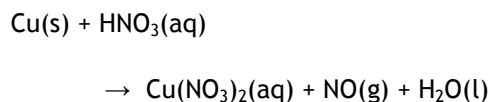


Step 7: Balance the rest of the equation by inspection.



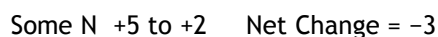
Balancing Redox Reactions Using the Oxidation Number Method:

Balance the following redox equation using either the “inspection” technique or the “oxidation number” method. Be sure to check that the atoms and the charge are balanced.

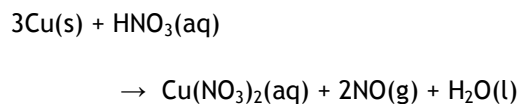


Solution:

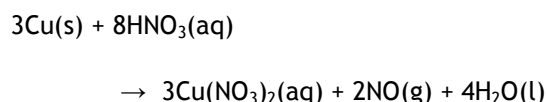
The nitrogen atoms and the oxygen atoms are difficult to balance by inspection, so we will go to Step 3. The copper atoms are changing their oxidation number from 0 to +2, and some of the nitrogen atoms are changing from +5 to +2. These changes indicate that this reaction is a redox reaction. We next determine the changes in oxidation number for the atoms oxidized and reduced.



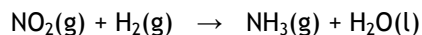
We need three Cu atoms (net change of +6) for every 2 nitrogen atoms that change (net change of -6). Although the numbers for the ratio determined in Step 5 are usually put in front of reactant formulas, this equation is somewhat different. Because some of the nitrogen atoms are changing and some are not, we need to be careful to put the 2 in front of a formula in which all of the nitrogen atoms are changing or have changed. We therefore place the 2 in front of the NO(g) on the product side. The 3 for the copper atoms can be placed in front of the Cu(s).



We balance the rest of the atoms using the technique described in Chapter 4, being careful to keep the ratio of Cu to NO 3:2.

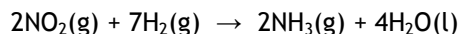


Balancing Redox Reactions Using the Oxidation Number Method Balance the following redox equation using either the “inspection” technique or the “oxidation number” method. Be sure to check that the atoms and the charge are balanced.



Solution:

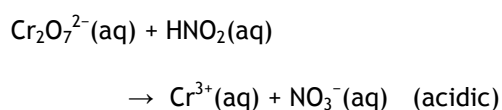
The atoms in this equation can be balanced by inspection. (You might first place a 2 in front of the H₂O to balance the O's, then 7/2 in front of the H₂ to balance the H's, and then multiply all the coefficients by 2 to get rid of the fraction.)



We therefore proceed to Step 2. For the reaction between NO_2 and H_2 , the net charge on both sides of the equation in Step 1 is zero. Because the charge and the atoms are balanced, the equation is correctly balanced.

Balancing Redox Equations for Reactions in Acidic Conditions Using the Half-reaction Method

Redox reactions are commonly run in acidic solution, in which case the reaction equations often include $\text{H}_2\text{O}(\text{l})$ and $\text{H}^+(\text{aq})$. This page will show you how to write balanced equations for such reactions even when you do not know whether the $\text{H}_2\text{O}(\text{l})$ and $\text{H}^+(\text{aq})$ are reactants or products. For example, you may know that dichromate ions, $\text{Cr}_2\text{O}_7^{2-}$, react with nitrous acid molecules, HNO_2 , in acidic conditions to form chromium ions, Cr^{3+} , and nitrate ions, NO_3^- . Because the reaction requires acidic conditions, you assume that $\text{H}_2\text{O}(\text{l})$ and $\text{H}^+(\text{aq})$ participate in some way, but you do not know whether they are reactants or products, and you do not know the coefficients for the reactants and products. An unbalanced equation for this reaction might be written



In order to balance equations of this type, we need a special technique called the half-reaction method or the ion-electron method.

Balancing Redox Equations Run in Acidic Conditions Using the Half-reaction Technique balance a redox equation and told that it takes place in an acidic solution, you can use the following procedure.

General Steps

Step 1: Write the skeletons of the oxidation and reduction half-reactions. (The skeleton reactions contain the formulas of the compounds oxidized and reduced, but the atoms and electrons have not yet been balanced.) See Examples.

Step 2: Balance all elements other than H and O.

Step 3: Balance the oxygen atoms by adding H_2O molecules where needed.

Step 4: Balance the hydrogen atoms by adding H^+ ions where needed.

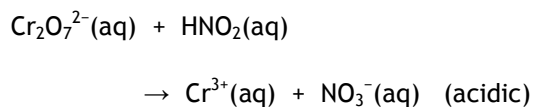
Step 5: Balance the charge by adding electrons, e^- .

Step 6: If the number of electrons lost in the oxidation half-reaction is not equal to the number of electrons gained in the reduction half-reaction, multiply one or both of the half- reactions by a number that will make the number of electrons gained equal to the number of electrons lost.

Step 7: Add the 2 half-reactions as if they were mathematical equations. The electrons will always cancel. If the same formulas are found on opposite sides of the half-reactions, you can cancel them. If the same formulas are found on the same side of both half-reactions, combine them.

Step 8: Check to make sure that the atoms and the charges balance.

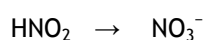
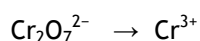
EXAMPLE - Balancing Redox Equations for Reactions Run in Acidic Conditions: Balance the following redox equation using the “half-reaction” method.



Solution:

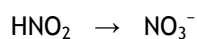
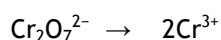
Step 1: Write the skeletons of the oxidation and reduction half-reactions.

You will usually be given formulas for two reactants and two products. In such cases, one of the reactant formulas is used in writing one half-reaction, and the other reactant formula is used in writing the other half-reaction. (In most cases, you do not need to know which reactant is oxidized and which is reduced.) The product formula in each half-reaction must include all of the elements in the reactant formula except hydrogen and oxygen. There are circumstances that make this step more complicated, but we will stick to simpler examples at this stage.



Step 2: Balance all elements other than H and O.

To balance the chromium atoms in our first half-reaction, we need a two in front of Cr^{3+} .

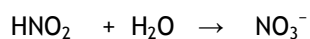


Step 3: Balance the oxygen atoms by adding H_2O molecules on the side of the arrow where O atoms are needed.

The first half-reaction needs seven oxygen atoms on the right, so we add seven H_2O molecules.

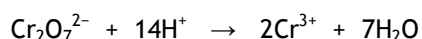


The second half-reaction needs one more oxygen atom on the left, so we add one H_2O molecule.

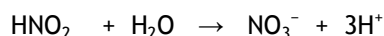


Step 4: Balance the hydrogen atoms by adding H^+ ions on the side of the arrow where H atoms are needed.

The first half-reaction needs 14 hydrogen atoms on the left to balance the 14 hydrogen atoms in the 7 H_2O molecules, so we add 14 H^+ ions to the left.



The second half-reaction needs three hydrogen atoms on the right to balance the three hydrogen atoms on the left, so we add 3 H^+ ions to the right.



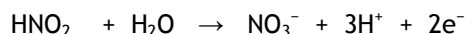
Step 5: Balance the charge by adding electrons, e^- .

The electrons go on the side of the equation with the highest charge (most positive or least negative). We add enough electrons make the charge on that side of the equation equal to the charge on the other side of the equation.

The sum of the charges on the left side of the chromium half-reaction is +12 (-2 for the $\text{Cr}_2\text{O}_7^{2-}$ plus +14 for the 14 H^+). The sum of the charges on the right side of the chromium half-reaction is +6 (for the 2 Cr^{3+}). If we add six electrons to the left side, the sum of the charges on each side of the equation becomes +6.



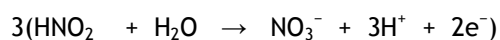
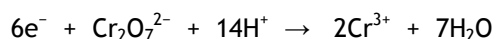
The sum of the charges on the left side of the nitrogen half-reaction is zero. The sum of the charges on the right side of the nitrogen half-reaction is +2 (-1 for the nitrate plus +3 for the 3 H^+). If we add two electrons to the right side, the sum of the charges on each side of the equation becomes zero.



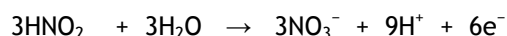
(Although it is not necessary, you can check that you have added the correct number of electrons by looking to see whether the net change in oxidation number for each half-reaction is equal to the number of electrons gained or lost. Because the two Cr atoms in $\text{Cr}_2\text{O}_7^{2-}$ are changing from +6 to +3, the net change in oxidation number is $2(-3)$ or -6. This would require six electrons, so we have added the correct number of electrons to the first half-reaction. The N atom in HNO_2 changes from +3 to +5, so the net change is +2. Two electrons would be lost in this change, so we have added the correct number of electrons to the second half-reaction.)

Step 6: If the number of electrons lost in the oxidation half-reaction is not equal to the number of electrons gained in the reduction half-reaction, multiply one or both of the half- reactions by a number that will make the number of electrons gained equal to the number lost.

For the chromium half-reaction to gain six electrons, the nitrogen half-reaction must lose six electrons. Thus we multiply the coefficients in the nitrogen half-reaction by 3.



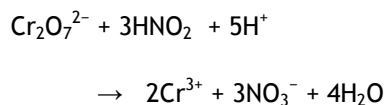
or



Step 7: Add the 2 half-reactions as if they were mathematical equations.

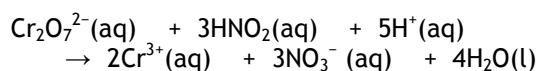
The 3 H_2O in the second half-reaction cancel three of the 7 H_2O in the first half-reaction to yield 4 H_2O on the right of the final equation.

The 9 H⁺ on the right of the second half-reaction cancel nine of the 14 H⁺ on the left of the first half-reaction leaving 5 H⁺ on the left of the final equation.



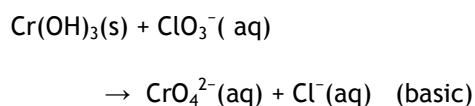
Step 8: Check to make sure that the atoms and the charge balance.

The atoms in our example balance and the sum of the charges is +3 on each side, so our equation is correctly balanced.



Balancing Redox Equations for Reactions in Basic Conditions Using the Half-reaction Method

Redox reactions are also commonly run in basic solution, in which case, the reaction equations often include H₂O(l) and OH⁻(aq). You may know the formulas for the reactants and products for your reaction, but you may not know whether the H₂O(l) and OH⁻(aq) are reactants or products. For example, you may know that solid chromium(III) hydroxide, Cr(OH)₃, reacts with aqueous chlorate ions, ClO₃⁻, in basic conditions to form chromate ions, CrO₄²⁻, and chloride ions, Cl⁻. Because the reaction requires basic conditions, you assume that H₂O(l) and OH⁻(aq) participate in some way, but you do not know whether they are reactants or products, and you do not know the coefficients for the reactants and products. An unbalanced equation for this reaction might be written



The process for balancing a redox reaction run in basic solution is very similar to the steps for balancing redox equations for acidic solutions. We first balance the equation as if it were in acidic solution, and then we make corrections for the fact that it is really in basic solution.

Balancing Redox Equations Run in Basic Conditions Using the Half-reaction Technique to balance a redox equation and told that it takes place in a basic solution, you can use the following procedure.

General Steps

Steps 1-7: Begin by balancing the equation as if it were in acid solution. If you have H⁺ ions in your equation at the end of these steps, proceed to Step 8. Otherwise, skip to Step 11.

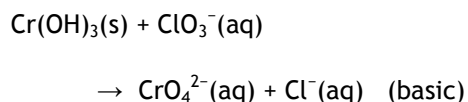
Step 8: Add enough OH⁻ ions to each side to cancel the H⁺ ions. (Be sure to add the OH⁻ ions to both sides to keep the charge and atoms balanced.)

Step 9: Combine the H⁺ ions and OH⁻ ions that are on the same side of the equation to form water.

Step 10: Cancel or combine the H₂O molecules.

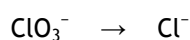
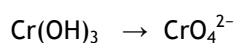
Step 11: Check to make sure that the atoms and the charge balance. If they do balance, you are done. If they do not balance, re-check your work in Steps 1-10.

EXAMPLE - Balancing Redox Reactions Using the Half-Reaction Method: Balance the following redox equation using the “half-reaction” method.



Solution:

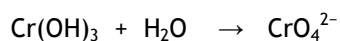
Step 1:



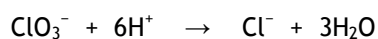
Step 2: (Not necessary for this example)



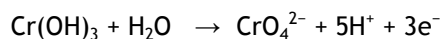
Step 3:



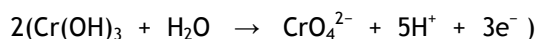
Step 4:



Step 5:

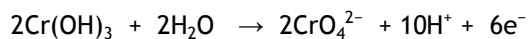


Step 6:

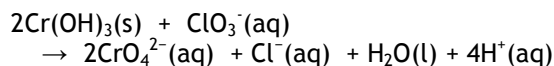


or

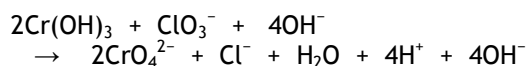
CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams



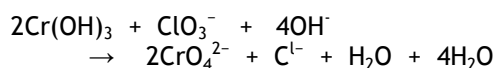
Step 7:



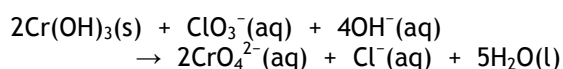
Step 8: Because there are 4 H⁺ on the right side of our equation above, we add 4 OH⁻ to each side of the equation.



Step 9: Combine the 4 H⁺ ions and the 4 OH⁻ ions on the right of the equation to form 4 H₂O.



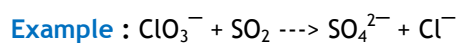
Step 10: Cancel or combine the H₂O molecules.



Step 11: The atoms in our equation balance, and the sum of the charges in each side is -5. Our equation is balanced correctly.

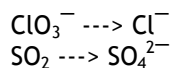
Points to remember:

- 1) Electrons NEVER appear in a correct, final answer. In order to get the electrons in each half-reaction equal, one or both of the balanced half-reactions will be multiplied by a factor.
- 2) Duplicate items are always removed. These items are usually the electrons, water and hydrogen ion.

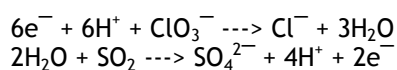


Solution:

1) Split into unbalanced half-reactions:

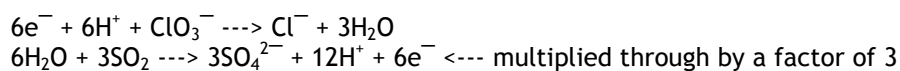


2) Balance the half-reactions:

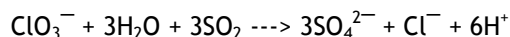


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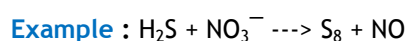
3) Make the number of electrons equal:



4) Add the two half-reactions for the final answer:

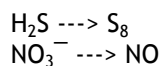


Note that items duplicated on each side were cancelled out. The duplicates are $6e^-$, $3H_2O$, and $6H^+$

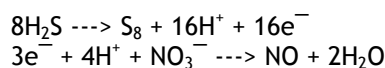


Solution:

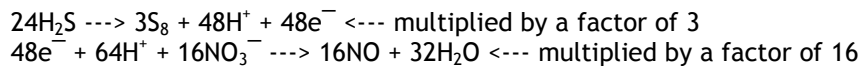
1) The unbalanced half-reactions:



2) balance each half-reaction:

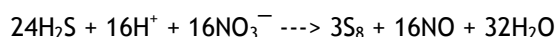


3) Make the number of electrons equal:

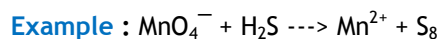


Note that 16 and 3 have no common factors except 1, so both 16 and 3 had to be used to obtain the lowest common multiple of 48 for the number of electrons.

4) Add:

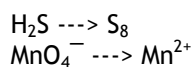


Comment: removing a factor of 8 does look tempting, doesn't it? However, the three in front of the S_8 (or the five in the next problem) makes it impossible. Also, note that duplicates of 48 electrons and 48 hydrogen ions were removed.

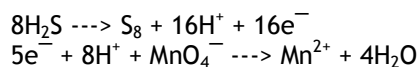


Solution:

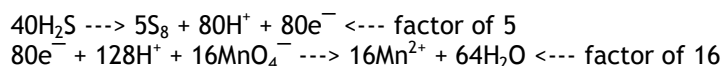
1) Half-reactions:



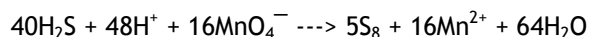
2) Balance:



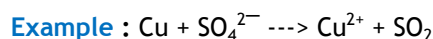
3) Make the number of electrons equal (note that there are no common factors between 5 and 16 except 1):



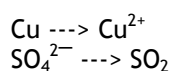
4) The final answer:



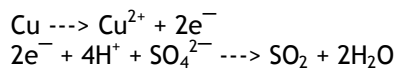
Another possibility of removing a factor of 8 destroyed by an odd number, in this case, the 5 in front of the S_8 .



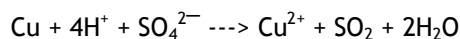
1) The unbalanced half-reactions:



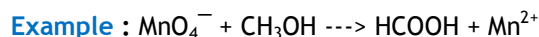
2) The balanced half-reactions:



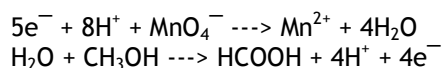
3) The final answer:



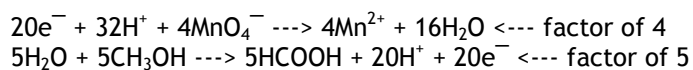
No need to equalize electrons since it turns out that, in the course of balancing the half-reactions, the electrons are equal in amount. Note how easy it was to balance the copper half-reaction. All you needed were the two electrons.



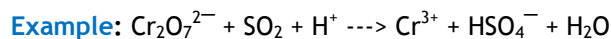
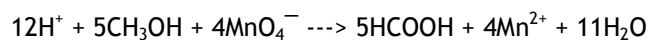
1) The balanced half-reactions:



2) Equalize electrons:

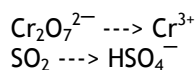


3) The final answer:

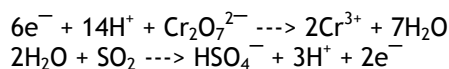


Solution:

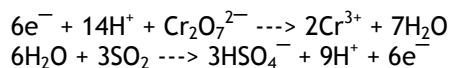
1) Half-reactions:



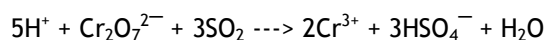
2) Balance in acidic solution:



3) Equalize electrons:

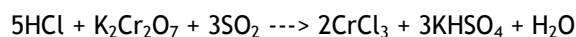


4) Add:

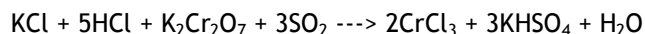


Sometimes you are given a net-ionic equation and asked to take it back to a full molecular equation. Sometimes, no context is added, so you have to make some informed predictions. Here's what I mean:

Since the equation is in acidic solution, you can use HCl or HNO₃. I'll use HCl. The most common dichromate that is soluble is potassium dichromate, so we will use that. Using those, we find this:



However, there is a problem. One too many K and Cl on the right-hand side. The solution is to add one KCl to the left-hand side:



You can write the equation using HNO₃ and the nitrate would simply replace the chloride.

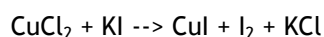
Using sulfuric acid can be done but (and this is part of the informed prediction) probably should not. The chromium(III) ion is presented as an ion, meaning it's soluble. Chromium(III) sulfate is not soluble, which means you would have to write the full formula. Since that was not done, we conclude that the chromium ion was part of a soluble compound.

If you don't have a net ionic equation to balance, that means you have what is usually called a molecular equation (or a complete molecular equation). These are harder to balance because the elements being oxidized and reduced are mixed in with substances that are not being reduced or oxidized.

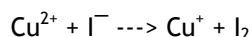
The solution is to, as much as possible, remove the "extraneous" substances: the ones that are neither oxidized or reduced. This gives you an unbalanced net ionic equation, which you proceed to balance. You then add back in the substances you had removed.

The problem? There is no explicit set of steps for how to do this. So, I will just let the technique evolve through some examples.

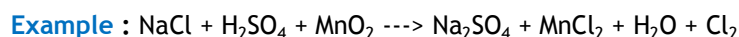
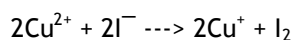
Comment: one thing that frustrates students learning the technique discussed in this tutorial is knowing how to decide what to eliminate and what not to. The easy answer to that is to advise you to eliminate everything but that which gets oxidized and reduced. For example, this equation:



You must be able to see that the Cu is reduced from +2 to +1 and that the I goes from -1 to zero. That means that the chloride and the potassium ion are spectator ions and we arrive at this:



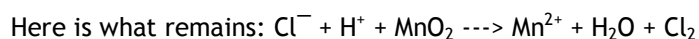
and eventually this:



Solution:

1) What to remove?

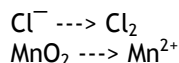
NaCl: sodium ion is a classic spectator ion and it will be removed.
 H_2SO_4 ; notice how only sulfate is present on the right-hand side. It will be removed.
 MnO_2 : this stays since Mn is reduced in the reaction.
 Cl_2 : it stays since the chloride from the left-hand side is oxidized.



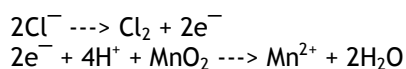
That's the net ionic.

Notice I kept the MnO_2 intact.

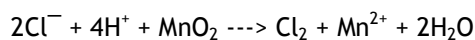
2) Now for the half-reactions:



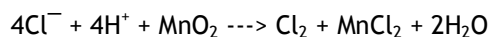
3) Balance them:



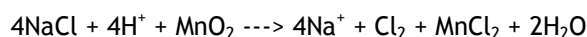
4) Since the electrons are already balanced, we add:



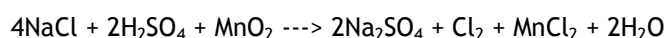
5) We add in two more chloride to make MnCl_2 :



6) We add in 4 sodium ion to make NaCl :



7) Add in four sulfate ions:



Example : $\text{SeCl}_2 \rightarrow \text{H}_2\text{SeO}_3 + \text{Se} + \text{HCl}$

Solution:

1) Here is what can be removed:

- a) the SeCl_2 can be changed to Se^{2+}
- b) the H_2SeO_3 can be changed to SeO_3^{2-}
- c) the HCl .

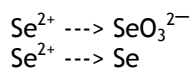
I dropped the chlorine and hydrogen because neither was oxidized or reduced. The prime skill needed in changing a molecular equation to a net ionic is recognizing which elements have had their oxidation states changed.

I will discuss the SeO_3^{2-} a bit more below. Also, the HCl tells me that this solution is to be balanced in acidic solution.

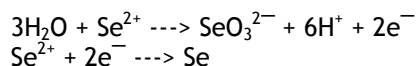
2) We now have this unbalanced net ionic equation:



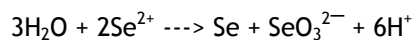
3) Here are the two half-reactions:



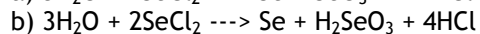
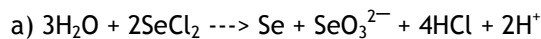
4) Balance the two half-reactions (in acidic solution):



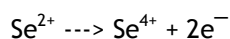
5) Add the two half-reactions and eliminate electrons:



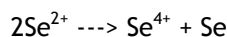
6) Restore items that were removed (shown in two steps). This gives the final answer:



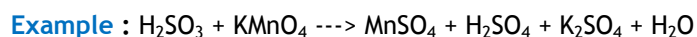
Why not drop the oxygen and get this half-reaction?



It does work because you get this balanced net ionic equation as an answer:



However, it seems to me to be a bit of a hassle to get back to the final answer. You might wish to try that on your own. Also, H_2SeO_3 is a weak acid. You might want to keep the full formula in its half-reaction and then balance. You can also get to the correct answer that way.



Solution:

You must be able to see that it is the Mn that gets reduced (from +7 to +2) and that the S gets oxidized (from +4 to +6).

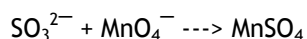
1) Here is what I will remove:

a) the H_2O (it will get back in via both half-reactions)

b) the H in H_2SO_3 and H_2SO_4

c) the potassium ion

Here is the unbalanced net-ionic equation that results:

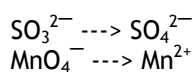


In order to make the half-reactions, I going to allow the MnSO_4 to ionize. Why?

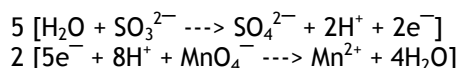
I know that the sulfate will play no role in balancing the reduction half-reaction, so I don't need it. How did I know? I know because the sulfur in the sulfate is being oxidized. I can't have an oxidation occurring in a reduction half-reaction. I will recombine the Mn^{2+} and the sulfate when I recover the balanced, molecular equation.

Also, suppose I keep the MnSO_4 unionized. That means I would have to include the permanganate in the equation, to keep Mn present on both sides. That means I have to balance the net-ionic equation.

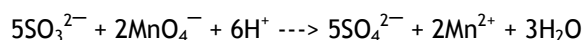
2) Here are the half-reactions that result:



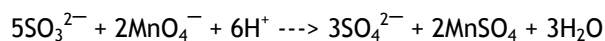
3) Here are the balanced half-reactions (note that it is acidic solution and that I have equalized the electrons):



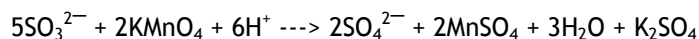
4) The final, balanced net ionic equation (extra water and hydrogen ion have been removed):



5) Make some MnSO_4 :

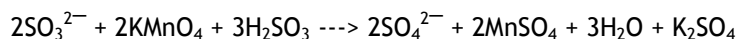


6) Make some potassium permanganate:

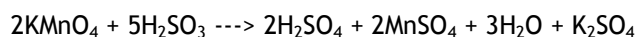


Notice how I made some potassium sulfate at the same time.

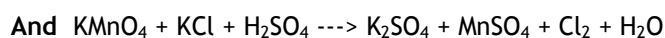
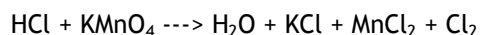
7) Make some H_2SO_3 :



8) Now, I will add 4 hydrogens on each side:



Example



We can eliminate the following:

H^+ from the HCl

H_2O

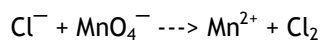
K^+

Cl^- , but only from the right-hand side

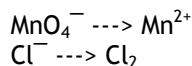
Why only from the right-hand side? It is because the Cl^- will be oxidized. I know this because there is Cl_2 on the right-hand side as well. This tells me the chlorine is going from a -1 oxidation state to zero. It is being oxidized. So, I need Cl^- on the left-hand side, but not the right-hand side.

CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

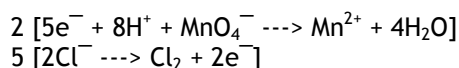
Here is the net-ionic equation:



From this, we get the half-reactions:

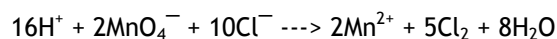


The balanced half-reactions:

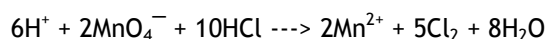


Note the addition of the factors 2 and 5, which will balance the electrons.

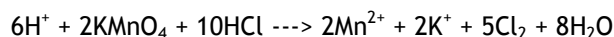
The balanced equation, in net-ionic form:



Now, we must re-create the molecular equation, but in balanced form. First, make some HCl:



Next, add potassium ion back in:

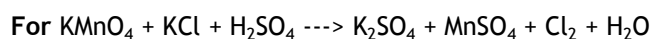


To both sides, add in six chlorine ions:



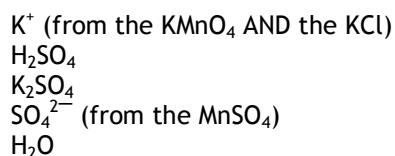
Where did they go? On the left-hand side, they hooked up with the hydrogen ion to make 6 HCl, giving a total of 16HCl. On the right-hand side, two went with the potassium ion to make KCl and the other 4 made 2MnCl₂.

I can add Cl⁻ back in since we know, from the starting equation, that it was always present. Some of the Cl⁻ reacted, to form Cl₂, and some remained as spectator ions.



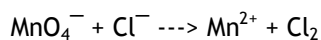
I'm going to answer this problem in two different ways. I'll link to the second way at the end of this file.

1) eliminate all spectator ions (this means anything that isn't reduced or oxidized). The list is:



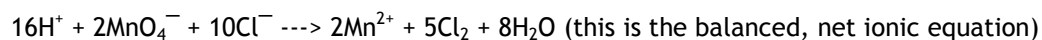
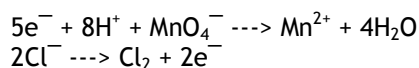
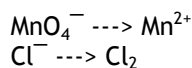
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That leaves this:



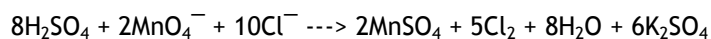
Why did I keep those? It's because they are the exact items oxidized (the Cl) or reduced (the Mn).

2) balance the net ionic reaction (in acidic solution because of the sulfuric acid):

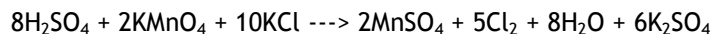


3) add back in the spectator ions (which I will do in a step-wise fashion):

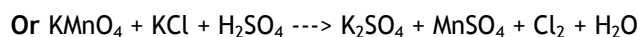
a) add back in 8 sulfates:



b) This added 12 potassium ions to the right side, so add 12 K⁺ to the left:



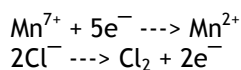
The last equation is the balanced, molecular equation.



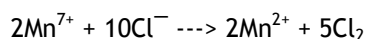
1) identify the atoms being oxidized and reduced:

Mn goes from +7 to +2; it is reduced
Cl goes from -1 to zero; it is oxidized

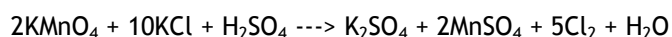
2) write the two half-reactions:



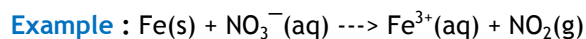
3) multiply the first reaction by 2 and the second by 5, and add them to get:



4) since this a complete redox reaction and the number of electrons are equal on both sides, we can now use these coefficients in the molecular equation to balance it:



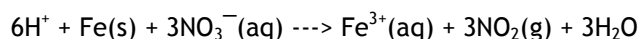
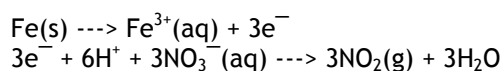
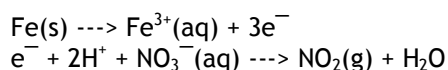
5) balancing the other atoms can be done easily now by 'trial and error' method



Solution:

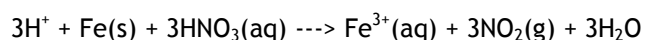
Notice that that reaction is already in net ionic form. I propose to balance it and then put it into molecular form.

Balance by half-reactions in acidic solution:

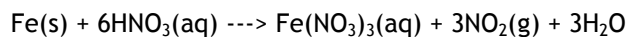


I knew to balance in acidic solution because of the nitrate. I needed positive ions coupled with the nitrate to give me a compound. Hydroxide did not fit my needs. Also, note that the iron(III) ion is in solution. In the presence of hydroxide, $\text{Fe}(\text{OH})_3$ would precipitate.

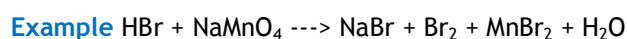
To make a molecular equation, join up some hydrogen ion with some nitrate ion:



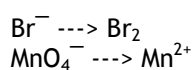
We need more nitrate ion to combine with the rest of the hydrogen ion AND the ferric ion:



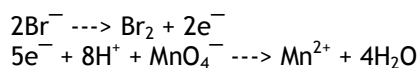
It's now a fully-balanced molecular equation. Note that iron(III) nitrate is soluble, making the three nitrate ions added in this last step as the only spectator ions in the reaction.



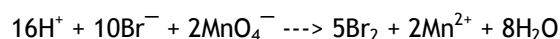
1) Half-reactions:



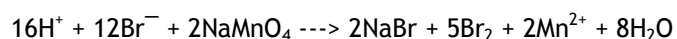
2) Balance them:



3) Equalize electrons, then combine half-reactions:



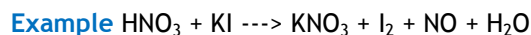
4) Add two sodium ions and two bromide ions to each side:



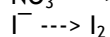
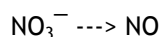
5) Add four bromide ions to each side:



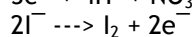
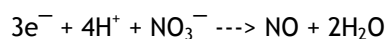
Note that, on the left-hand side, I also combined the 16 hydrogen ions with the 16 bromide ions.



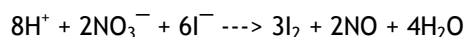
1) Half-reactions:



2) Balance them:



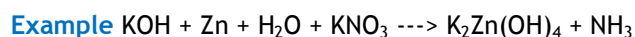
3) Equalize electrons, then combine half-reactions:



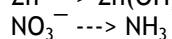
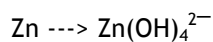
4) Add in six potassium ions and 6 nitrate ions:



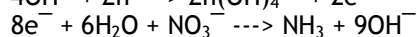
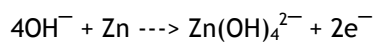
Note that, on the left-hand side, I also combined the 8 hydrogen ions with the 8 nitrate ions.



1) Half-reactions:

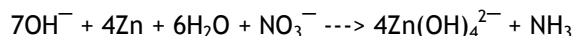


2) Balance:

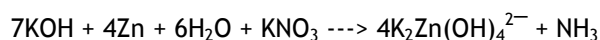


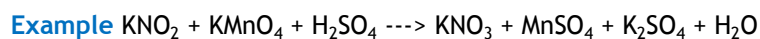
I first balanced the second half-reaction in acidic solution, then changed it over to basic.

3) Equalize electrons, then combine half-reactions:

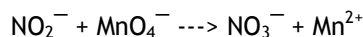


4) Add eight potassium ions to each side:

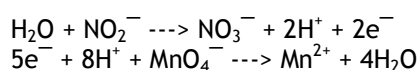
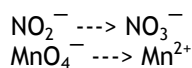




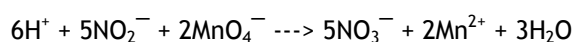
1) Write the net ionic equation:



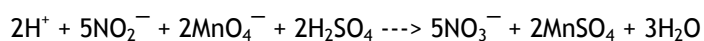
2) Half-reactions and balance:



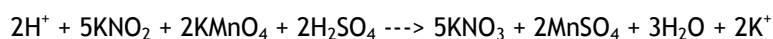
Top half-reaction by 5, bottom by 2; then add and eliminate water and hydrogen ion.



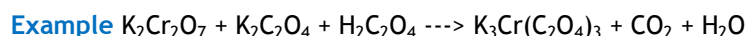
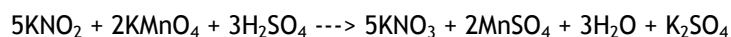
3) Add sulfate to the Mn^{2+} :



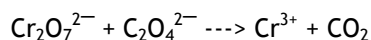
4) Add seven potassium ions:



5) Add one more sulfate:

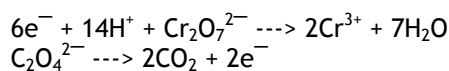
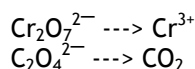


1) Write the net ionic equation:

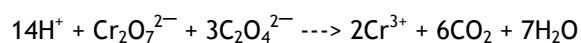


The potassium ion is one of the usual suspects when it comes to spectator ions, so that's easy. Be sure to notice, however, that the oxalate is both a spectator ion and the species oxidized (the C going from +3 to +4). That means that only some of the oxalate in the final answer gets oxidized.

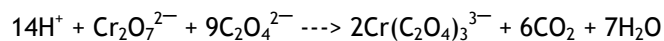
2) Half-reactions and balance:



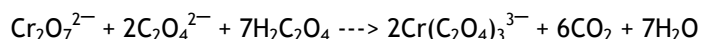
3) Equalize electrons and add:



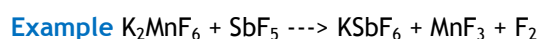
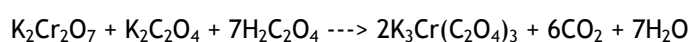
4) Add six oxalate ions to each side:



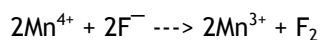
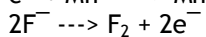
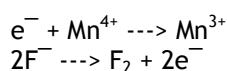
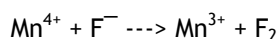
5) Make seven oxalic acids:



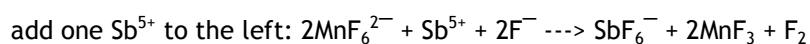
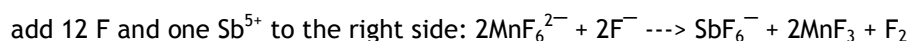
6) Add six potassium ions to recover the final answer:



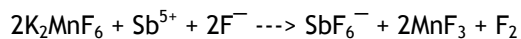
1) Net ionic, half-reactions and balanced net ionic:



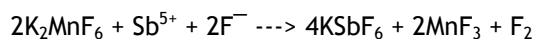
2) Add 12 F^- and one Sb^{5+} to each side:



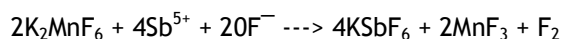
3) Add 4 potassium ions to the left:



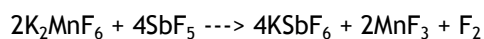
4) This means we MUST add 4 potassium to the right side:

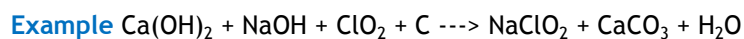


5) This means we MUST add 3 Sb and 18 F to the left side. I'll do it as ions first:

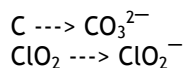


6) Combine ions for the final answer:

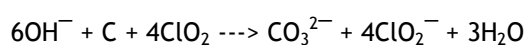
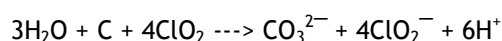
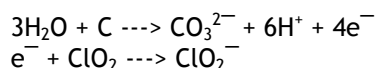




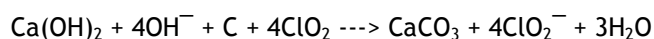
1) Half-reactions:



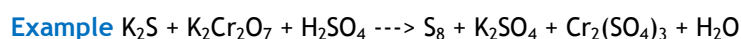
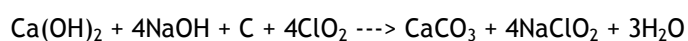
2) Balance using acid solution & write net-ionic in basic solution:



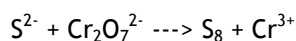
3) Add one calcium ion back in:



4) Add 4 sodium ions:



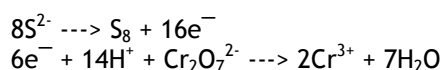
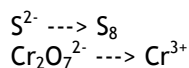
1) Write the net ionic equation:



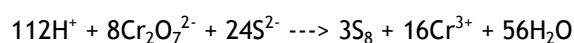
Note that the only chemical species in the net ionic equation are the ions (which includes polyatomic ions) which were oxidized or reduced.

Also, the chromium(III) sulfate is a precipitate, yet I deleted the sulfate ion. Why? Because I know the sulfates are not involved in the production of elemental sulfur. How do I know that? Below, I already have a half-reaction producing elemental sulfur. To introduce a third half-reaction of sulfate to elemental sulfur is unnecessary. At the end, I'll just reform chromium(III) sulfate when I remake the balanced molecular equation.

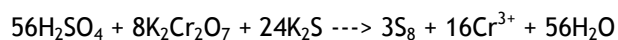
2) Write the half-reactions and balance:



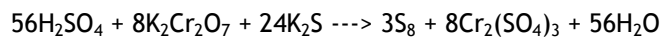
Use a factor of three for the first half-reaction and eight for the second half-reaction.



3) Add this to the left-hand side: $56 \text{ sulfate} + 16 \text{ K}^+ + 48 \text{ K}^+$

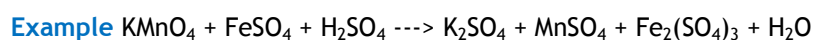
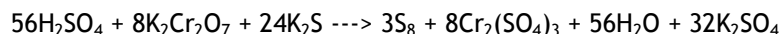


4) Add 24 sulfates to the right-hand side:

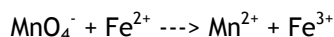


Note how the coefficient went from 16 to 8.

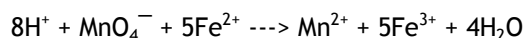
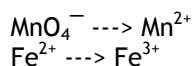
5) Pick up the remaining 32 sulfates and 64 potassium ions:



1) Write the net ionic equation:



2) Half-reactions and balance in net ionic form:



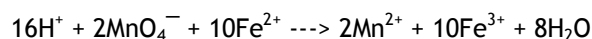
However, there will be a major problem, so much so that the balanced net ionic equation will be insufficient for what lies ahead.

The problem has to do with adding the potassium back in to make the molecular equation. On the left-hand side we have potassium permanganate (with only one potassium per formula unit) and on the right-hand side, the only place to add potassium is with potassium sulfate (with two potassium per formula unit). I can never balance the potassium with the net ionic as written above. (Yes, I could put a 2 in front of KMnO_4 . Try it and see what happens. It will probably be much harder to figure out than what I'm going to do below.)

So, how to solve?

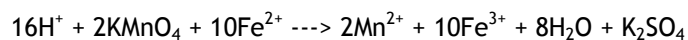
Notice that I said the balanced net ionic is insufficient, not incorrect.

In the net ionic above, I used factors of 1 and 5 to multiply through so that, when I added the two half-reactions, the electrons cancel out. To solve my potassium problem, I will use factors of 2 and 10 to get this:

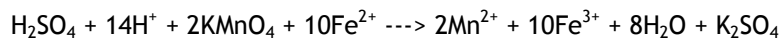


Notice that I will now use 2KMnO_4 (and one K_2SO_4) to balance the potassium. So, let's do that:

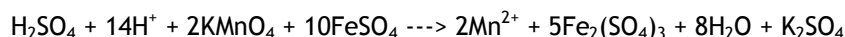
3) Balance the potassium:



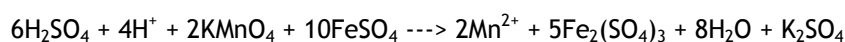
I balance the sulfate introduced on the right like this:



4) Add sulfates to the iron(II) and iron(III) ions (follow this carefully):

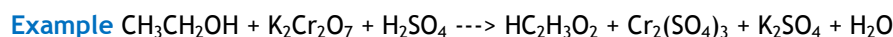


The problem is that I added 10 sulfates to the left and 15 to the right. So add 5 sulfates to the left:

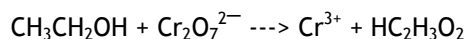


Notice how the sulfuric acid goes from 1 to 6 and the hydrogen ion goes down by 10.

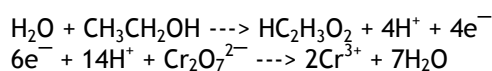
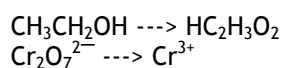
5) Add two more sulfates to get the final answer:



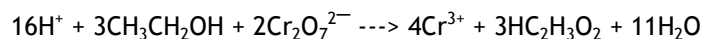
1) Write the net ionic equation:



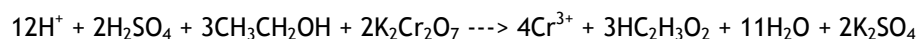
2) Half-reactions and balance:



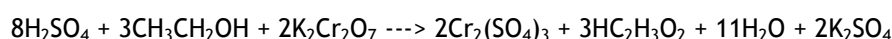
Top half-reaction by 3, bottom by 2; then add and eliminate water and hydrogen ion.



3) Add 4 K⁺ to the left, then the right. Add two sulfate to the right (thus making the potassium sulfate), then to the left:



4) Add six sulfates to the Cr(III) ion, then make the rest of the sulfuric acid. Result:



Example

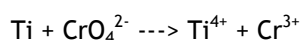
In the reaction of titanium metal with excess potassium chromate and sulfuric acid, the products are titanium (IV) sulfate, potassium sulfate, chromium (III) sulfate, and water. Write and balance the equation and calculate the coefficient for the potassium sulfate in the balanced equation.

Solution:

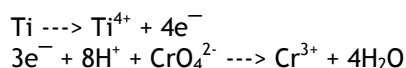
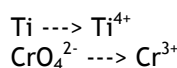
1) Write the equation (with correct formulas!):



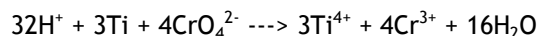
2) Convert it to net ionic:



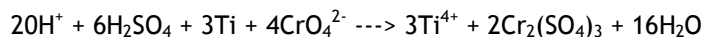
3) Write and balance half-reactions:



4) Balance net ionic equation:

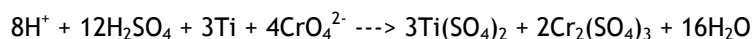


5) Make chromium(III) sulfate:



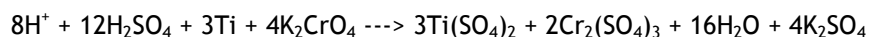
Note how six sulfuric acid has been added in as well. This balances the six sulfates added.

6) Make titanium(IV) sulfate:



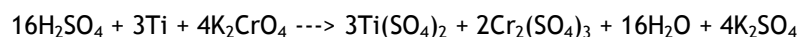
Note how another six sulfuric acid has been added in as well. This balances the six sulfates added. Also, see the hydrogen ion decreasing by 12 each time, for a total of 24 so far.

7) Make potassium chromate:



Notice how 4 potassium sulfate showed up on the right. That's to balance the potassium. Now, I'll fix the extra 4 sulfates that currently exist on the right-hand side of the equation.

8) Introduce 4 sulfates to the left-hand side of the equation:

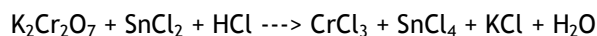


CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

Did you see what I did? I simply introduced 4 more sulfuric acids. I took the 8 hydrogen ion already there and combined them with 4 sulfate ions I needed to add to the left-hand side. Notice that the coefficient of the sulfuric acid went from 12 to 16.

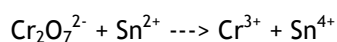
It's balanced and the answer the problem wants is 4.

Example

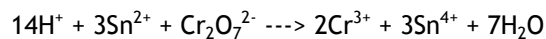
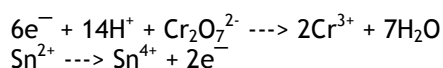
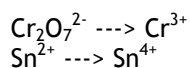


Solution:

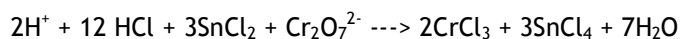
1) Write the net ionic equation:



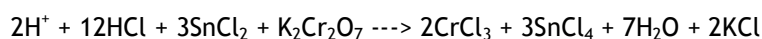
2) Break into half-reactions and balance:



3) Add chloride to the Cr(III) and Sn(IV) ions:

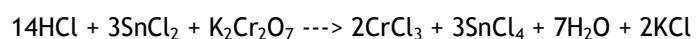


4) Add potassium ion:

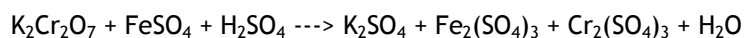


Notice that there are now two extra chlorides on the right-hand side.

5) Add two chlorides to the left-hand side:

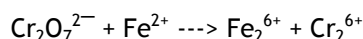


Example



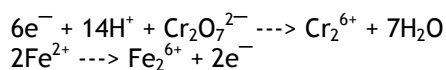
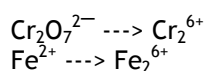
Solution:

1) Write the net ionic equation:

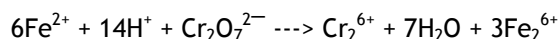


Notice how I preserved the subscripts for the Fe(III) ion and the Cr(III) ion on the right-hand side. In the next example, I do not employ this little trick. In several other problems, I use the above trick. One way will be effective for some and the other way will be effective for others.

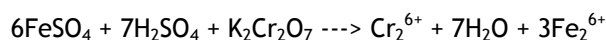
2) Write the half-reactions and balance them:



3) The balanced net ionic equation:

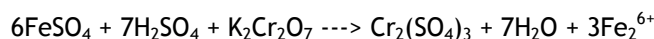


4) I'm going to add everything to the left-hand side and nothing to the right-hand side:



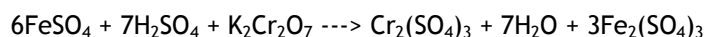
I added thirteen sulfates and two potassium ions. Now, I have to do the same to the right-hand side.

5) Add sulfate to the chromium(III) ion:



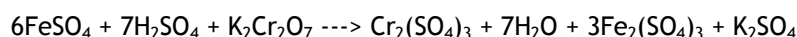
That's three (of thirteen).

6) Add sulfate to the iron(III) ion:

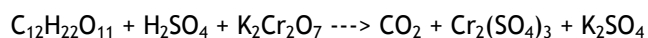


That's nine more (remember the coefficient of three in front of the iron(III) on the right-hand side), for a total of twelve. One more sulfate to go.

7) Pick up the last sulfate with the two potassium ions still unbalanced:

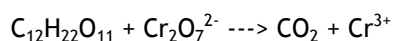


Example

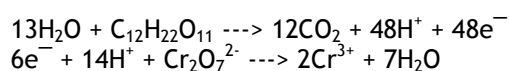
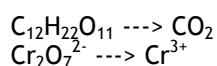


Solution:

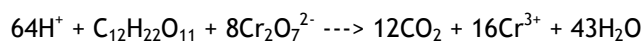
1) Write the net ionic equation:



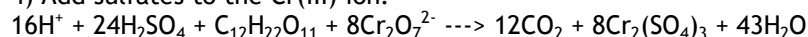
2) Write the half-reactions and balance them:



3) The balanced net ionic equation:

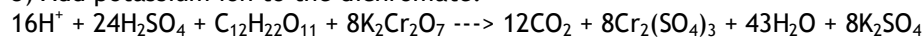


4) Add sulfates to the Cr(III) ion:



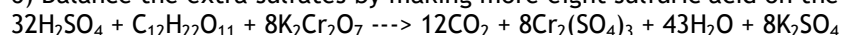
Notice how the sulfates are balanced with sulfuric acid. Notice also that this consumes 48 of the 64 hydrogen ions.

5) Add potassium ion to the dichromate:



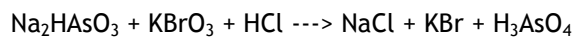
Notice how the potassium is balanced with potassium sulfate. This introduces eight extra sulfate on the right-hand side.

6) Balance the extra sulfates by making more eight sulfuric acid on the left-hand side:



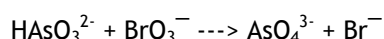
Notice how the 16 remaining hydrogen ions are included in the sulfuric acid.

Example



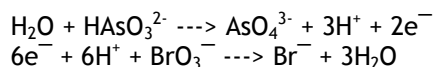
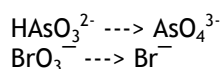
Solution:

1) Write the net ionic equation:

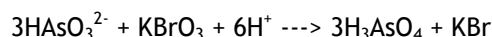


2) Write the half-reactions and balance:

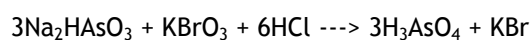
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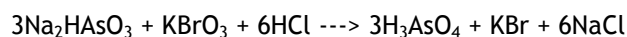
3) Add one potassium to each side:



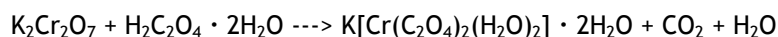
4) Add six sodium and six chloride to the left-hand side:



5) Add six sodium chloride to the right-hand side:

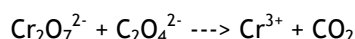


Example

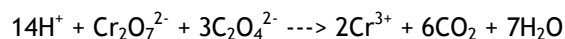
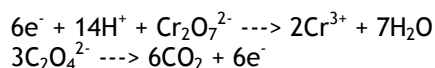
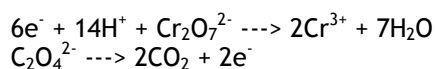
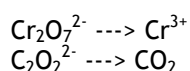


Solution:

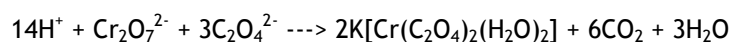
1) Strip out spectator ions:



2) Balance in acidic solution (because of the oxalic acid):



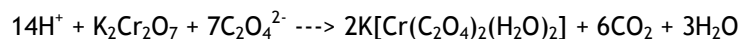
3) To restore the molecular equation the trick, to me, is to restore the right-hand side and then deal with the left:



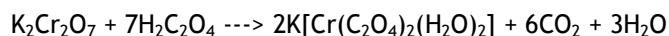
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Notice how I also reduced the water on the right-hand side. I will also ignore the water of hydration for the moment.

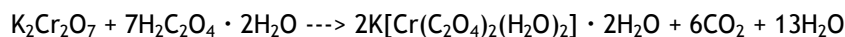
4) The net effect is that I have 4 oxalates and two potassium on the right that still need to be balanced. Let's do both of them:



5) Reform the oxalic acid:



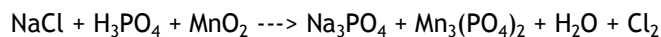
6) When I add in the water of hydration, keep in mind that there is a 7 in front of the oxalic acid. That means 14 waters will be added to the left-hand side. On the right, the waters of hydration will only add 4, so I have to add 10 more to the $3\text{H}_2\text{O}$:



7) Check the balance and find this:

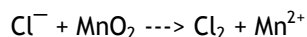
42 hydrogens and 49 oxygens; I won't bother with the others.

Example



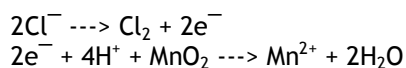
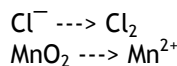
Solution:

1) Write the net ionic equation:

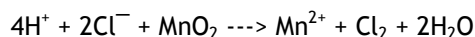


The usual practice is keep the formula MnO_2 untouched. Eventually, those oxygens will combine with hydrogen ion to make water.

2) Separate into half-reactions and balance:

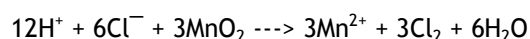


3) Add:

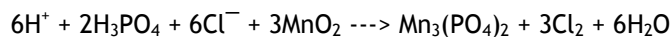


4) Notice the formula $\text{Mn}_3(\text{PO}_4)_2$. It requires three manganese and we have only one in the net ionic. Multiply through by three:

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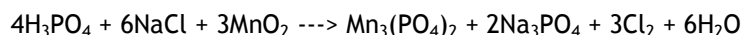


5) I will make the $\text{Mn}_3(\text{PO}_4)_2$ by adding in two phosphates:



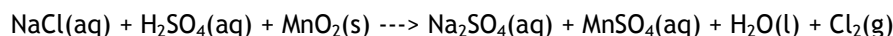
Notice how I also made two phosphoric acids.

6) I'm going to make 2 more phosphoric acid as well as six NaCl:



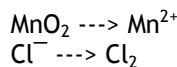
Note how two sodium phosphate were added to the right-hand side.

Example

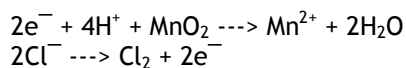


Solution:

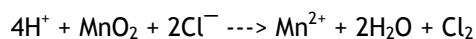
1) Half-reactions:



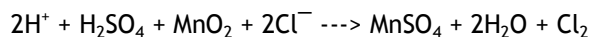
2) Balanced:



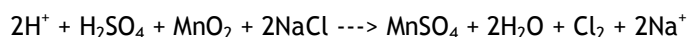
3) Add them:



4) Add in one sulfate:



5) Add in two Na^+ :

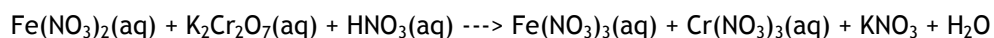


6) Add in one more sulfate:



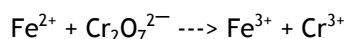
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Example

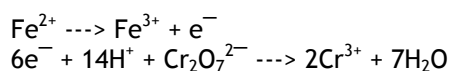
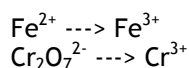


Solution:

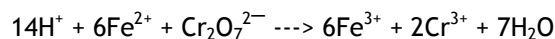
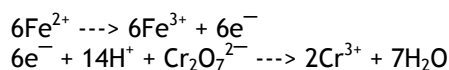
1) Net ionic:



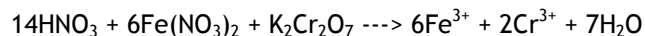
2) Half-reactions and balance:



3) Equalize electrons and add:

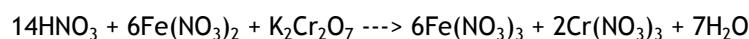


4) Add nitrate (and two potassium ions) to the left-hand side:

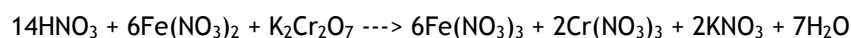


That's 26 nitrates (and two potassium) that have to go on the right-hand side.

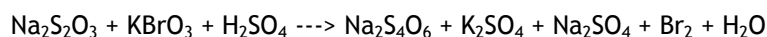
5) Eighteen nitrates go with the 6Fe^{3+} and six with the 2Cr^{3+} :



6) That leaves us with two nitrates to account for as well as the two potassium ions:

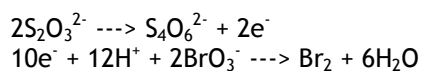


Example

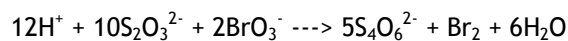
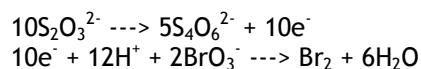


Solution:

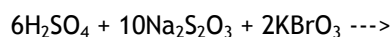
1) Write balanced net ionic half-reactions:



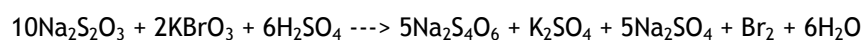
2) Equalize electrons and add:



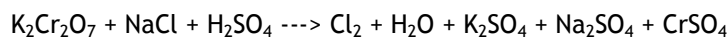
3) Add six sulfates, 20 sodium ions and two potassium ions to the left-hand side only:



4) Only 10 sodium ions can be accounted for by making $5\text{Na}_2\text{S}_4\text{O}_6$. Everything else is accounted for by the spectator ions:

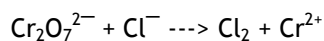


Example

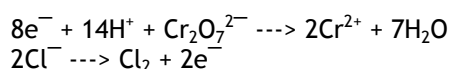
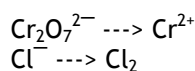


Solution:

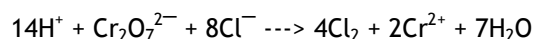
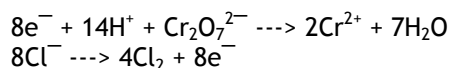
1) Write the net ionic:



2) Write half-reactions and balance:



3) Equalize electrons and write balanced net ionic:

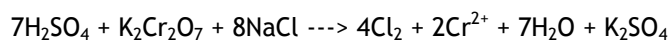


4) Add everything to the left-hand side:

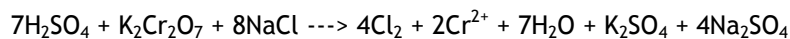


I added two potassium ions, eight sodium ions and seven sulfate ions.

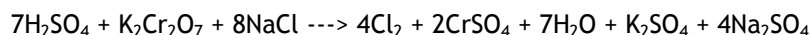
5) Add two potassium ions and one sulfate to the RHS:



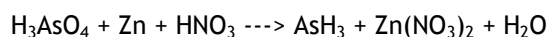
6) Add eight sodium ions and four sulfate ions to the RHS:



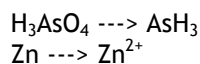
7) Add the last two sulfate ions to create the final answer:



Example

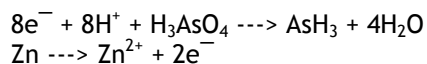


1) Write the net ionic half-reactions:

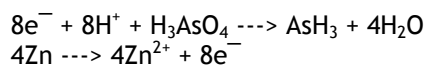


I could have written AsO_4^{3-} if I had wanted to. I would have just re-formed H_3AsO_4 at the end.

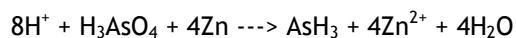
2) Balance in acidic solution:



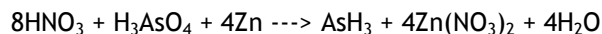
3) Equalize electrons:



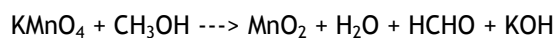
4) Add:



5) Bring back to molecular:

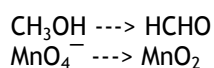


Example

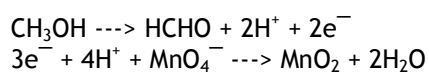


Solution:

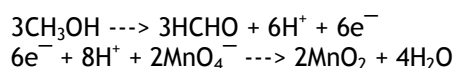
1) Half-reactions:



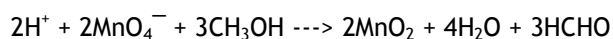
2) Balance in acidic solution:



3) Equalize electrons:



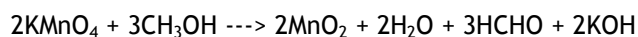
4) Add half reactions and eliminate hydrogen ion and electrons:



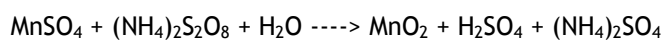
5) Change to basic by adding 2 hydroxides and then eliminating water:



6) Add in two potassium ions:

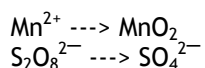


Example

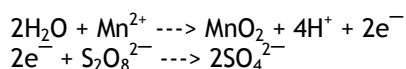


Solution:

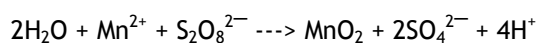
1) Half-reactions:



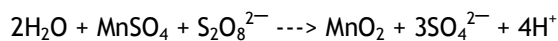
2) Balance:



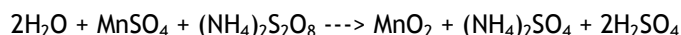
3) Add:



4) Add one sulfate:

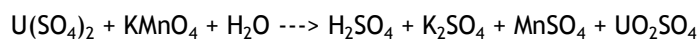


5) Add two ammonium ions:



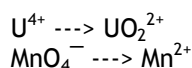
Note that I made two sulfuric acid with the four hydrogen ions and two sulfate ions. The third sulfate ion went to make the ammonium sulfate.

Example

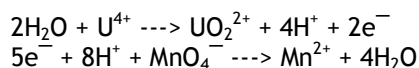


Solution:

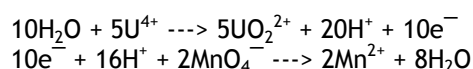
1) Half-reactions:



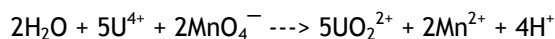
2) Balance:



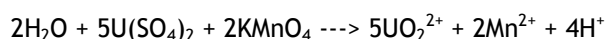
3) Make electrons equal:



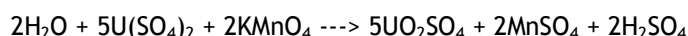
4) Add and eliminate electrons as well as excess water and hydrogen ion:



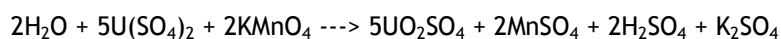
5) Add 10 sulfates and two potassium ions to the left-hand side:



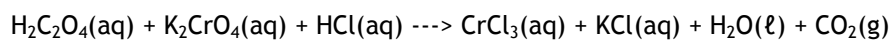
6) Add five sulfates to UO_2^{2+} , two sulfates to Mn^{2+} and two sulfate to the H^+ :



7) Add one K_2SO_4 to the right to account for the 10th sulfate and the two potassium ions:

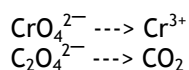


Example

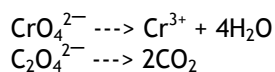


Solution:

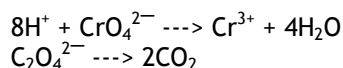
1) The half-reactions are these:



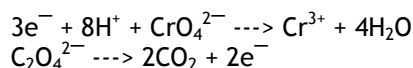
2) Balance for oxygen (C also gets balanced):



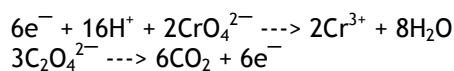
3) Balance for H:



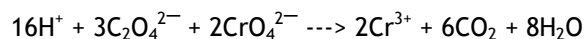
4) Balance for charge:



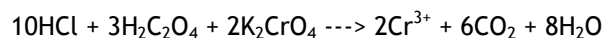
5) Equalize charge:



6) Add:

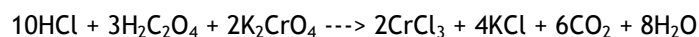


7) To recover the molecular, you can add stuff back in to the left-hand side:



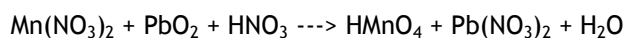
I added 10 Cl^- (note six H^+ went to the $\text{H}_2\text{C}_2\text{O}_4$) and I also added four K^+

8) Now, we need to add the same amount to the right-hand side:



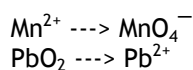
Six Cl^- went to make the 2CrCl_3 and the other four Cl^- paired with the four K^+ to make 4KCl .

Example

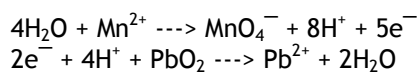


Solution:

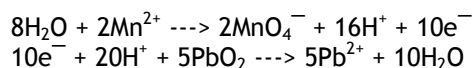
1) Half-reactions:



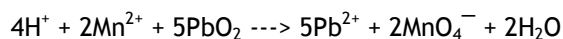
2) Balance:



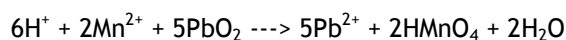
3) Equalize electrons:



4) Add. Eliminate electrons as well as excess hydrogen ions and water:

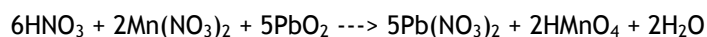


5) What needs to be added in is mostly nitrate. The only other item would be two hydrogens intended to make HMnO_4 . Add them in before adding the nitrates:



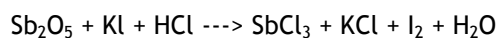
I made the decision to add hydrogen back in first based mainly on experience. It now makes it possible to add in the necessary nitrates in one step.

6) Ten nitrates finish the problem:



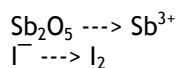
You are welcome to add some nitrate in first and then add in two hydrogens. What will happen is that you'll have two unattached nitrates on the left that will become HNO_3 when you add in the two hydrogen.

Example

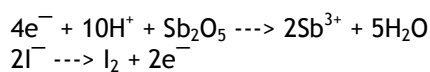


Solution:

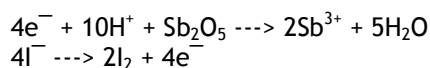
1) Half-reactions:



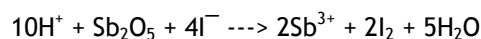
2) Balance:



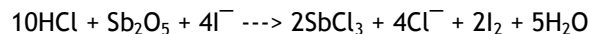
3) Equalize electrons:



4) Add:

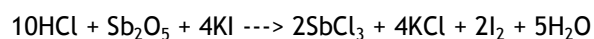


5) Add 10 chlorides to each side:

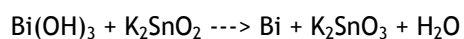


Note that 4 chlorides on the right are left as ions.

6) Add four potassium ions to each side:

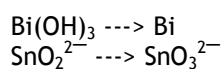


Example

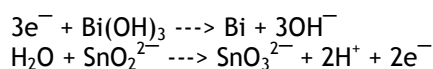


Solution:

1) Half-reactions:

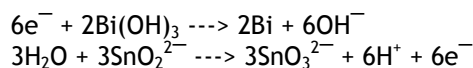


2) Balance:

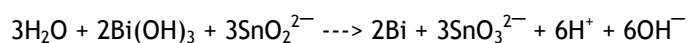


It does not matter that one half-reaction is in basic and the other in acid. That will be fixed.

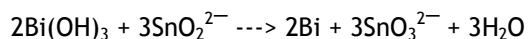
3) Equalize electrons:



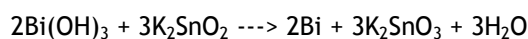
4) Add:



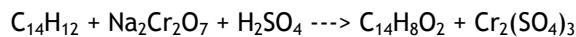
$6\text{H}^+ + 6\text{OH}^- = 6\text{H}_2\text{O}$ and then cancel three H_2O .



5) Add six potassium ions to each side:

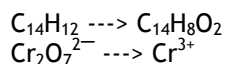


Example

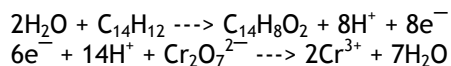


Solution:

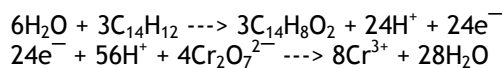
1) Half-reactions:



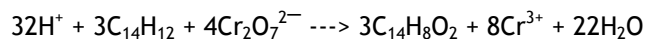
2) Balance:



3) Equalize electrons:

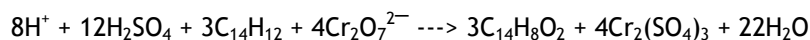


4) Add:

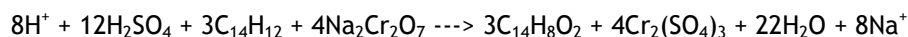


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SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

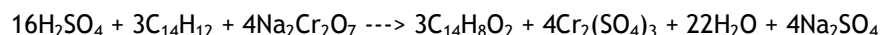
5) Add 12 sulfates to both sides (to make the $\text{Cr}_2(\text{SO}_4)_3$):



6) Add eight sodium ions to each side (to make the $\text{Na}_2\text{Cr}_2\text{O}_7$):

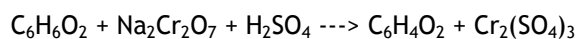


7) Add four more sulfates:



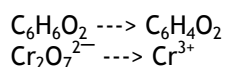
This last step made four more sulfuric acids as well as four sodium sulfates. Note how the sodium sulfate was not part of the equation that was originally given.

Example

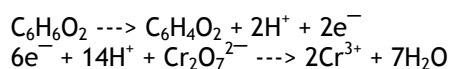


Solution:

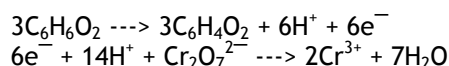
1) Half-reactions:



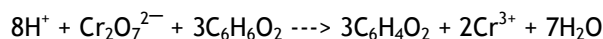
2) Balance:



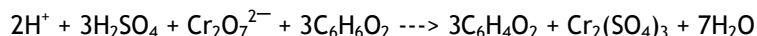
3) Equalize electrons:



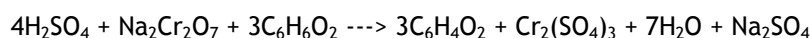
4) Add:



5) Put three sulfates in (to make $\text{Cr}_2(\text{SO}_4)_3$):



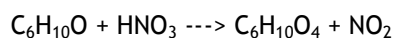
6) Add two sodium ions and one sulfate to the left:



I also added one sodium sulfate to the right-hand side to balance everything.

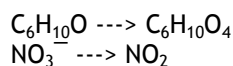
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Example

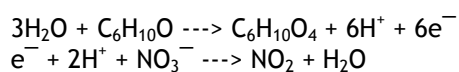


Solution:

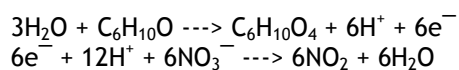
1) Half-reactions:



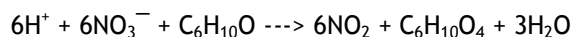
2) Balance:



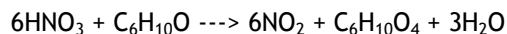
3) Equalize electrons:



4) Add:



5) Nothing needs to be added back in. Only one recombination:

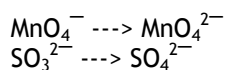


Example

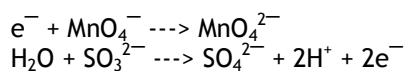


Solution:

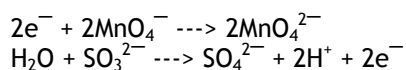
1) Half-reactions:



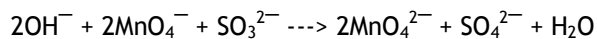
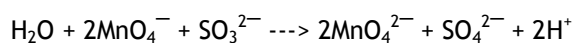
2) Balance:



3) Equalize electrons:

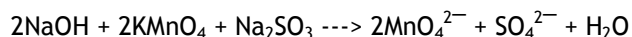


4) Add and convert to basic:



5) Add four sodium ion and two potassium ion to each side:

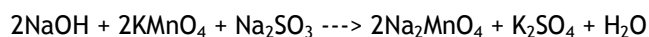
First, add to the left-hand side:



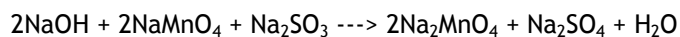
Now, to the RHS:



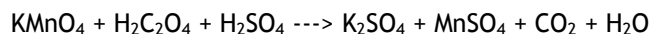
In case you were mildly curious, depending on the compounds selected by the question writer, the following answers could have been written:



or

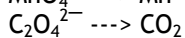
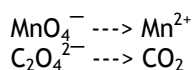


Example

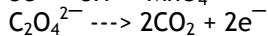
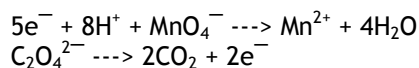


Solution:

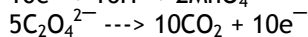
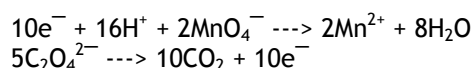
1) Half-reactions:



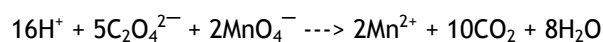
2) Balance:



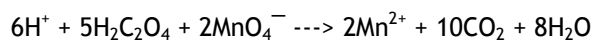
3) Equalize electrons:



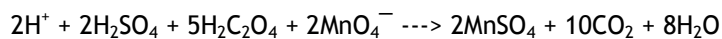
4) Add:



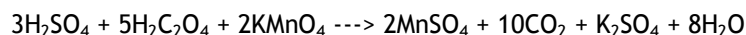
5) Make five undissociated oxalic acids:



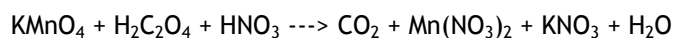
6) Add two sulfates to each side:



7) Add two potassium ions and one more sulfate:



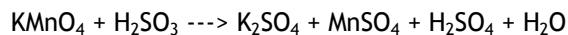
8) The same problem with nitric acid:



balanced:

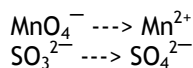


Example

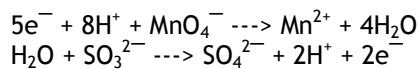


Solution:

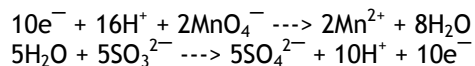
1) Half-reactions:



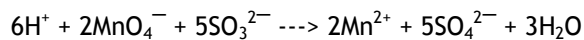
2) Balance:



3) Equalize electrons:



4) Add:



5) Add four hydrogen ion to each side:



Two sulfates went to sulfuric acid, two sulfates went to MnSO_4 and one sulfate is still to be dealt with.

6) Add two potassium ions to finish it:

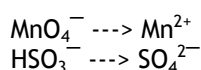


Example

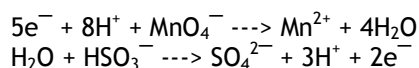


Solution:

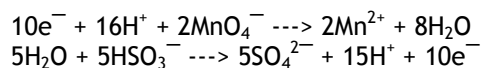
1) Half-reactions:



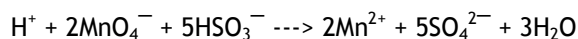
2) Balance:



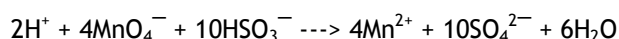
3) Equalize electrons:



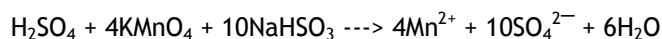
4) Add:



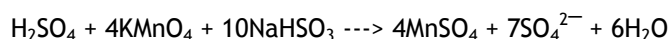
5) We know that there will be at least one H_2SO_4 , but we have only one H^+ on the left-hand side. Double everything to get two H^+ :



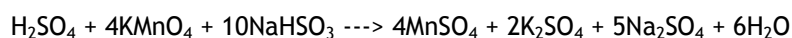
6) Add one sulfate, four potassium ions and ten sodium ions to the left-hand side:



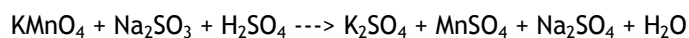
7) I'm going to reunite the 4Mn^{2+} with four sulfates and I will add in one sulfate to the right:



8) Add in the 10 sodium ions (using up five sulfates) and the four potassium (using up two sulfates):

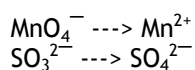


Example

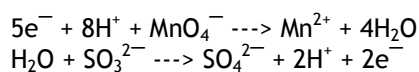


Solution:

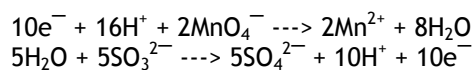
1) Half-reactions:



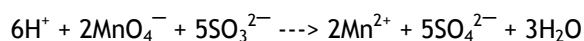
2) Balance:



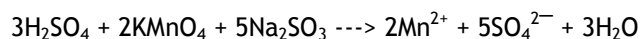
3) Equalize electrons:



4) Add:

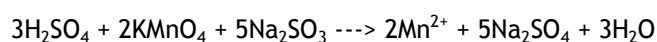


5) Add all the required spectator ions, but only do it on the left-hand side:



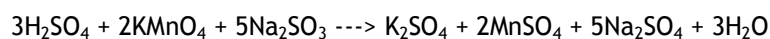
I added 3 sulfate ions, two potassium ions, and 10 sodium ions.

6) Add 10 sodium ions to the right-hand side:



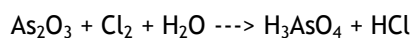
I did that simply because I had five sulfate ions already present to take up the ten sodium ions.

7) Now, the three sulfate ions:



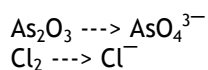
Two of the sulfates went to the potassium sulfate and the other one went to the manganese(II) sulfate. Notice I also added in the two potassium ions.

Example

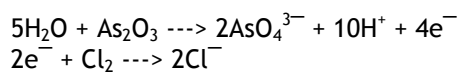


Solution:

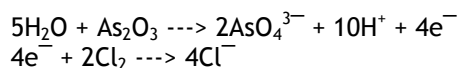
1) Half-reactions:



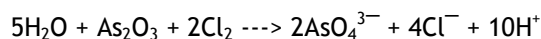
2) Balance:



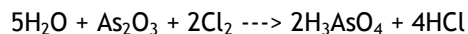
3) Equalize electrons:



4) Add:

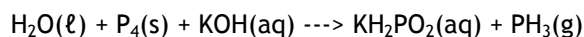


5) Reunite ions on the right-hand side:



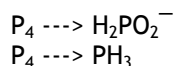
Note that no spectator ions needed to be added in.

Example

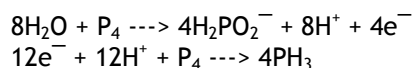


Solution:

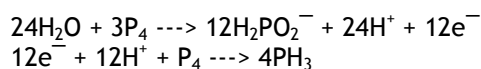
1) Half-reactions:



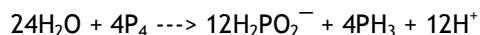
2) Balance in acid (change to basic at the end):



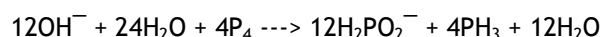
3) Equalize electrons (still in acid):



4) Add (then change to basic):



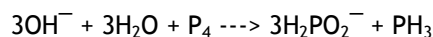
Add 12 hydroxide:



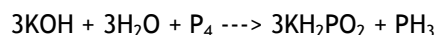
Remove 12 waters:



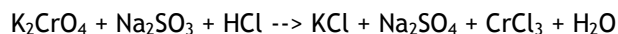
5) Remove factor of 4:



6) Add three potassium ions:

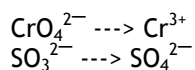


Example

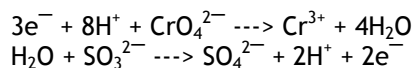


Solution:

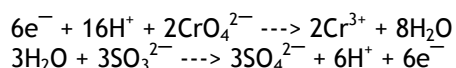
1) Half-reactions:



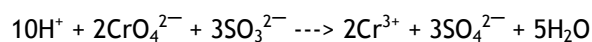
2) Balance:



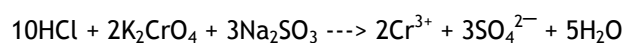
3) Equalize electrons:



4) Add:



5) Add 10 chlorides, four potassium ions and six sodium ions to the left-hand side:

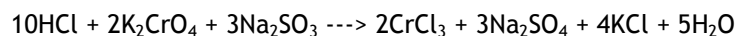


6) On the right-hand side:

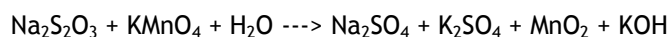
six chlorides go to the 2Cr^{3+}

six sodium go to the 3SO_4^{2-}

The remaining four K^+ and four Cl^- for 4KCl

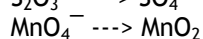
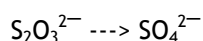


Example

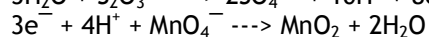
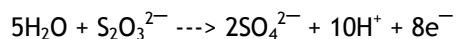


Solution:

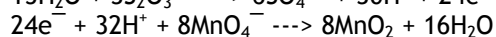
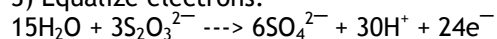
1) Half-reactions:



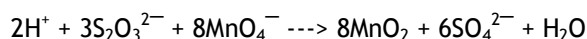
2) Balance (in acid, change to base later):



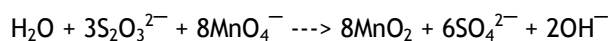
3) Equalize electrons:



4) Add, then change to basic:

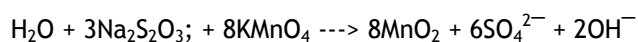


Add two hydroxide to each side:



One excess water was also eliminated.

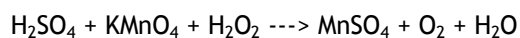
5) Add six sodium and eight potassium to the left-hand side:



6) On the right-hand side, the six sodium will be distributed among three sulfates. Six potassium will take care of the other three sulfates and the last two potassium will form KOH.

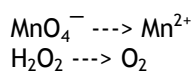


Example

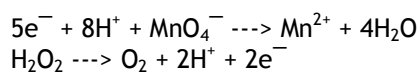


Solution:

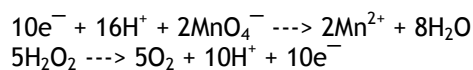
1) Half-reactions:



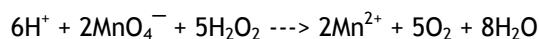
2) Balance:



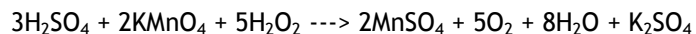
3) Equalize electrons:



4) Add:

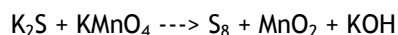


5) Adding in spectator ions:



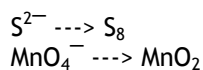
Three sulfates and two potassium ions were added back in.

Example

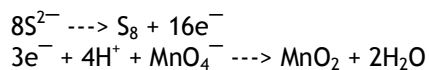


Solution:

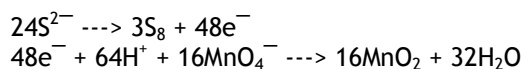
1) Half-reactions:



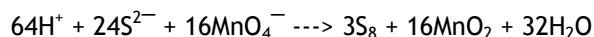
2) Balance as if in acidic solution:



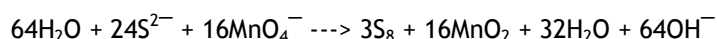
3) Equalize electrons:



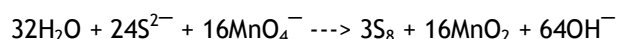
4) Add:



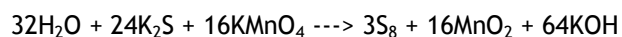
5) Change to basic by adding 64 hydroxide ions to each side:



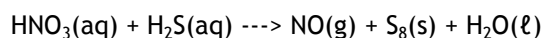
eliminate the water:



6) The only spectator ion is potassium:

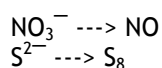


Example

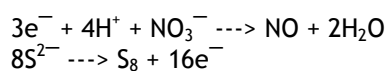


Solution:

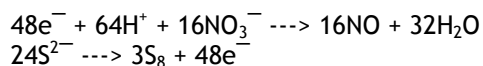
1) Half-reactions:



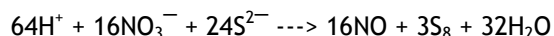
2) Balance:



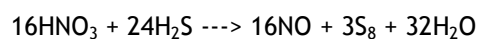
3) Equalize electrons:



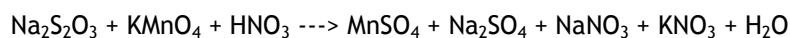
4) Add:



5) Distribute the 64 hydrogen ions:

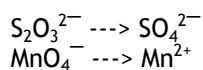


Example

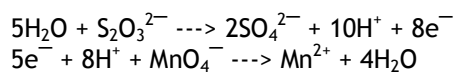


Solution:

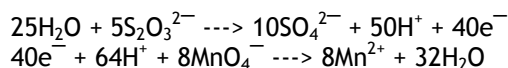
1) Half-reactions:



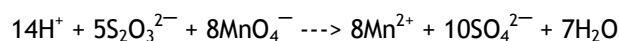
2) Balance:



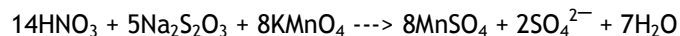
3) Equalize electrons:



4) Add:



5) Add 14 nitrates, 10 sodium and 8 potassium to the left:

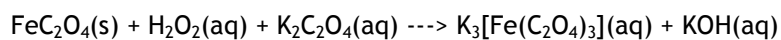


I also formed 8 MnSO₄ on the right side.

6) Four sodium with the two sulfates, the other six sodium with six nitrates and the eight potassium with the remaining 8 nitrates:

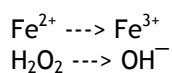


Example

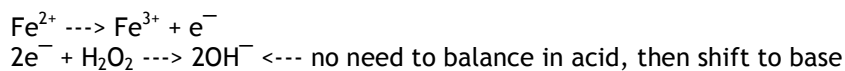


Solution:

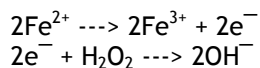
1) Half-reactions:



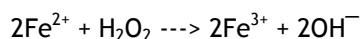
2) Balance:



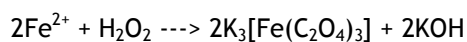
3) Equalize electrons:



4) Add:

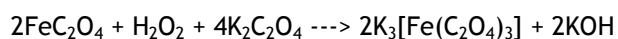


5) Make molecular formulas on the right:

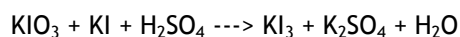


I added eight potassium ions as well as six oxalate ions.

6) Add two oxalates to the two ferrous ions and make four potassium oxalates:

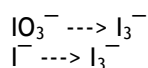


Example

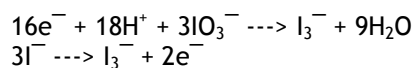


Solution:

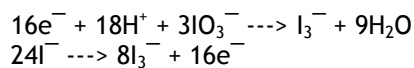
1) Half-reactions:



2) Balance:



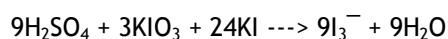
3) Equalize electrons:



4) Add:

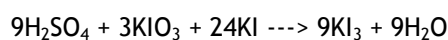
$18\text{H}^+ + 3\text{IO}_3^- + 24\text{I}^- \rightarrow 9\text{I}_3^- + 9\text{H}_2\text{O}$ <--- I could take out a factor of three before making everything molecular. I missed that when I answered this question on Yahoo Answers, but I get rid of the factor of 3 at the end.

5) Make the left-hand side molecular:

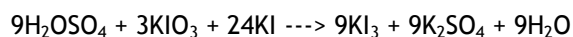


I did that by adding nine sulfates and 27 potassium ion.

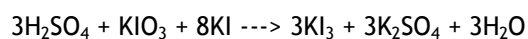
6) Add 9 potassium ion to the right:



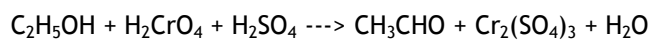
7) I have 18 K^+ and 9 SO_4^{2-} still to add:



8) Remove a factor of 3:

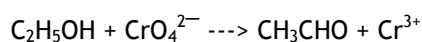


Example

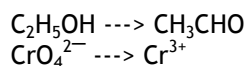


Solution:

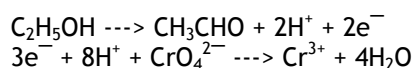
1) Write the net-ionic equation:



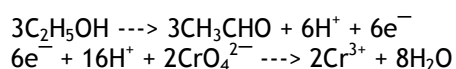
2) Half-reactions:



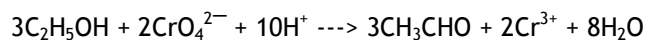
3) Balance in acidic solution:



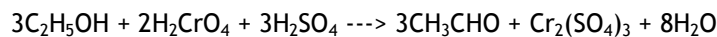
4) Equalize electrons:



5) Add:



6) Add in three sulfate ions:

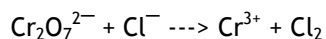


Example

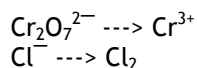


Solution:

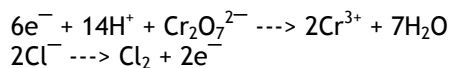
1) Write the net-ionic equation:



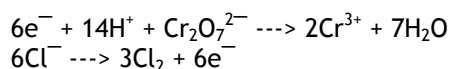
2) Half-reactions:



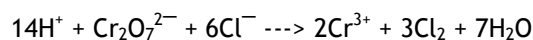
3) Balance half-reactions in acidic solution:



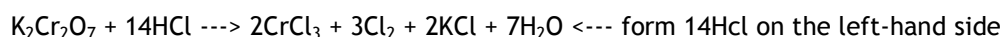
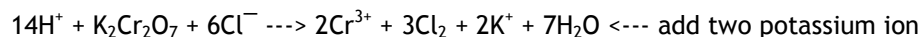
4) Equalize electrons:



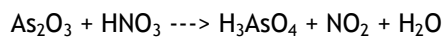
5) Add:



6) Restore molecular equation:

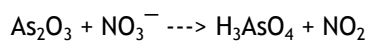


Example

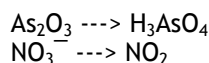


Solution:

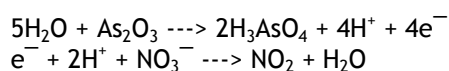
1) Write the net-ionic equation:



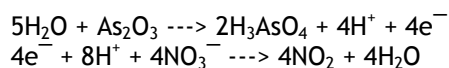
2) Half-reactions:



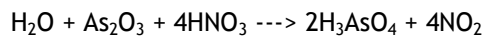
3) Balance:



4) Equalize electrons:



5) Add:



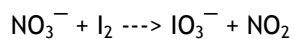
I put the 4 hydrogen ions and the 4 nitrate ions back together as well.

Example

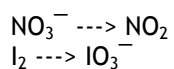


Solution:

1) Write the net-ionic equation:

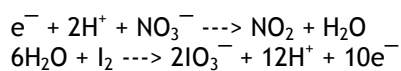


2) Half-reactions:

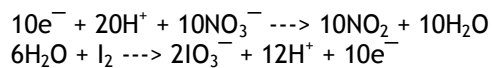


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SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

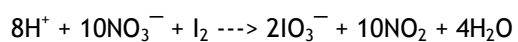
3) Balance:



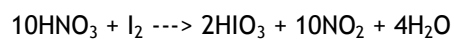
4) Equalize electrons:



5) Add:



6) Add two hydrogen ion and make nitric acid as well as iodic acid:



-

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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 :

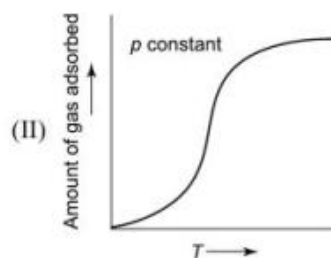
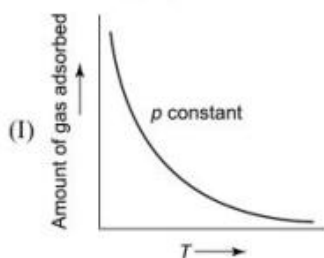
The stability of lyophobic colloidal particles is due to the preferential adsorption of common ion from the solution. Each colloidal particle has the same charge and are thus kept away from each other due to electronic repulsion (choice a).

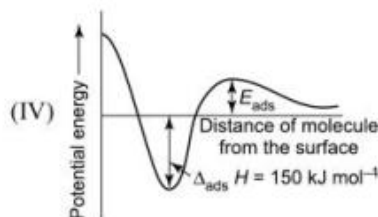
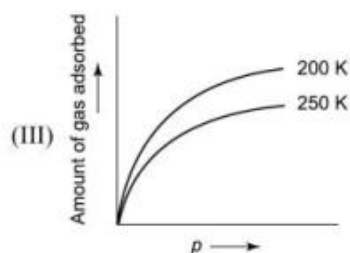
There exists potential difference between the fixed and diffused layer of opposite charge (choice d).

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

Physisorption 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

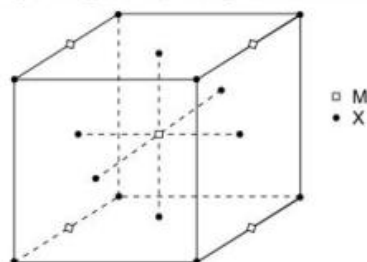
Graph III represents physisorption

Graph II represents chemisorption

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.

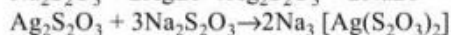
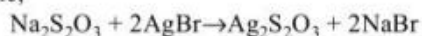
HCl HBr and HI react with $AgNO_3$ to give a precipitate that dissolves in $Na_2S_2O_3$

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,



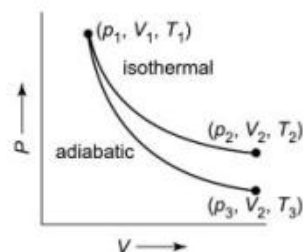
AgF is soluble in water.

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 expense 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 | $K_a = \frac{[H^+][A^-]}{[HA]}$ |
| Adiabatic 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 | $\Delta T_b = i K_b \times \text{molality}$ |
| Buffer Design Equation | $pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$ |
| Cell Voltage | $E_{cell} = E_{cell}^\circ - \frac{RT}{n\mathfrak{F}} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q$ |
| 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 | $E_n = -R_H \left(\frac{1}{n^2} \right) = \frac{-2.178 \times 10^{-18}}{n^2} \text{joule}$ |

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 | $E_{cell} = E_{cell}^{\circ} - \frac{RT}{n\mathcal{F}} \ln Q = E_{cell}^{\circ} - \frac{0.0592}{n} \log Q$ |
| Electric Current | $I = \frac{q}{t}$ |
| Reaction Quotient | $Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ where $aA + bB \rightarrow cC + dD$ |
| 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 | $K_w = [OH^-][H^+] = K_a \times K_b$ $= 1.0 \times 10^{-14}$ at $25^{\circ}C$ |
| 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

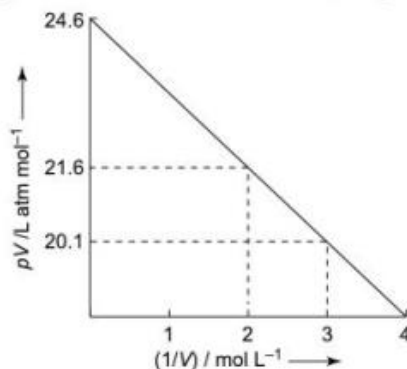
| DESCRIPTION | EQUATION |
|---------------------------|---|
| Adiabatic change | $PV = k$ |
| Boiling Point Elevation | $\Delta T_b = iK_b \times \text{molality}$ |
| Charles' Law | $\frac{V}{t} = k$ |
| Combined Gas Law | $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$ |
| Density of a Material | $D = \frac{m}{V}$ |
| Freezing Point Depression | $\Delta T_f = iK_f \times \text{molality}$ |
| 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 | $\frac{KE}{\text{mole}} = \frac{3}{2}RT$ |
| Kinetic Energy per Mole | $\frac{KE}{\text{mole}} = \frac{3}{2}RT$ |

Thermochemistry

| DESCRIPTION | EQUATION |
|--------------------------|--|
| Acid Ionization Constant | $K_a = \frac{[H^+][A^-]}{[HA]}$ |
| Adiabatic 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 | $\Delta T_b = i K_b \times \text{molality}$ |
| Buffer Design Equation | $pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$ |
| Cell Voltage | $E_{cell} = E_{cell}^\circ - \frac{RT}{n\mathcal{F}} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q$ |
| 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) $1.0 \text{ L}^2 \text{ atm mol}^{-2}$ (b) $4.5 \text{ L}^2 \text{ atm mol}^{-2}$ (c) $1.5 \text{ L}^2 \text{ atm mol}^{-2}$ (d) $3.0 \text{ L}^2 \text{ atm mol}^{-2}$

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 $\frac{(20.1 - 21.6) \text{ L atm mol}^{-1}}{(3.0 - 2.0) \text{ mol L}^{-1}} = -1.5 \text{ L}^2 \text{ atm mol}^{-2}$

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

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 $K_b = 0.76 \text{ K kg mol}^{-1}$) 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

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

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

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{n_2}{m_1/M_1} = \frac{(2/7.6) \text{ mol}}{(100 \text{ g}/18 \text{ g mol}^{-1})} = \frac{36}{760}$$

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

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

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

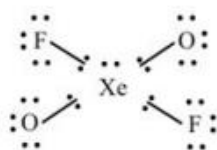
Shape of XeO_2F_2 molecule is seesaw

The shape of XeO_2F_2 molecule is

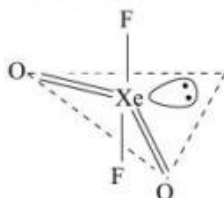
- (a) trigonal bipyramidal (b) square planar (c) tetrahedral (d) see-saw

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 pairs of electrons around Xe. To accommodate these, Xe undergoes dsp^3 hybridization leading to the trigonal bipyramidal arrangement of five pairs 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 , $1^\circ X$, $2^\circ X$, $3^\circ X$,

Increasing reactivity sequence of S_N2 displacement of halogen: CH_3X , $1^\circ X$, $2^\circ X$, $3^\circ X$.

Increasing reactivity of alcohols towards gaseous HBr:

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

Increasing order of reactivity towards E2 dehydrohalogenation of the bromides:

ethyl bromide, *n*-propyl 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:

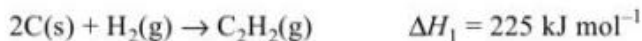
2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane

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 C₂H₂.

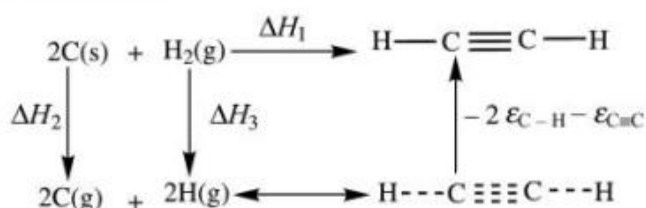


Take the bond energy of C—H bond equal to 350 kJ mol⁻¹.

- (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 $\Delta H_1 = \Delta H_2 + \Delta H_3 - 2\varepsilon_{\text{C-H}} - \varepsilon_{\text{C}\equiv\text{C}}$

This gives

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

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

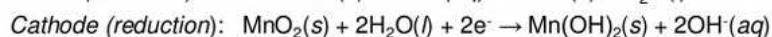
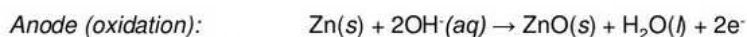
Most ionic compound = CsF

Strongest base = Cs (OH)

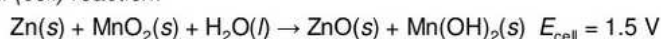
Strongest basic oxide = Cs₂O

Most conducting metal = Ag

Zinc and Magnesium Oxide Battery

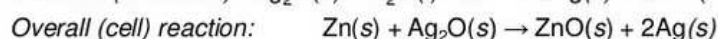
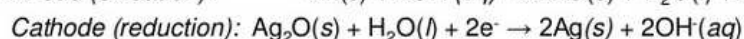
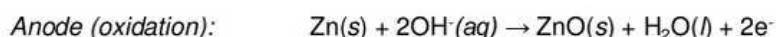


Overall (cell) reaction:



-

Zinc and Magnesium Oxide Battery



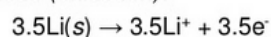
$$E_{\text{cell}} = 1.6 \text{ V}$$

The mercury battery uses HgO as the oxidizing agent instead of Ag₂O and has cell potential of 1.3 V.

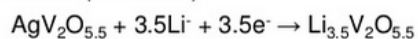
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The Lithium Batteries use Silver Vanadium Pentoxide as cathode

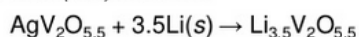
Anode (oxidation):



Cathode (reduction):



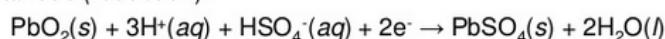
Overall (cell) reaction:



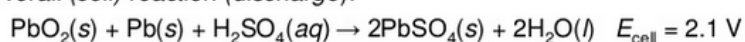
The most commonly used Battery is Lead-Acid Battery



Cathode (reduction):



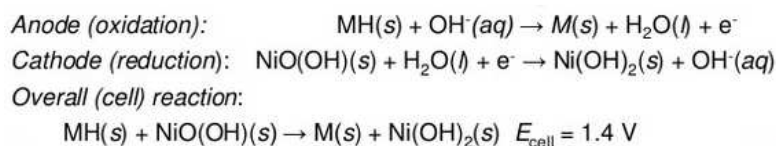
Overall (cell) reaction (discharge):



Overall (cell) reaction (recharge):

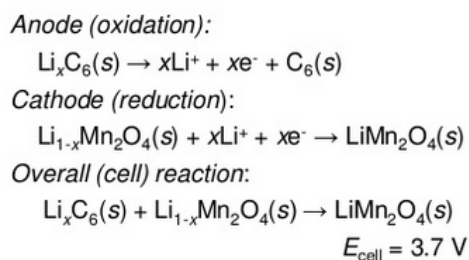


Nickel Metal Hydride Battery



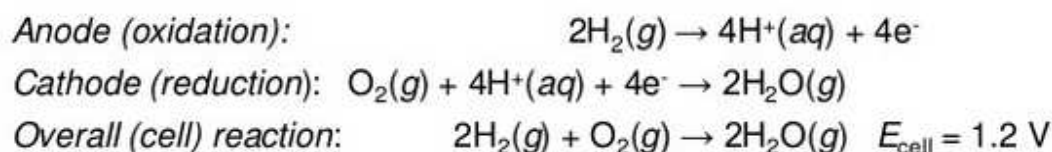
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Laptops, Cell-phones most commonly use Lithium ion Batteries



-

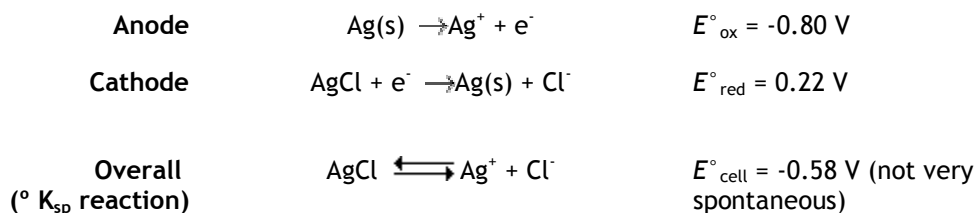
Hydrogen Fuel Cell



-

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:



$$\ln K = \frac{nFE^\circ}{RT} = \frac{1 \times 96485 \frac{C}{mol} (-0.58V)}{8.3145 \frac{J}{mol K} \times 298.15K} = 22.5744$$

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

Ion Concentrations can also be calculated...

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

The overall reaction is $\text{Cu}^{2+} + \text{H}_2 \rightarrow \text{Cu} + 2\text{H}^+$.

The Nernst equation is

$$E = E^\circ - \frac{8.31451 \frac{\text{J}}{\text{mol K}} \times 298.15 \text{ K}}{2 \text{ mol} \times 96485 \frac{\text{C}}{\text{mol}}} \times \ln \left(\frac{a(\text{H}^+)^2}{a(\text{Cu}^{2+}) \times a(\text{H}_2)} \right)$$
$$E = E^\circ - \frac{.0257 \text{ V}}{2} \times \ln \left(\frac{a(\text{H}^+)^2}{a(\text{Cu}^{2+}) \times a(\text{H}_2)} \right) \quad \text{since}$$

$$\frac{8.31451 \frac{\text{J}}{\text{mol K}} \times 298.15 \text{ K}}{96485 \frac{\text{C}}{\text{mol}}} = .0256928 \text{ V}$$

If $[\text{Cu}^{2+}] = 1 \text{ M}$ and $P(\text{H}_2) = 1 \text{ bar}$ (both their activities are 1) then

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

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

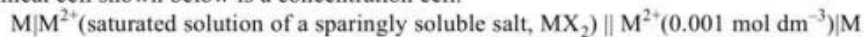
$$E = E^\circ + 0.05917 \text{ V} (-\log [\text{H}^+])$$

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

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.



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.

Q The solubility product (K_{sp}) of MX_2 at 298 K based on the information available for the given concentration cell (take $2.303 RT/F = 0.059 \text{ V}$ at 298 K) is

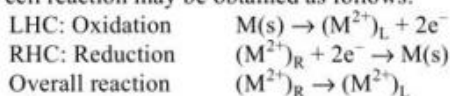
- (a) $1 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$ (b) $4 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$
(c) $1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$ (d) $4 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

Q The value of ΔG for the given cell reaction (take $1F = 96500 \text{ C mol}^{-1}$) is

- (a) -5.7 kJ mol^{-1} (b) 5.7 kJ mol^{-1} (c) 11.4 kJ mol^{-1} (d) $-11.4 \text{ kJ mol}^{-1}$

Solutions :

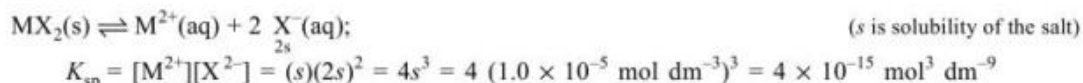
The cell reaction may be obtained as follows.



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



The ΔG of the cell reaction is

$$\Delta G = -nFE = -(2)(96500 \text{ C mol}^{-1})(0.059 \text{ V}) = -11387 \text{ J mol}^{-1} = -11.4 \text{ kJ mol}^{-1}$$

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 , loses electrons, it is getting oxidized. Metals are basic. Metals lose electrons and get oxidized. The metals which lose electron very easily, get oxidized very easily. So these are better reducing agents.

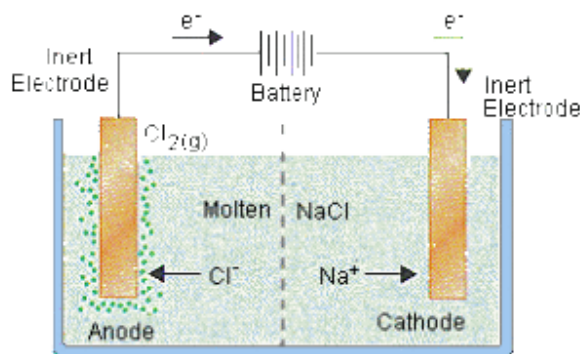
Adding of Oxygen, or Halogens (F, Cl, Br, I) or other p-Block elements which accept electrons, is oxidation. So if Potassium (K) gets Oxygen (attaches to O) to form K_2O or KO_2 (Superoxide), K is getting oxidized. If Cs attaches with F then Cs is getting oxidized, while F is being reduced. Cs is a reducing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



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)



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

Reaction at the ANODE:

- Cl^- ions are attracted to the anode.

CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams

- 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.
- $Mg^{2+}(l) + 2e^- \rightarrow Mg(s)$

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.
- $2MgO(l) \rightarrow 2Mg(s) + O_2(g)$

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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 $\text{A B} \rightleftharpoons \text{A}^+ + \text{B}^-$

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

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

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

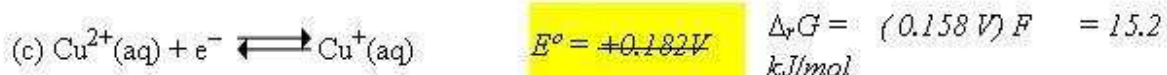
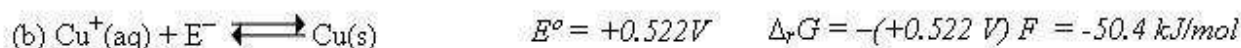
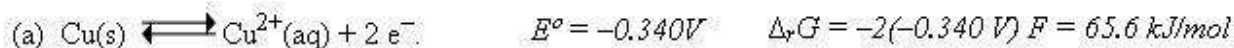
This equation represents the variation of degree of dissociation with dilution and is known as **Ostwald dilution law**. This is law of mass action applied to weak electrolytes. In case of weak electrolytes, the value of a is very small as compared to unity and hence may be neglected in the denominator.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

Gyan Question :

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

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.

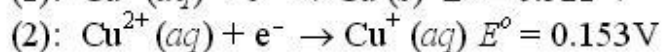
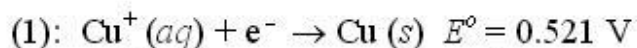
The two reactions that will occur are:



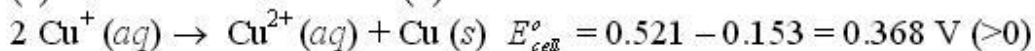
Now, since $E^\circ = -v \Delta_r G/F = -0.158\text{V}$ ($v = 1$ in the final equation)

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

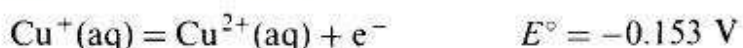
If the final reaction is a complete cell reaction, with no electrons remaining, then we can skip to just adding the cell potentials because the factor v would be the same in all equations and hence, cancel out.



(1) is reduction and drives (2) as oxidation



Which means $E_{\text{cell}}^\circ > 0$ and $\Delta G_{\text{rxn}}^\circ < 0$ spontaneous. Yes it disproportionates.



We have value of K

$$\begin{aligned} \ln K &= \frac{nFE^\circ}{RT} \\ &= \frac{(1)(96485)(0.368)}{(8.314)(298.15)} = 14.3. \end{aligned}$$

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

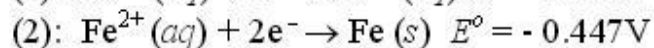
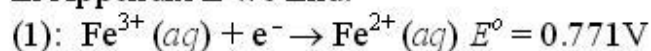
The large K indicates that the point of equilibrium in the **reaction** is far toward products, and disproportionation will occur until a_{Cu^+} becomes very

small

Discuss Disproportion of Iron

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

In Appendix E we find:



In order for $\text{Fe}^{2+}(\text{aq})$ to disproportionate reaction (1) would have to be driven backwards (oxidation): $3\text{Fe}^{2+} \rightarrow \text{Fe}(\text{s}) + 2\text{Fe}^{3+}(\text{aq})$

And $E^\circ = -0.447 - (+0.771) = -1.218\text{V} (< 0)$ and $\Delta G_{\text{rxn}}^\circ > 0$ (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) $10x$ (b) $100x$ (c) $10^5 / x$ (d) $10^5 x$

$$C = 0.01\text{ M} = 0.01\text{ N (for HCN)}$$

$$\therefore V = \frac{1}{0.01} = 100 \text{ litres/eq}$$

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

$$kv = \frac{1}{\text{Specific resistance}}$$
$$= \frac{1}{x} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductance

$$\lambda_v = kv \times V$$

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

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

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, 3.292×10^{-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,

$$\frac{\text{Weight of } H_2}{\text{Weight of Cu}} = \frac{\text{Eq. Wt. of } H_2}{\text{Eq. Wt. of Cu}} = \frac{1.008}{31.78}; \quad \frac{\text{Weight of Cu}}{\text{Weight of Ag}} = \frac{\text{Eq. Wt. of Cu}}{\text{Eq. Wt. of Ag}} = \frac{31.78}{107.88}$$

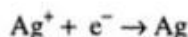
The quantity of electricity required to liberate one gm equivalent of each element is calculated as,

$$\text{Hydrogen} : [1.008/1.036 \times 10^{-5}] = \mathbf{96515 \text{ Coulombs}}$$

$$\text{Copper} : [31.78/3.292 \times 10^{-4}] = \mathbf{96567 \text{ Coulombs}}$$

$$\text{Silver} : [107.88/1.118 \times 10^{-3}] = \mathbf{96494 \text{ Coulombs}}$$

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



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 deposit 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

$$F = e \times N = 1.603 \times 10^{-19} \times 6.023 \times 10^{23} = \mathbf{96500 \text{ Coulombs.}}$$

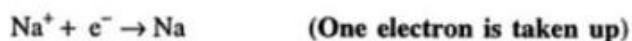
This fact can be used in calculating the electrochemical equivalents. For example,

$$\text{Electrochemical equivalent of silver} = \frac{\text{Eq. Wt of Ag}}{96500} = \frac{107.88}{96500} = 1.118 \times 10^{-3} \text{ g.}$$

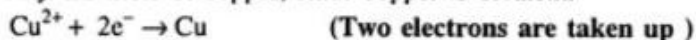
$$\text{Electrochemical equivalent of copper} = \frac{\text{Eq. Wt of Cu}}{96500} = \frac{31.78}{96500} = 3.292 \times 10^{-4} \text{ g.}$$

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 6.023×10^{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.



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.



If one Faraday 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.



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,

$$M = e.Z.F \quad \text{..... (3)}$$

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

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

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 ($=c \times t$) 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

$$\frac{1 \text{ gm. Atomic Weight}}{2} = \frac{63.5}{2} = 31.8 \text{ g.}$$

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

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

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

$$\lambda_v = K_v \times V \quad \dots (9)$$

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 sufficiently 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

$$\lambda_m = K_v \times V \quad \dots (10)$$

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 in order to get specific conductivity. This factor is known as **cell constant**. We know

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

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

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

In order 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°C has been found to be 0.002765 mhos. The cell is placed in a thermostat at 25°C and the resistance and hence the conductivity of the solution is determined. Thus

$$\text{Cell Constant} = \frac{0.002765}{\text{Observed conductivity}}$$

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

The important conditions for the cell to be reversible are :

- 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.
- 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.
- 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.
- 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 (because 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

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

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. $\text{CdI}_2 \rightleftharpoons \text{Cd}^{2+} + 2\text{I}^-$. (b) That with increase in concentration, CdI_2 takes on I^- ions and forms complex, $\text{CdI}_2 + 2\text{I}^- \rightleftharpoons [\text{CdI}_4]^{2-}$

Thus the concentrated solution contains both +vely charged Cd^{2+} ions and negatively charged $[\text{CdI}_4]^{2-}$ 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 concentration of electrolyte CdI_2 , higher the concentration of CdI_2 greater would be the proportion of the complex $[\text{CdI}_4]^{2-}$ ion. Thus, if anion $[\text{CdI}_4]^{2-}$ 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, $(\text{Hg}^{2+} + \text{Ag} \rightarrow \text{Ag}^+ + \text{Hg})$

Comment on the feasibility of the reaction under the different concentrations of ions given below

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

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

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

(B) For a process, $\text{Water} \rightleftharpoons \text{ice}$, the enthalpy change $\Delta H = -500 \text{ J/mol}$; $T = 100\text{K}$; $P = 1 \text{ atm}$.

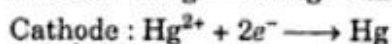
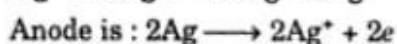
What will be the values of

(i) Entropy change ΔS

(ii) Free energy change ΔG ?

Sol. (A) $E^0_{\text{cell}} = E^0_{\text{C}} - E^0_{\text{A}} = 0.79 - 0.80 = -0.01 \text{ V}$

The net cell reaction is



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

So Reaction not feasible as $E(\text{cell})$ is negative

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

∴ Feasible because E_{cell} is + ve.

(B) The given process is



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

(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,

$$\lambda_{\infty} = \lambda_a + \lambda_c \quad \dots(12)$$

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,

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

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)**.

$$\text{Thus,} \quad U = \frac{\lambda_a}{96500} \quad V = \frac{\lambda_c}{96500}$$

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

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

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 $\lambda_{\infty} = \lambda_a + \lambda_c$)

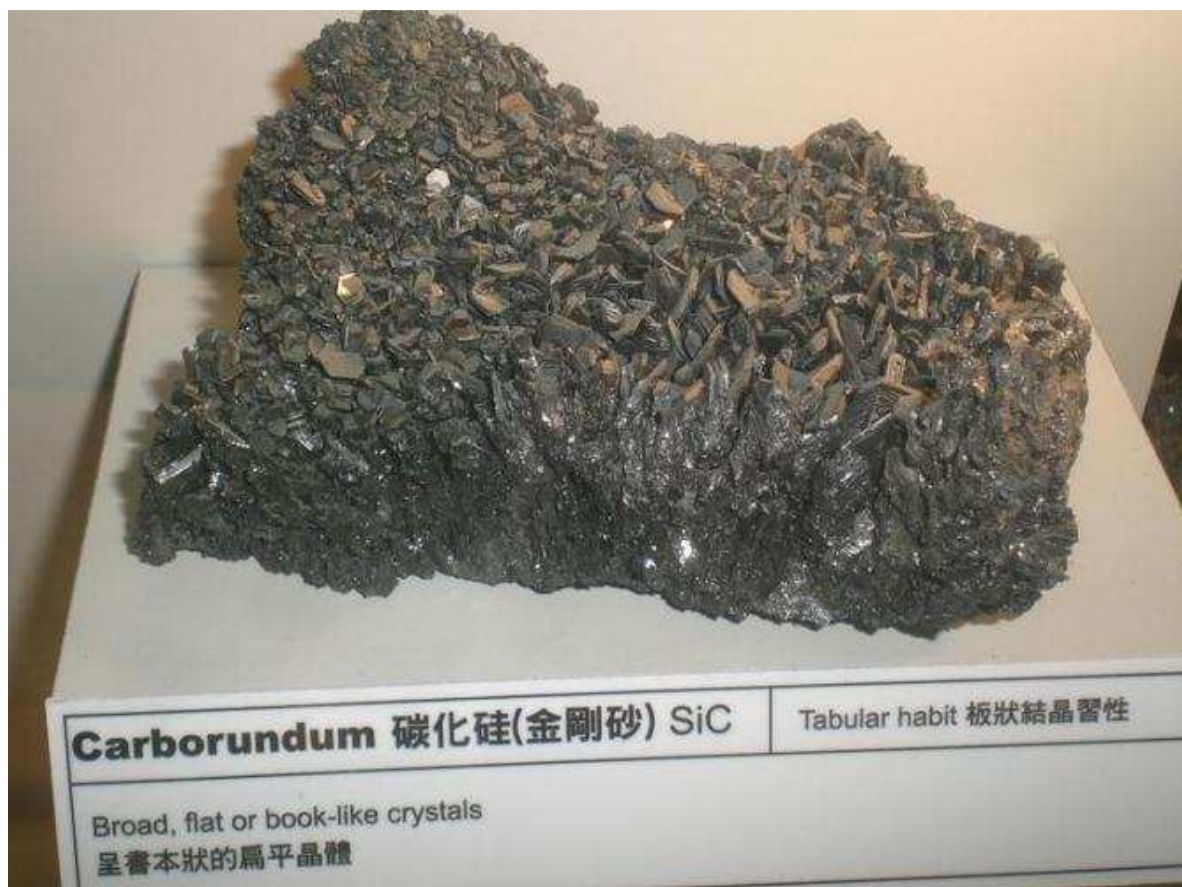
Gyan Question :

Q : What is carborundum ? Does it conduct electricity ?

Ans :

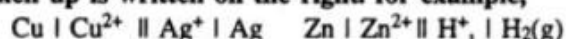
Silicon carbide, also known as carborundum, is a compound of silicon and carbon with chemical formula SiC . It occurs in nature as the extremely rare mineral moissanite. Silicon carbide powder has been mass-produced since 1893 for use as an abrasive.

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.



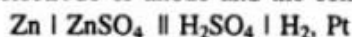
Relative tendencies of electrodes to liberate electrons – When two electrodes are connected to from a cell, a competition sets in between the two electrodes to liberate electrons. For example, if the cell consists of zinc and copper electrodes, as in Daniell cell, the electrons flow from negative zinc 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,



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

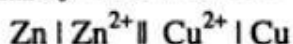
Also remember that the metal which goes into the solution in the form of its salt is undergoing oxidation and thus will act as negative electrode (anode), while the other metal acts as positive electrode (cathode). For example, in the reaction $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$, the Zn is oxidised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



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 :



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

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

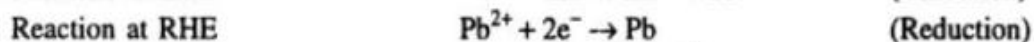
Reaction at RHE $Cu^{2+} + 2e^- \rightleftharpoons Cu$ (Reduction)

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

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

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

To calculate the E°_{CELL} of the cell $\text{Zn} | \text{Zn}^{2+} || \text{Pb}^{2+} | \text{Pb}$



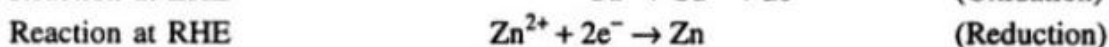
$$E^{\circ}_{\text{CELL}} = E^{\circ}_{\text{RHE}} - E^{\circ}_{\text{LHE}} = E^{\circ}_{(\text{Pb}^{2+}, \text{Pb})} - E^{\circ}_{(\text{Zn}^{2+}, \text{Zn})} = -0.130 - (-0.76) = -0.130 + 0.76 = +0.640 \text{ V.}$$

As the E°_{CELL} is **positive**, the above reaction is **spontaneous and thus cell is a source of electricity**.

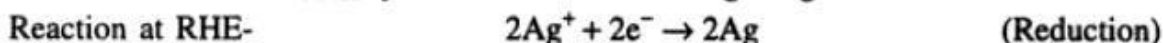
To calculate E°_{CELL} of the cell $\text{Cu} | \text{Cu}^{2+} | \text{Zn}^{2+} | \text{Zn}$

$$E^{\circ}_{\text{CELL}} = E^{\circ}_{\text{RHE}} - E^{\circ}_{\text{LHE}} = E^{\circ}_{(\text{Zn}^{2+}, \text{Zn})} - E^{\circ}_{(\text{Cu}^{2+}, \text{Cu})} = -0.76 - (+0.34) = -1.10 \text{ Volts.}$$

Since the E°_{CELL} is **negative**, the reaction, $\text{Cu} + \text{Zn}^{2+} \rightleftharpoons \text{Cu}^{2+} + \text{Zn}$ is **non-spontaneous**.



To calculate E°_{CELL} of the cell $\text{Cu} | \text{Cu}^{2+} || \text{Ag}^{+} | \text{Ag}$

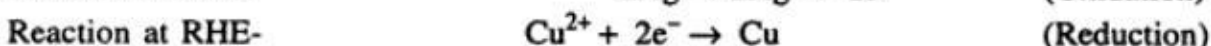


$$E^{\circ}_{\text{CELL}} = E^{\circ}_{\text{RHE}} - E^{\circ}_{\text{LHE}} = E^{\circ}_{(\text{Ag}^{2+}, \text{Ag})} - E^{\circ}_{(\text{Cu}^{2+}, \text{Cu})} = 0.8 - 0.34 = 0.46\text{V}$$

Since the E°_{CELL} is **positive**, the cell reaction is **spontaneous**.

To calculate E°_{CELL} of the cell $\text{Ag} | \text{Ag}^{+} || \text{Cu}^{2+} | \text{Cu}$

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

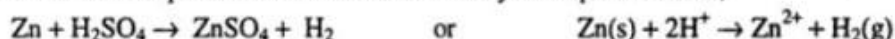


Since E°_{CELL} is **negative**, the above reaction is **non-spontaneous**.

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 $M_1 \rightarrow M_1^{+} + \text{e}^{-}$ and M_2^{+} is reduced as $M_2^{+} + \text{e}^{-} \rightarrow M_2$. 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 $\text{Al} | \text{Al}^{3+}$ (+1.66V) is greater than $\text{Ni} | \text{Ni}^{2+}$ (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 reducing agent. Hence lower the reduction potential stronger the reducing agent. The decreasing order of the reducing property of some of the metals is $\text{Na} > \text{Mg} > \text{Zn} > \text{Fe} > \text{Cu} > \text{Ag}$ (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,



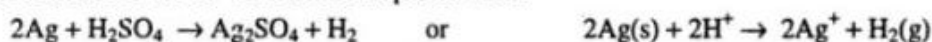
This reaction is a combination of two half cells.



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, $\text{Zn, Zn}^{2+} \parallel \text{H}^+, \text{H}_2(\text{g}), \text{Pt}$

$$\text{Thus } E_{\text{CELL}}^{\circ} = E_{\text{RHE}}^{\circ} - E_{\text{LHE}}^{\circ} = E_{\text{(H}^+, \text{H}_2)}^{\circ} - E_{\text{(Zn}^{2+}, \text{Zn})}^{\circ} = 0 - (-0.76\text{V}) = +0.76 \text{ V}$$

Since E_{CELL}° is positive, the reaction of zinc with hydrogen is spontaneous or feasible. Now consider the reaction of silver with dilute sulphuric acid.



The cell may be represented as $\text{Ag, Ag}^+ \parallel \text{H}^+, \text{H}_2(\text{g}), \text{Pt}$

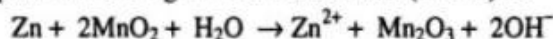
$$E_{\text{CELL}}^{\circ} = E_{\text{(H}^+, \text{H}_2)}^{\circ} - E_{\text{(Ag}^+, \text{Ag})}^{\circ} = 0 - (0.80) = -0.80 \text{ V}$$

Since E_{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.

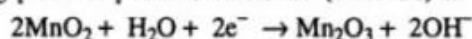
Secondary cells – A secondary cell once used can be recharged by passing current through it and it may, therefore, be used over and over again. Certain chemical changes occur when the cell is charged with electricity and these changes are reversed during discharge.

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



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



The net cell reaction is :

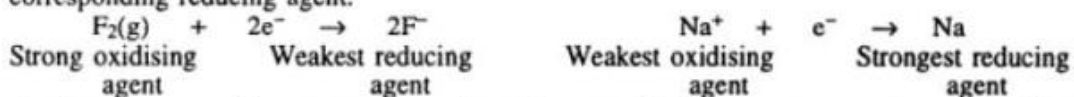


During the electrolysis of fused NaCl, chloride ions are oxidised at anode. If current is passed into the solution of an electrolyte, anions move towards anode and cations move towards cathode. In the electrolysis of dilute H₂SO₄ using platinum electrodes H₂ is evolved at cathode and O₂ is evolved at anode. Electrolytes when dissolved in water dissociate into ions because the forces of electrostatic attraction are broken down by water. Magnesium can liberate H₂ 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 F₂(g) > MnO₄⁻ > Br₂(aq) > Ag⁺ > Cu²⁺ > H⁺ > Pb²⁺ > Zn²⁺ > Na⁺.

Fluorine gas (F₂) 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 > H₂ > Cu > Ag > Br⁻ > Mn²⁺ > 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.



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 $Ag | Ag^+ = 0.8 V$, $2Hg | Hg^{2+} = 0.79 V$, $Cu | Cu^{2+} = 0.34 V$ and $Mg | Mg^{2+} = -2.37 V$. 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.

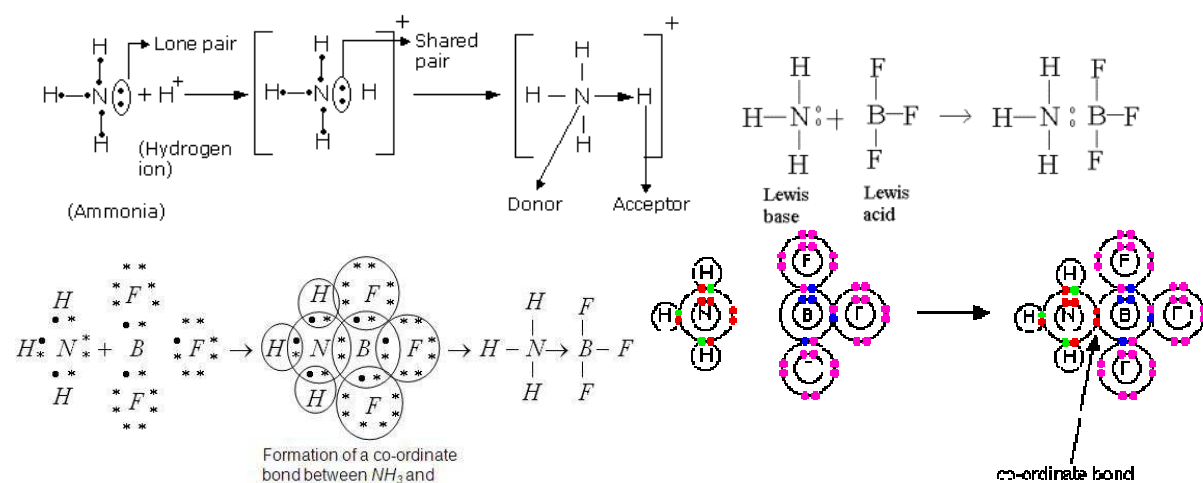
One coulomb = 6.28×10^{28} electrons. **One electric charge** = 1.6×10^{-19} coulombs. In galvanic cell electrical energy is generated at the expense of chemical energy. In an electrolytic cell the chemical energy is generated at the expense of electrical energy. **In an electrolytic cell current flows 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

absorb a large volume of gas, but the process may actually be adsorption on the high surface area of internal pores in the material.

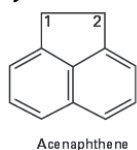
2. The process in which electromagnetic radiation, particles, or sound waves lose energy in passing through a medium. Absorption involves conversion of one form of energy into another.

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.

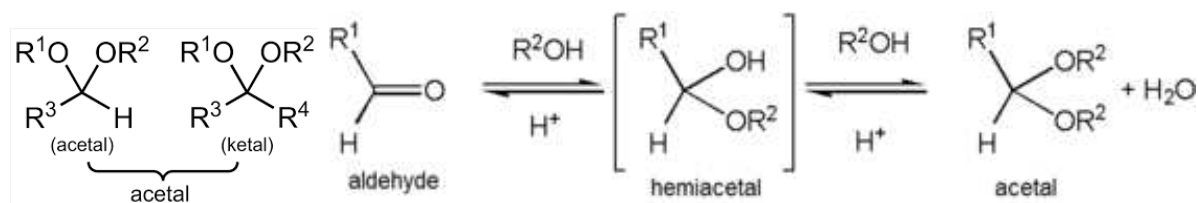
Acceptor - The atom or group to which a pair of electrons is donated in forming a COORDINATE BOND.



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



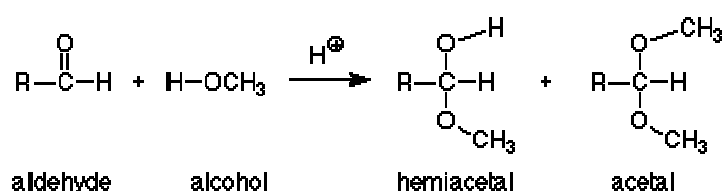
Acetal - A type of compound formed by reaction of an alcohol with either an aldehyde or a ketone. The first step in formation of an acetal is the formation of an intermediate, known as a hemiacetal. For example, ethanal (acetaldehyde; CH_3CHO) reacts with ethanol (C_2H_5OH) as follows: $CH_3CHO + C_2H_5OH \rightleftharpoons CH(OH)(CH_3)(C_2H_5O)$ 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 R_1COR_2 with the alcohol R_3OH is:
 $R_1COR_2 + R_3OH \rightleftharpoons CR_1R_2(OH)(OR_3)$



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 positive 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 hemiacetals with another molecule of alcohol leads to a full acetal. For example:
 $\text{CH}(\text{OH})(\text{CH}_3)(\text{OC}_2\text{H}_5) + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$

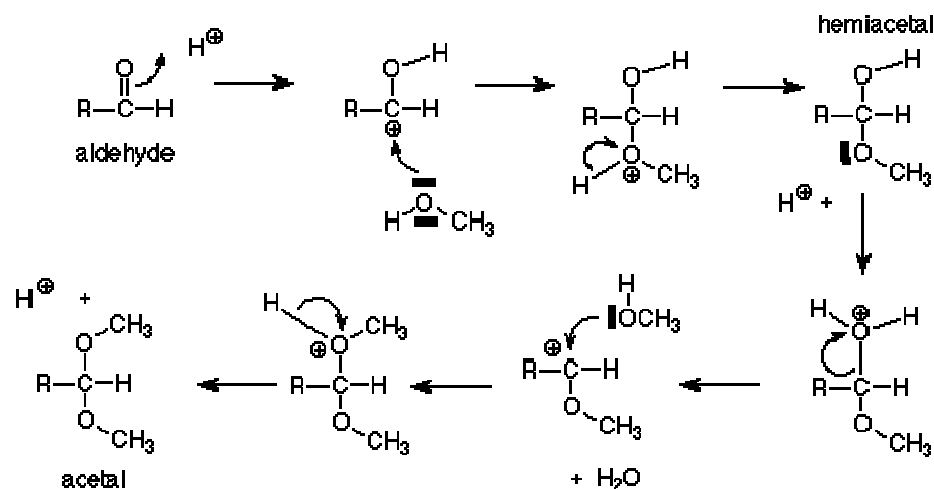


The overall reaction of an aldehyde or ketone with an alcohol to give an acetal can be written: $\text{R}_1\text{COR}_2 + \text{R}_3\text{OH} \rightleftharpoons \text{CR}_1\text{R}_2(\text{OR}_3)_2$

It is also possible to have 'mixed' acetals with the general formula $\text{CR}_1\text{R}_2(\text{OR}_3)(\text{OR}_4)$. 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.

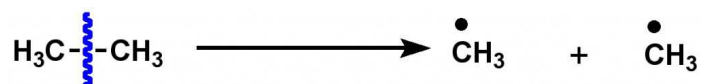


Achiral - Describing a molecule that does not have chiral properties; i.e. one that does not exhibit OPTICAL ACTIVITY.

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.

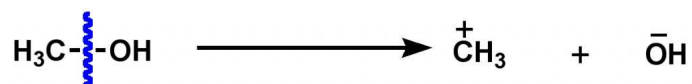
Homolytic fission



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).

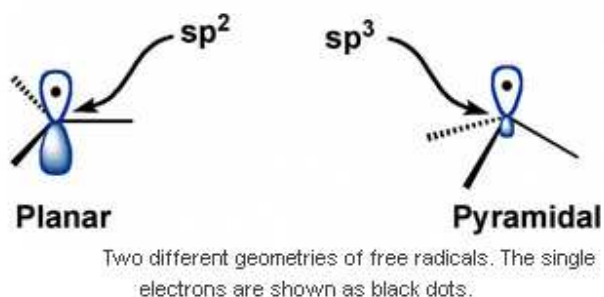
Free radicals

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:

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

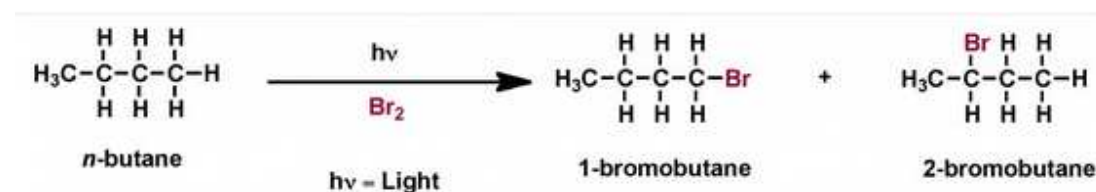
There has been a certain degree of debate as to what the shape and geometry of a free radical is like. Revisiting the theory of hybridization, there can be two basic shapes of these radicals.

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 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.



So to summarize free radicals:

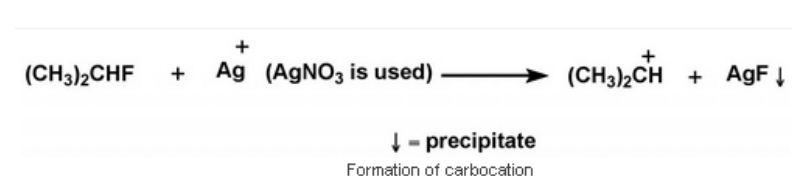
- Formed under activation by light or use of additional compounds called Radical Initiators.
- They are very reactive, because they have an unpaired electron which wants to get paired up.
- They are either pyramidal or planar with the lone electron in their sp^3 or p orbitals respectively.
- Because 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.



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.]

$\text{RX} + \text{NaI} \longrightarrow \text{RI} + \text{NaX}$ 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 $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$ 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 sp² 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 (sp² 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 be 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 sp³ hybridized.

Carbanions are also stable in polar solution (electrostatic stabilization).

To summarize carbanions:

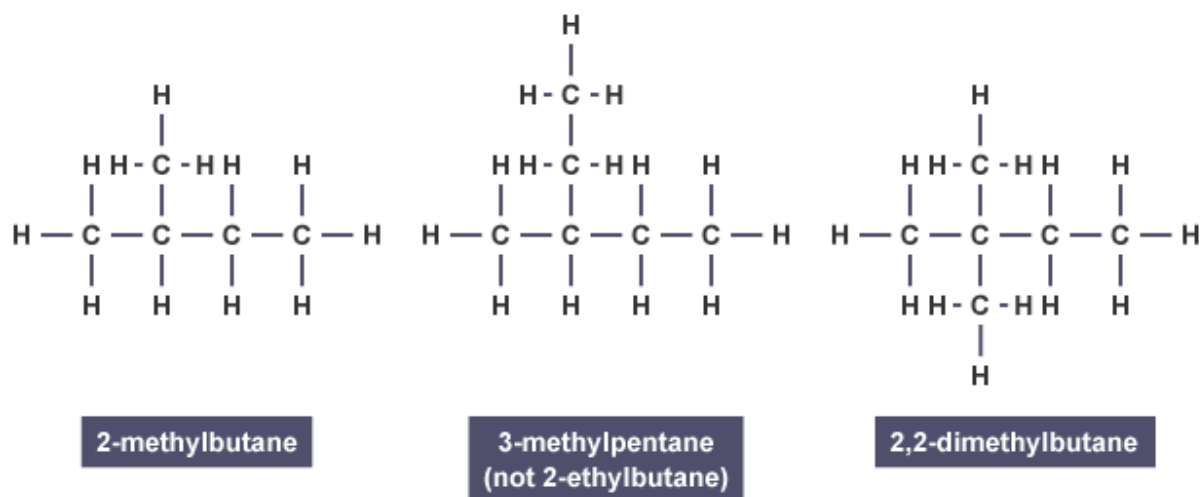
- Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.
- Pyramidal in shape (sp³ hybridized) with the excess electrons placed in one sp³ hybrid orbital.
- Reactive towards positively charged (electron deficient species).

Stability of intermediates

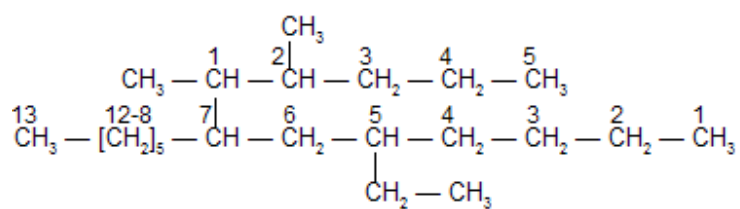
Most organic reactions take place via formation of intermediates. So the study of different intermediates would help us predict the course of the reaction and the main aspect to look at would be their stability. No organic mechanism has been conclusively 'PROVEN', all the mechanisms we see are the most 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.

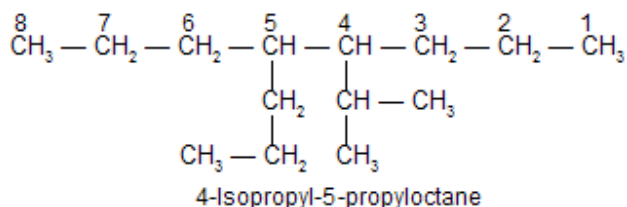
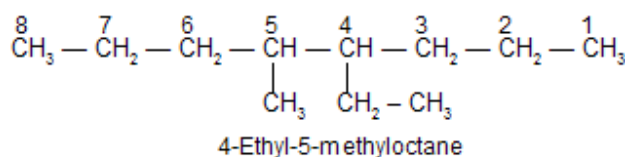


The name of a complex radical is considered to start with the first letter of its complete name.

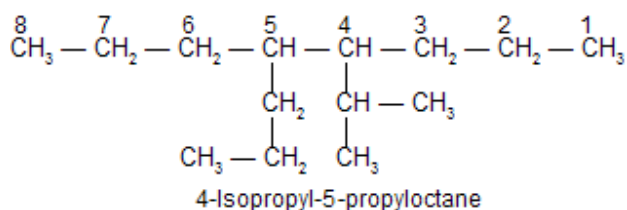
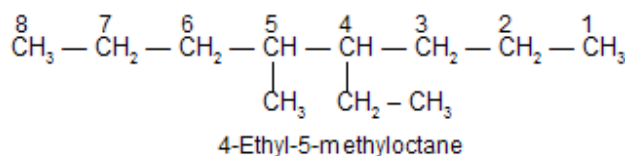


dimethylpentyl (as a complete single substituent) is alphabetized under "d", thus 7-(1,2-Dimethylpentyl)-5-ethyltridecane

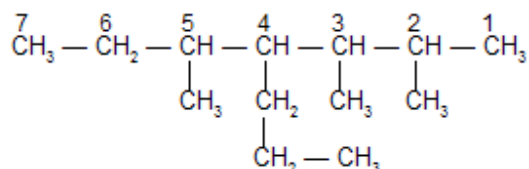
In cases where names of complex radicals are composed of identical words, preference for citation is given to that radical which contains the lowest locant at the first cited point of difference in the radical.



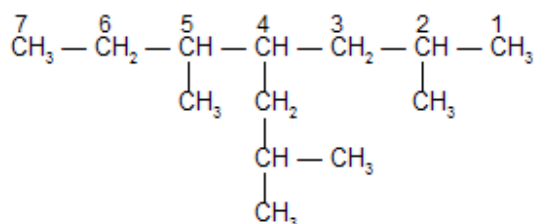
If two or more side chains are in equivalent positions the one to be assigned the lower number is that cited first in the name.



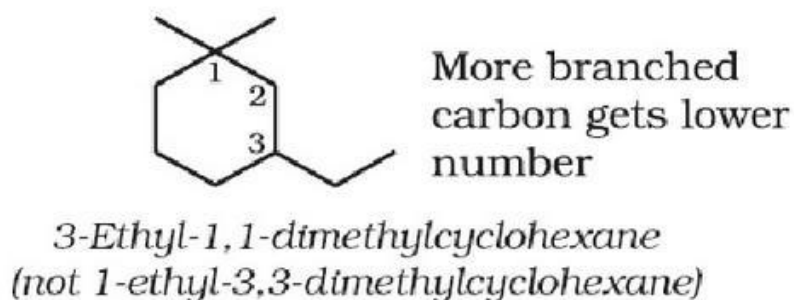
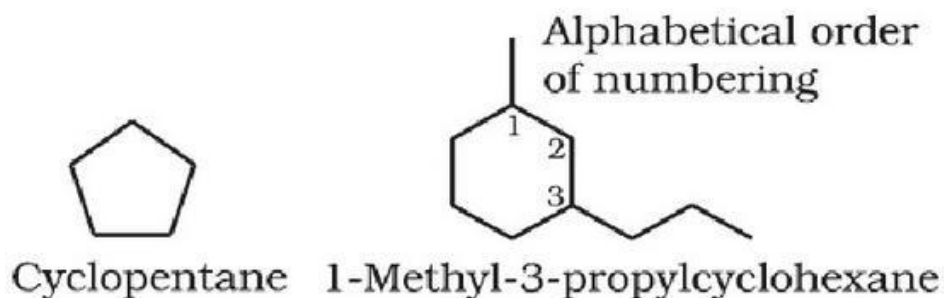
The lowestsum rule.



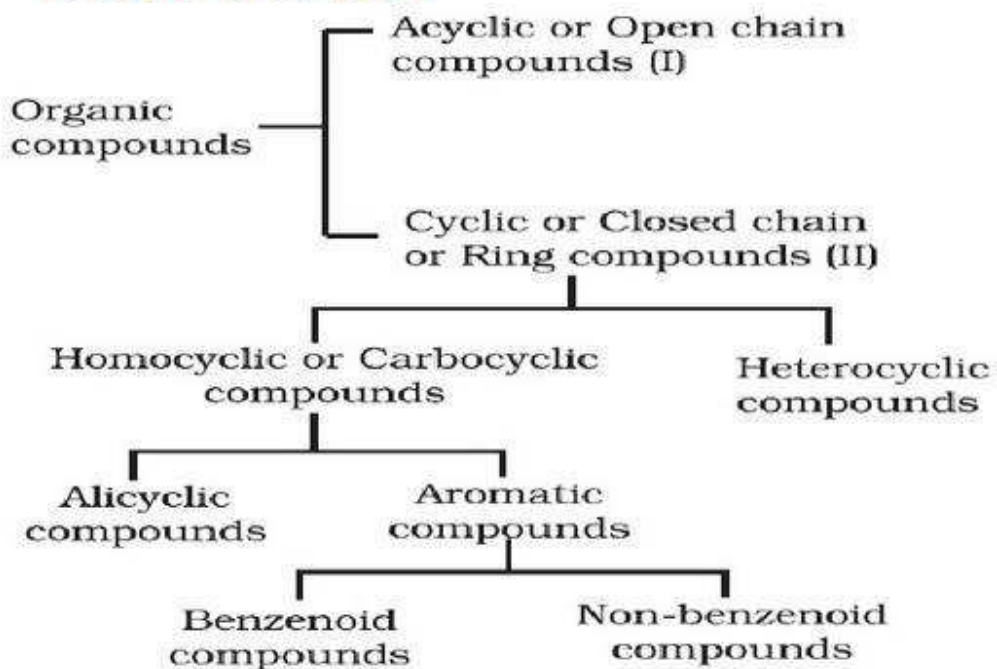
2,3,5-Trimethyl-4-propylheptane (not 3,5,6-Trimethyl-4-propylheptane)



4-Isobutyl-2,5-dimethylheptane (not 4-Isobutyl-2, 6-dimethylheptane)



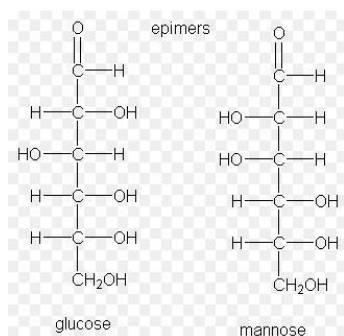
CLASSIFICATION OF ORGANIC COMPOUNDS



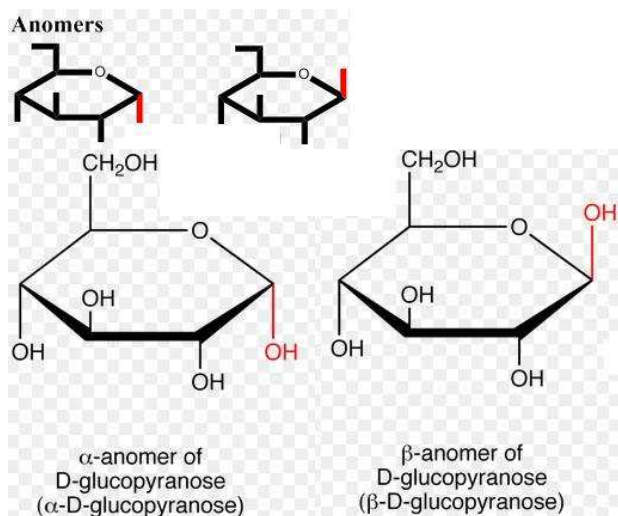
Heating with ethanolic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodamide in an inert solvent shifts the bond towards the end of chain.

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: $-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{COOR}$ ($\text{R}=\text{alkyl group}$), COCl , $-\text{CONH}_2$, $-\text{CN}$, $-\text{HC}=\text{O}$, $>\text{C}=\text{O}$, $-\text{OH}$, $-\text{NH}_2$, $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$.**

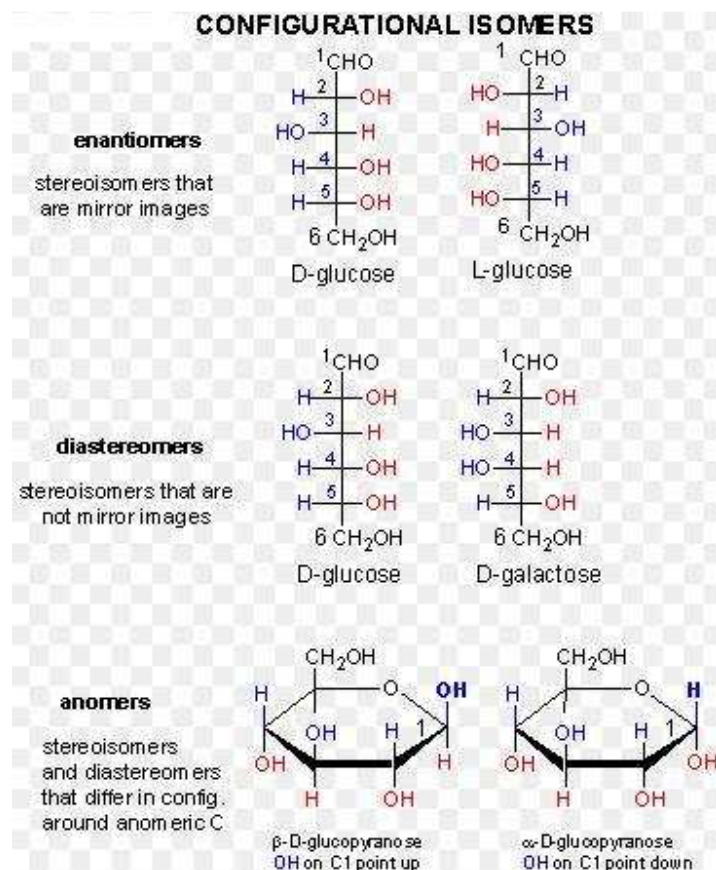
Epimers



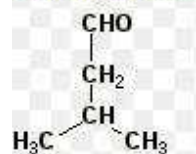
Anomers



Epimer Anomer comparison



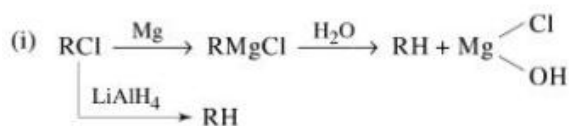
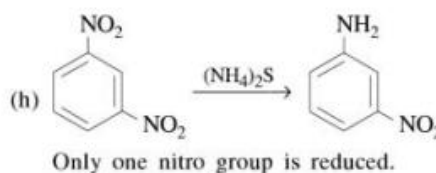
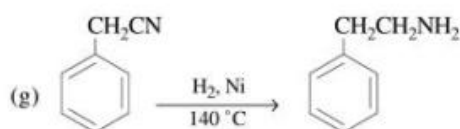
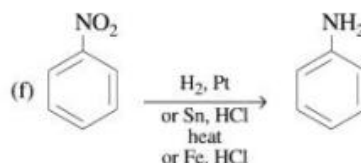
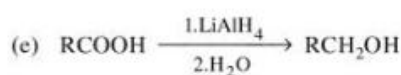
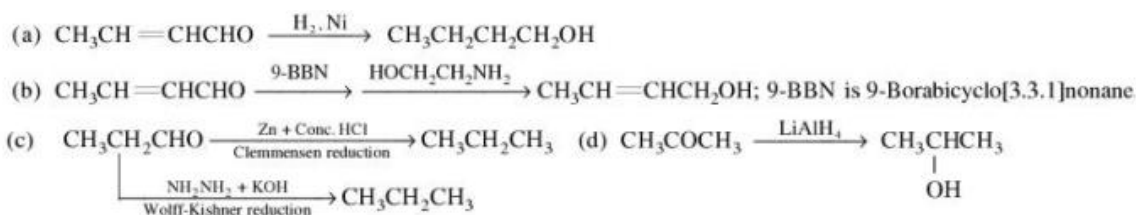
3-Methylbutanal



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 configuration.

Various Methods of Reduction used in Organic Chemistry

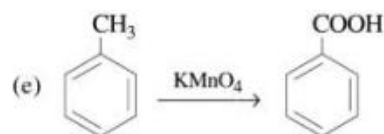
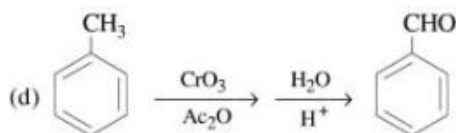
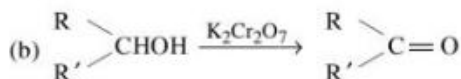
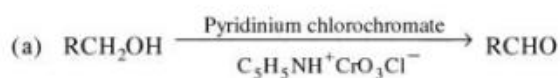


(j) Rosenmund's reduction



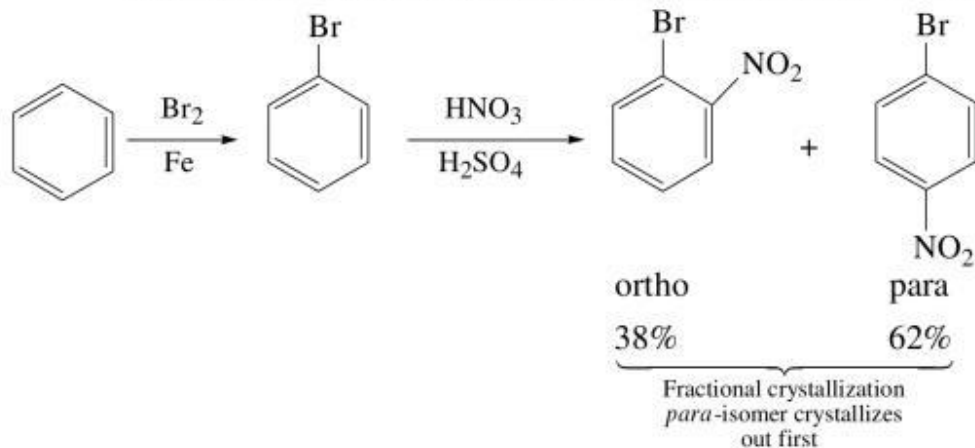
Various methods of Oxidation

Oxidation

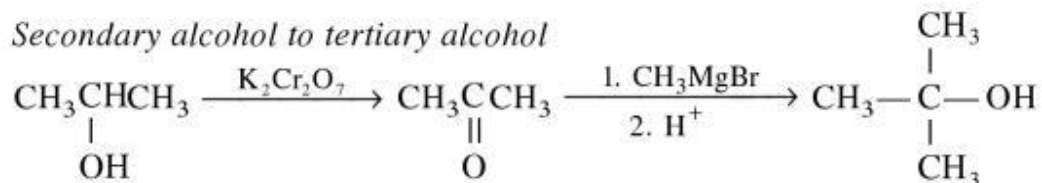


Synthesis of *p*-bromonitrobenzene in 2 steps

a synthesis of *p*-bromonitrobenzene from benzene in two steps.

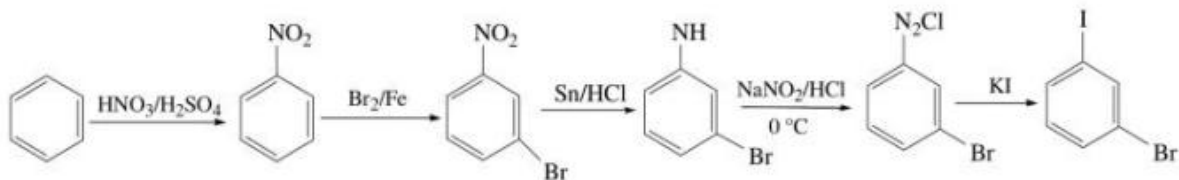


Secondary alcohol to tertiary alcohol

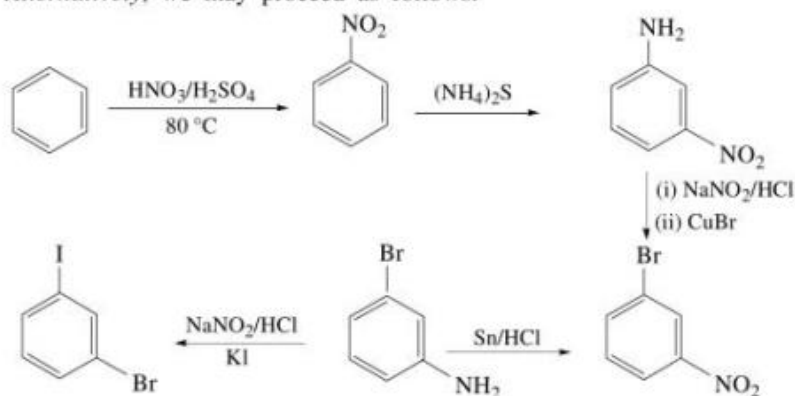


Prepare *m*-bromiodobenzene from benzene

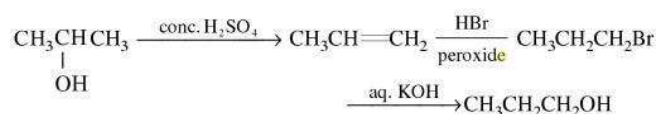
prepare *m*-bromiodobenzene from benzene (in not more than 5-7 steps)?



Alternatively, we may proceed as follows:



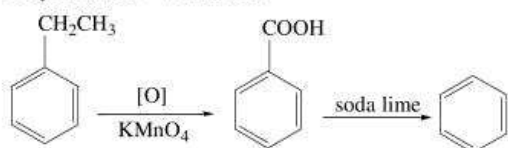
Secondary alcohol to Primary alcohol



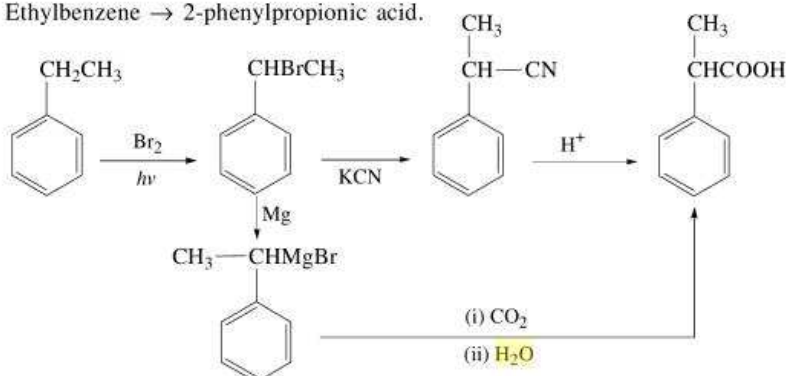
To convert Ethylbenzene to Benzene and Ethylbenzene to phenylpropionic acid

Show the steps to carry out the following transformations.

(i) Ethylbenzene \rightarrow benzene



(ii) Ethylbenzene \rightarrow 2-phenylpropionic acid.

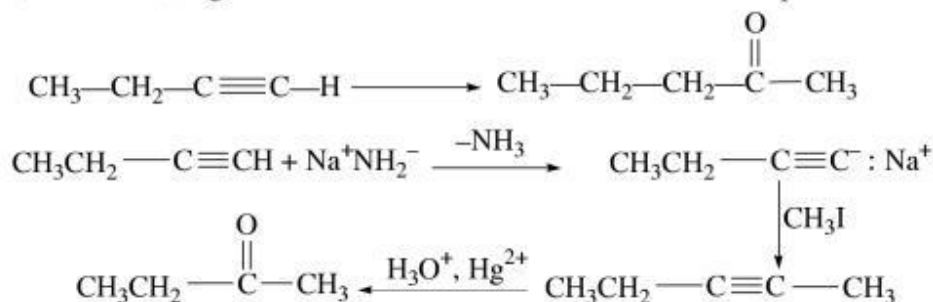


Alcohol to alcohol with one carbon more

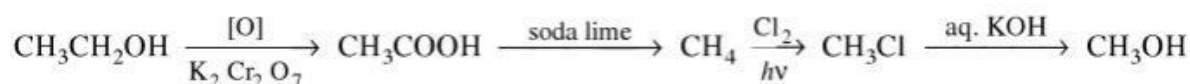


Carry out the transformations 1-Butyne to ketone

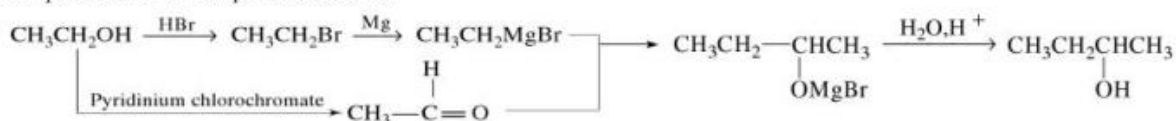
Carry out the following transformation in not more than three steps.



Alcohol to alcohol with one carbon less



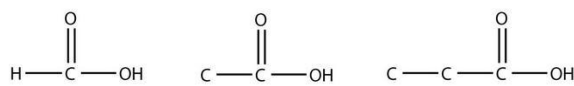
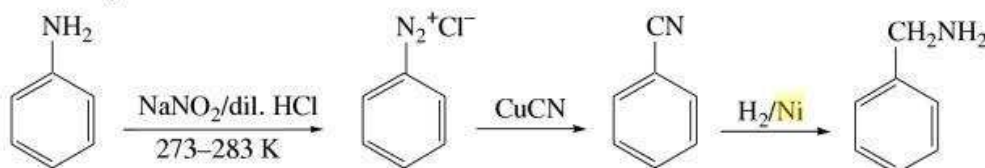
Simple alcohol to complicated alcohol



Conversion of Aniline to Benzylamine

How would you bring about the following conversion (in 3 steps)?

Aniline → Benzylamine



Methanoic acid

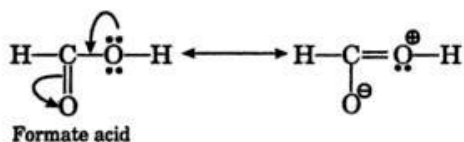
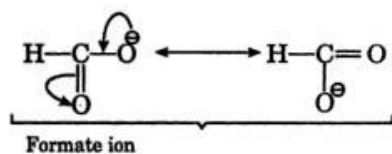
Ethanoic acid

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.

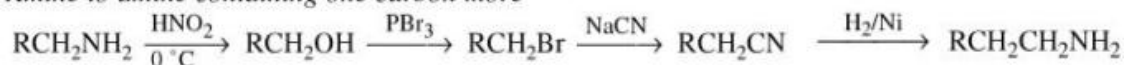
Solution. (i) In sodium formate, the contributing structures for the anion are equivalent while these are not the same in formic acid.



Thus, carbon-oxygen bond length in formate ion is the same for both the bonds while these are different in formic acid.

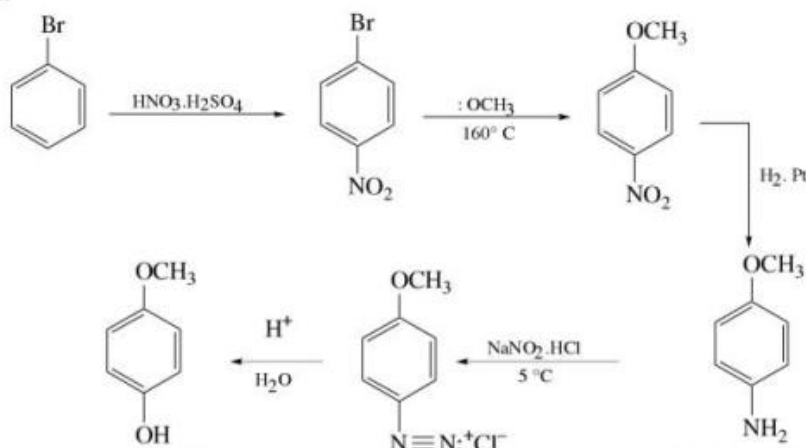
(ii) In phenate ion, the negative charge is dispersed only one electronegative oxygen atoms while there are two available oxygen atoms in benzoate ion to disperse the negative charge.

Amine to amine containing one carbon more

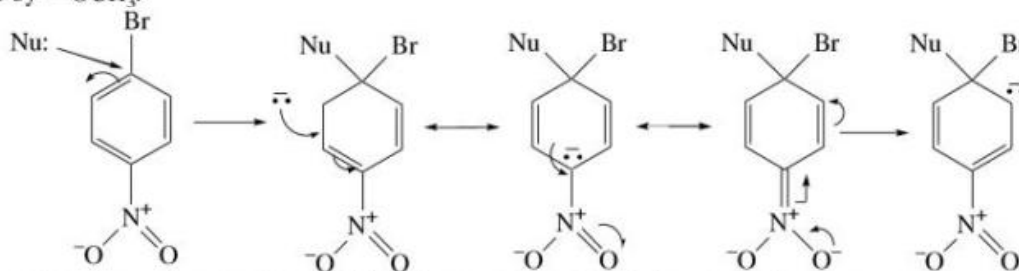


Synthesis of 4-methoxyphenol from bromobenzene

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 $-\text{NO}_2$ group at *para* position in bromobenzene facilitates the nucleophilic replacement of $-\text{Br}$ by $-\text{OCH}_3$.



The negative charge is strongly stabilised by resonance involving *para*-nitro group.

Write chemical tests to distinguish

between:

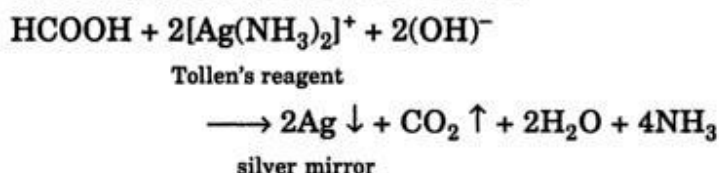
Solution. Formic acid $\left(\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{OH} \end{array} \right)$ contains

both an aldehyde $\left(\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{O} \end{array} \right)$ as well as carboxyl

group $\left(\begin{array}{c} -\text{C}-\text{OH} \\ || \\ \text{O} \end{array} \right)$ but acetic acid contain only a

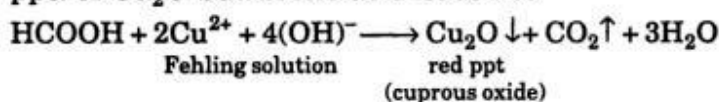
carboxyl group. Formic acid behaves as reducing agent whereas acetic acid does not.

(a) Formic acid reduces Tollen's reagent to metallic silver but acetic acid does not.

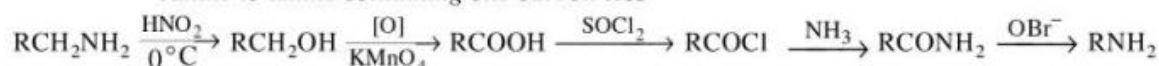


No silver mirror is formed with acetic acid.

(b) Formic acid reduced Fehling solution to red ppt. of Cu_2O but acetic acid does not.



Amine to amine containing one carbon less

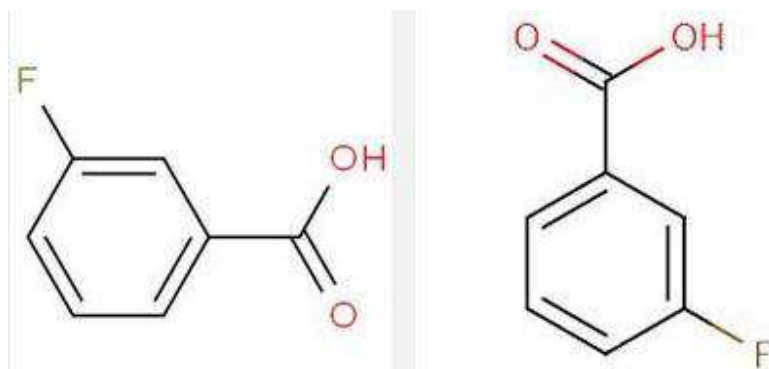


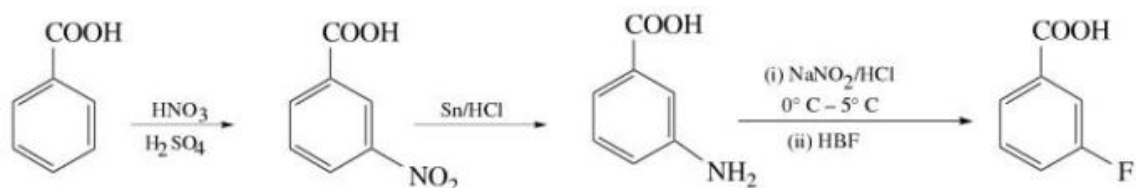
Convert Benzoic acid to meta fluorobenzoic acid (2-fluorobenzoic acid)

Convert

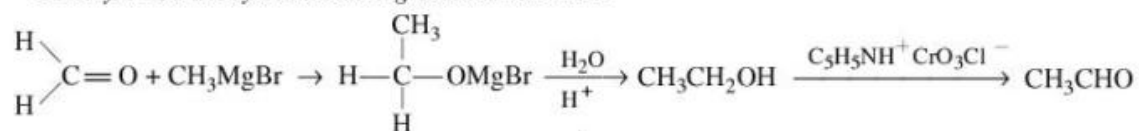


metafluoro benzoicacid

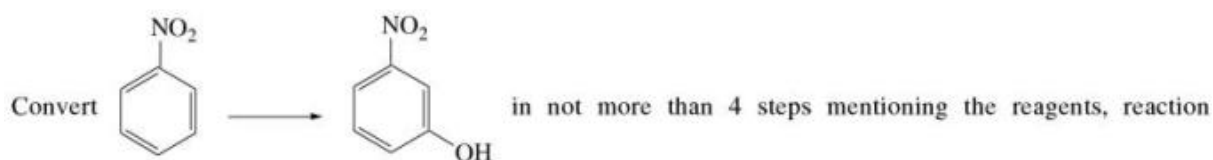




Aldehyde to aldehyde containing one carbon more

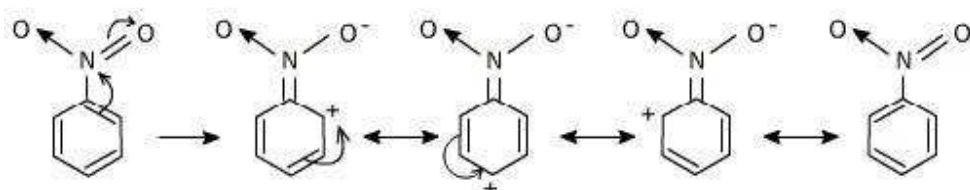


Convert Nitrobenzene to meta hydroxynitrobenzene (or 4-nitrophenol)

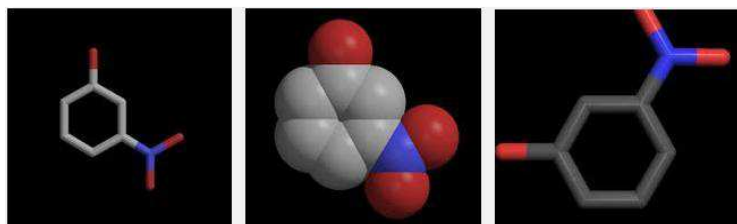


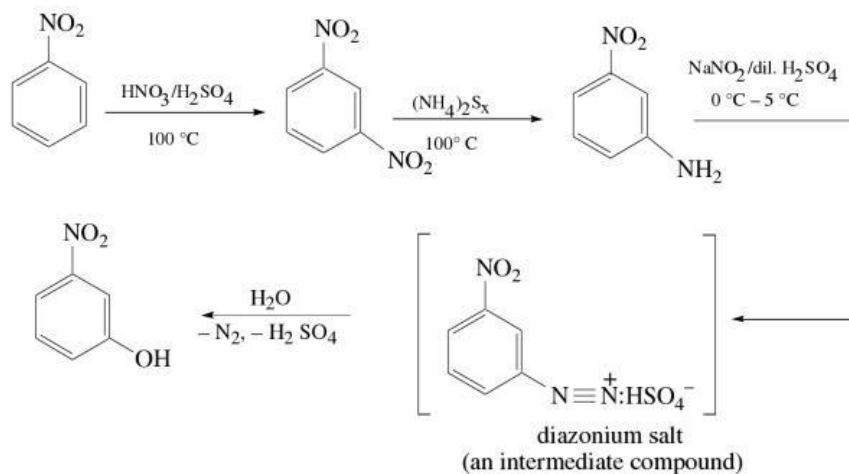
The given conversion can be carried out as follows.

Nitrobenzene resonance structure



4 nitrophenol or metahydroxynitrobenzene

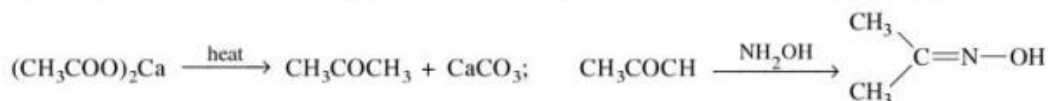
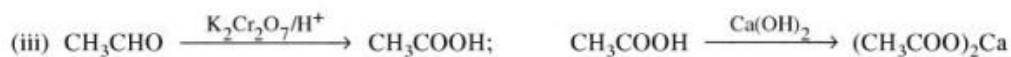
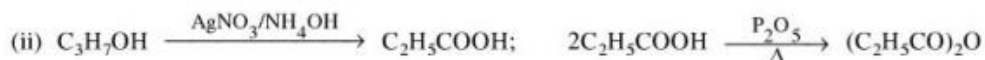
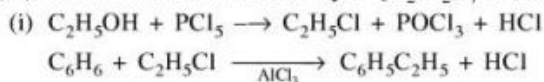




Many conversions or preparations

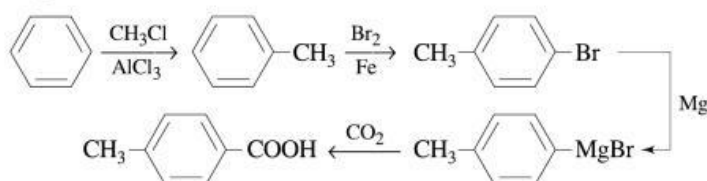
Write down the reactions involved in the preparation of the following using the reagents indicated against each in paranthesis

- (i) Ethylbenzene from benzene [$\text{C}_2\text{H}_5\text{OH}$, PCl_5 , anhydrous AlCl_3]
- (ii) Propanoic anhydride from propanol [$\text{AgNO}_3/\text{NH}_4\text{OH}$, P_2O_5]
- (iii) Acetoxime from acetaldehyde [$\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+$, $\text{Ca}(\text{OH})_2$ and $\text{NH}_2\text{OH} \cdot \text{HCl}$]



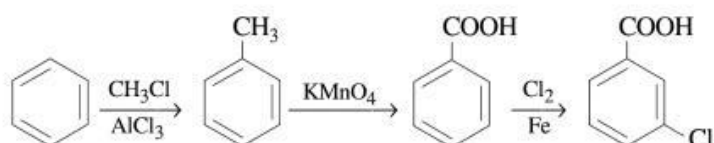
Benzene to *p*-toluic acid

Benzene to *p*-toluic acid



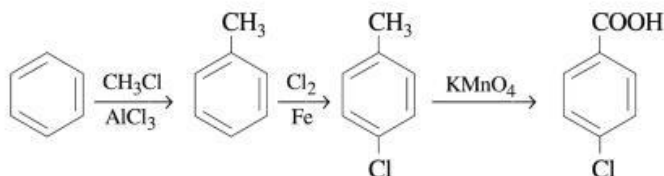
Benzene to *m*-chlorobenzoic acid

Benzene to *m*-chlorobenzoic acid



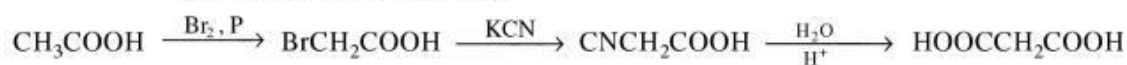
Benzene to *p*-chlorobenzoic acid

Benzene to *p*-chlorobenzoic acid



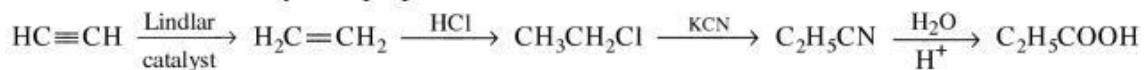
Acetic acid to Malonic acid

Acetic acid to malonic acid



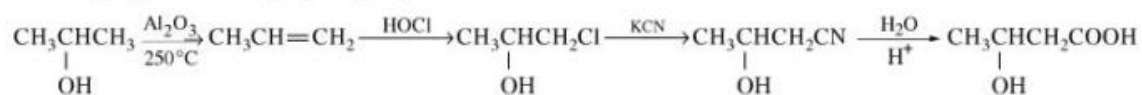
Ethyne to propanoic acid

Ethyne to propanoic acid



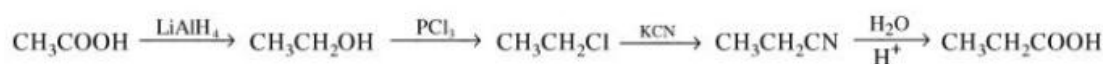
Isopropyl alcohol to β -hydroxybutyric acid

Isopropyl alcohol to β -hydroxybutyric acid



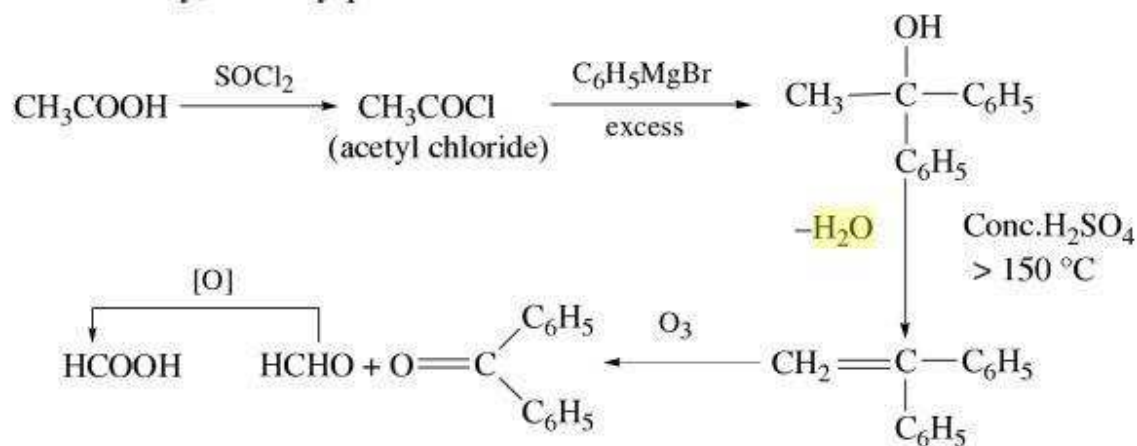
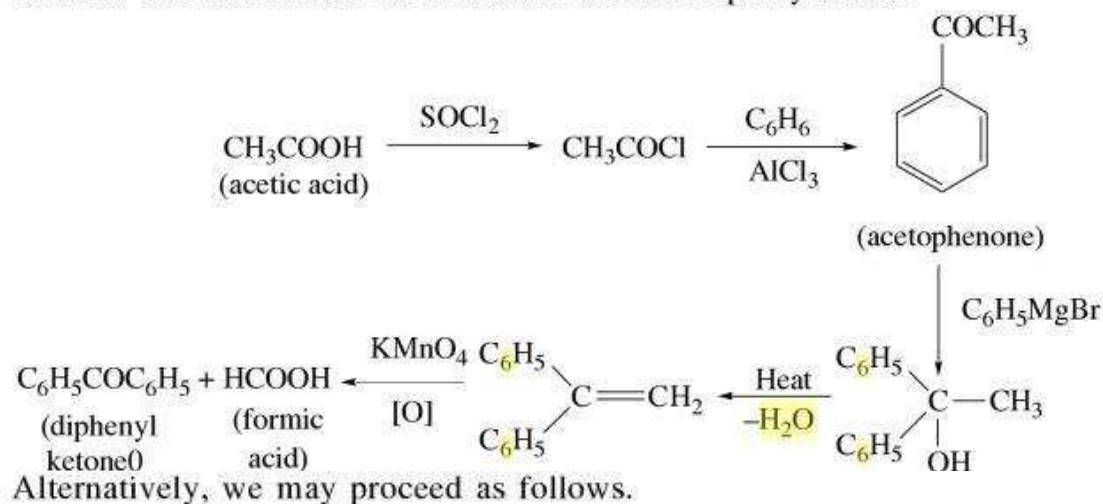
Acetic acid to Propanoic acid

Acetic acid to propanoic acid



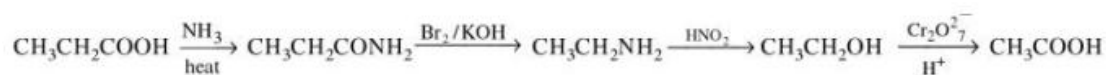
Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

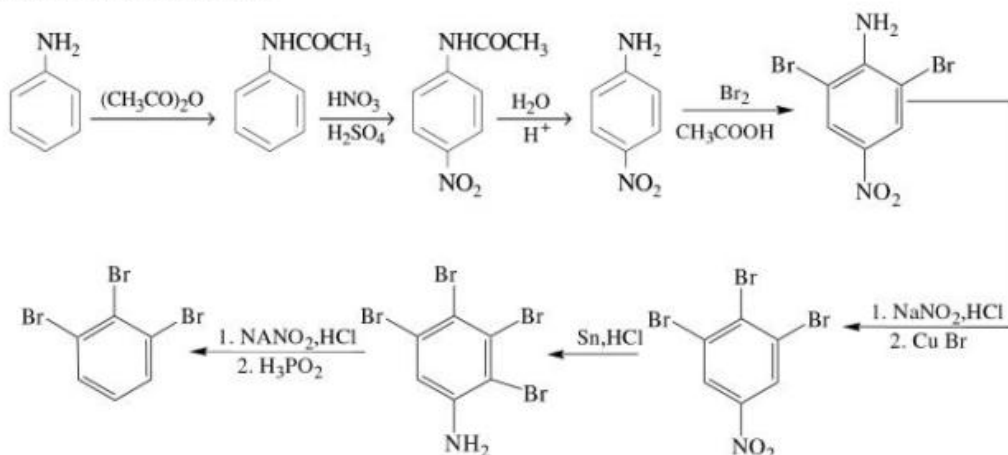


Propanoic acid to acetic acid

Propanoic acid to acetic acid

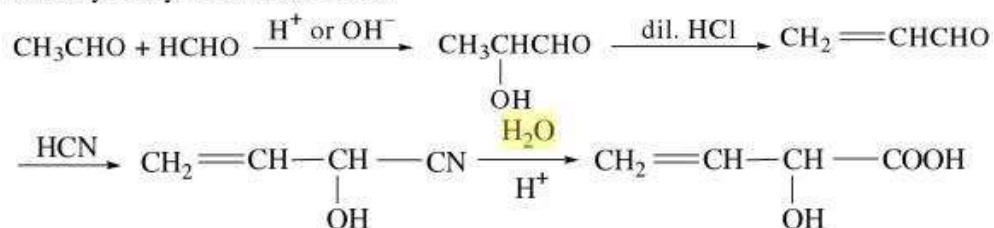


Aniline to 1, 2, 3-tribromobenzene



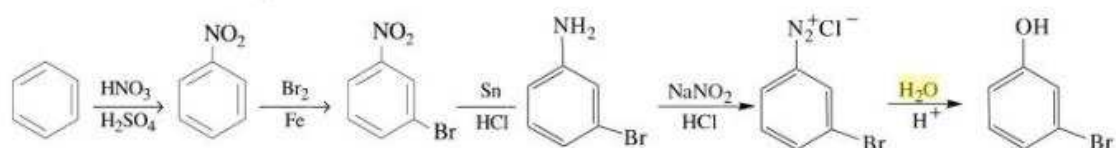
Ethanal to 2-hydroxy-3-butenic acid

Ethanal to 2-hydroxy-3-butenic acid



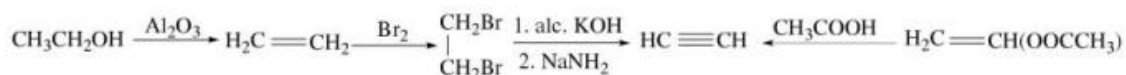
Benzene to m-bromophenol

Benzene to m-bromophenol



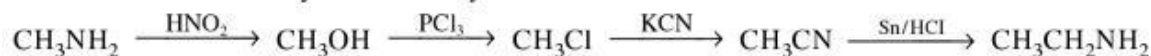
Ethyl alcohol to Vinyl alcohol

Ethyl alcohol to vinyl acetate

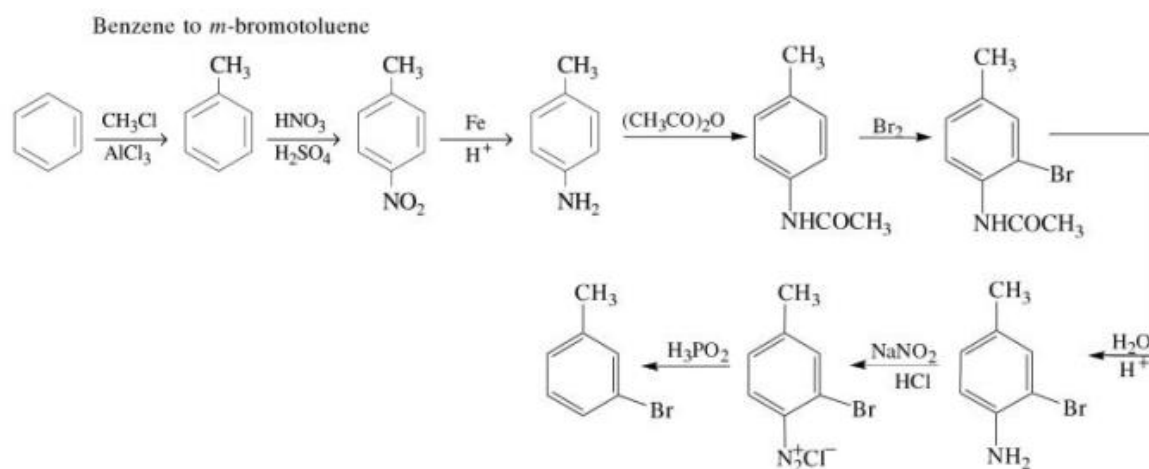


Methylamine to ethylamine

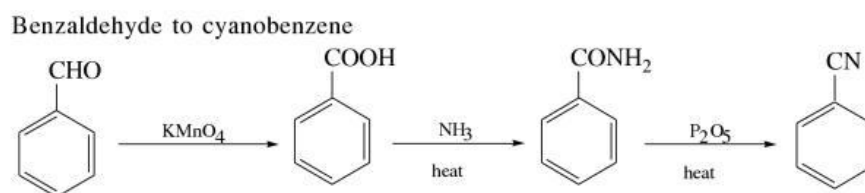
Methylamine to ethylamine



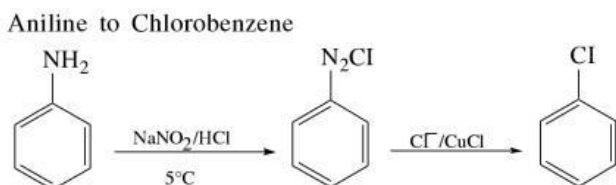
Benzene to *m*-bromotoluene



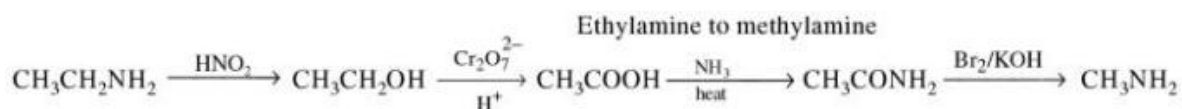
Benzaldehyde to cyanobenzene



Aniline to Chlorobenzene

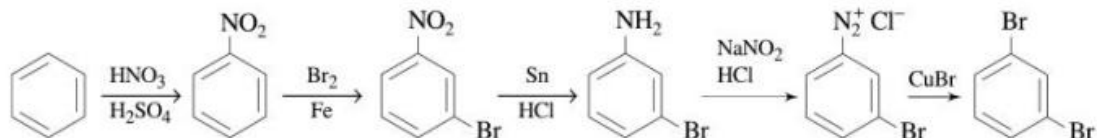


Ethylamine to Methylamine



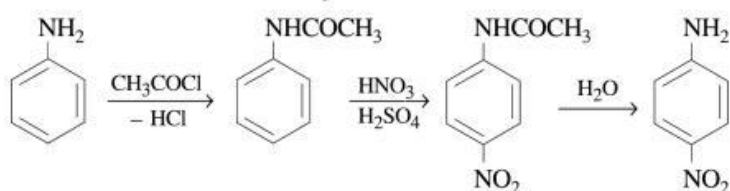
Benzene to *m*-dibromobenzene

Benzene to *m*-dibromobenzene



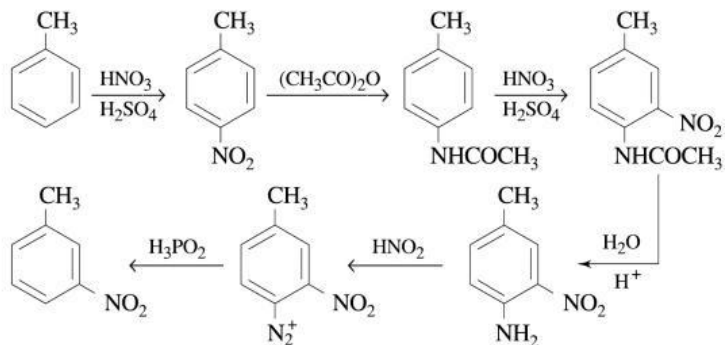
Aniline to *p*-nitroaniline

Aniline to *p*-nitroaniline



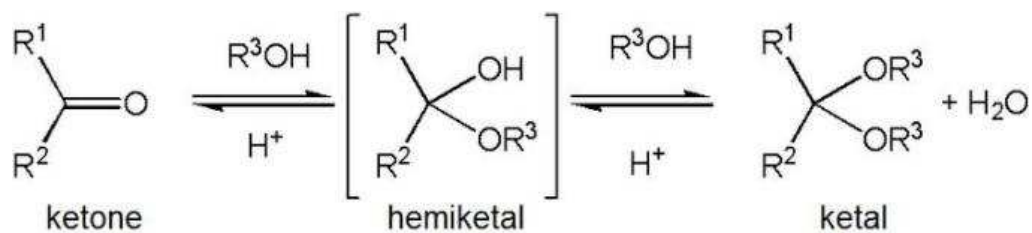
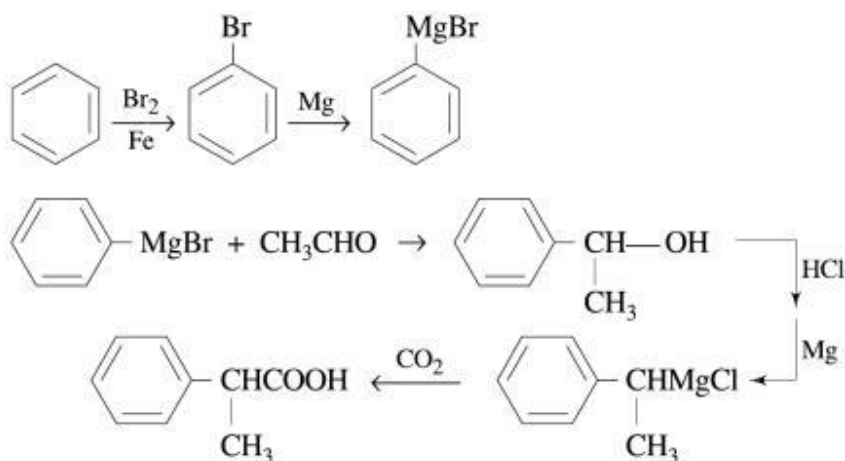
Toluene to *m*-nitrotoluene

Toluene to *m*-nitrotoluene



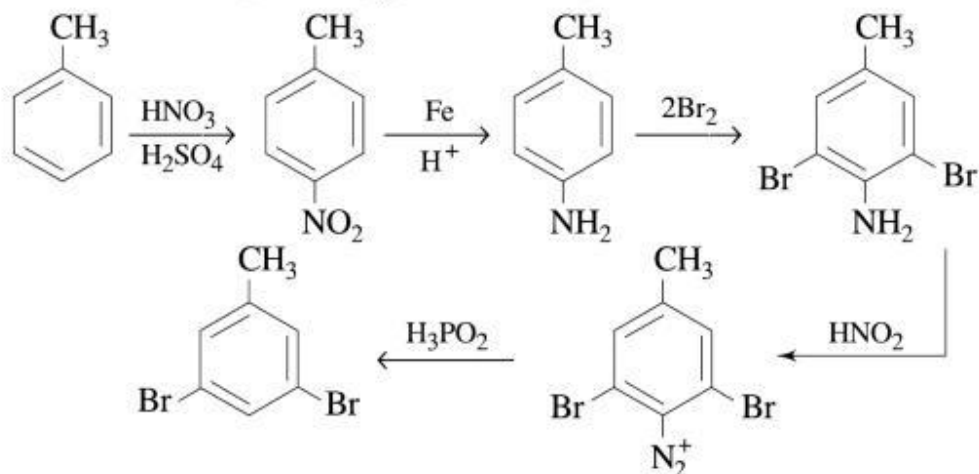
Convert Benzene + Alcohol to α -methylphenylacetic acid

Benzene + alcohol to α -methylphenylacetic acid



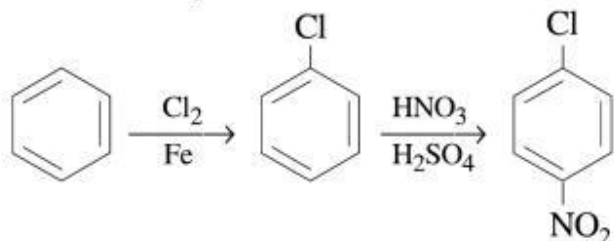
Toluene to 3,5-dibromotoluene

Toluene to 3,5-dibromotoluene



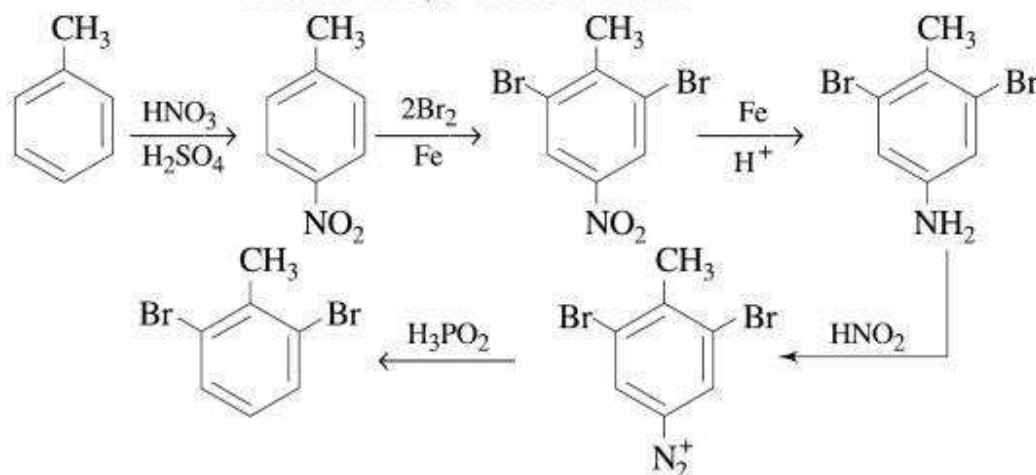
Benzene to *p*-chloronitrobenzene

Benzene to *p*-chloronitrobenzene



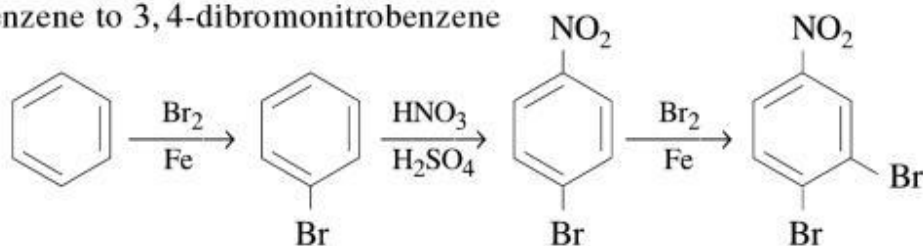
Toluene to 2,6-dibromotoluene

Toluene to 2,6-dibromotoluene

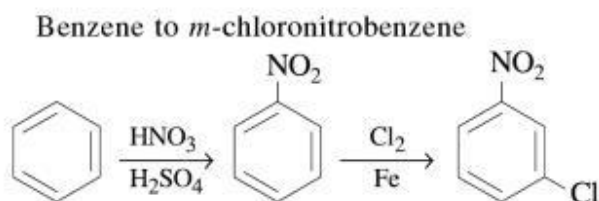


Benzene to 3,4-dibromonitrobenzene

Benzene to 3,4-dibromonitrobenzene

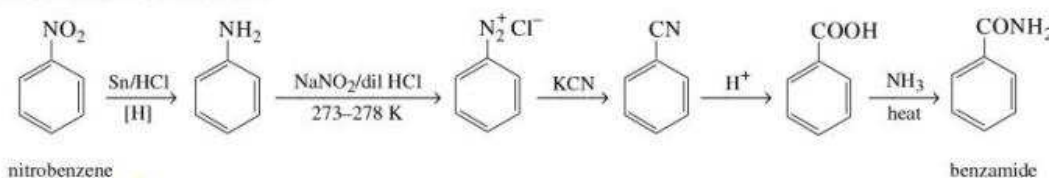


Benzene to *m*-chloronitrobenzene



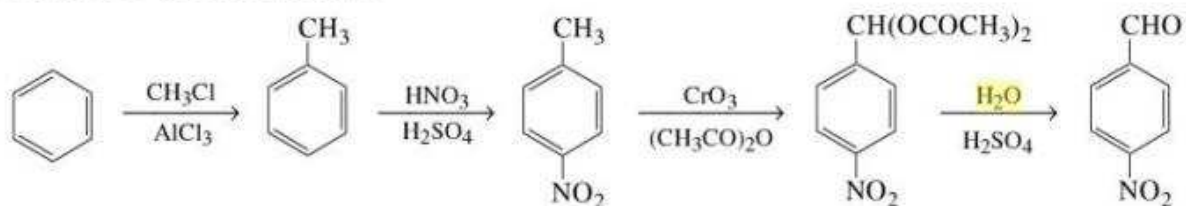
Nitrobenzene to benzamide

Nitrobenzene to benzamide



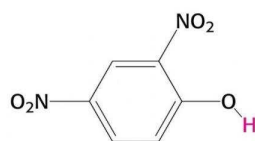
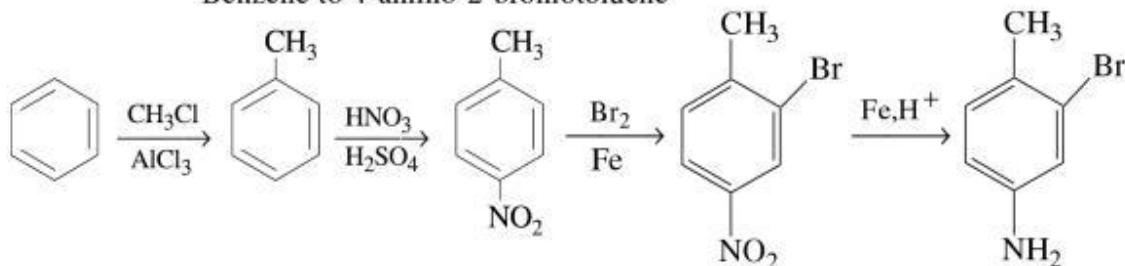
Benzene to 4-nitrobenzaldehyde

Benzene to 4-nitrobenzaldehyde



Benzene to 4-amino-2-bromotoluene

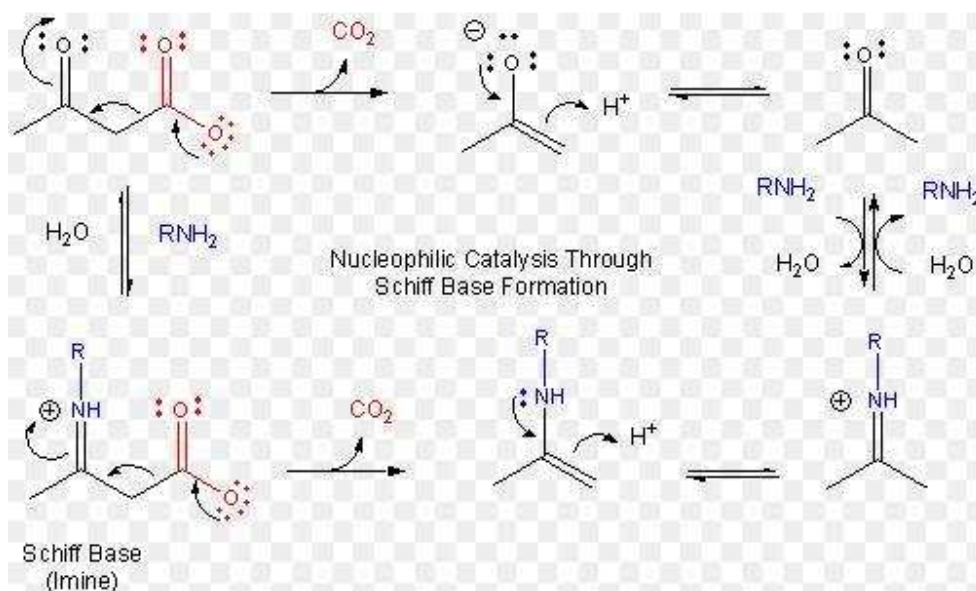
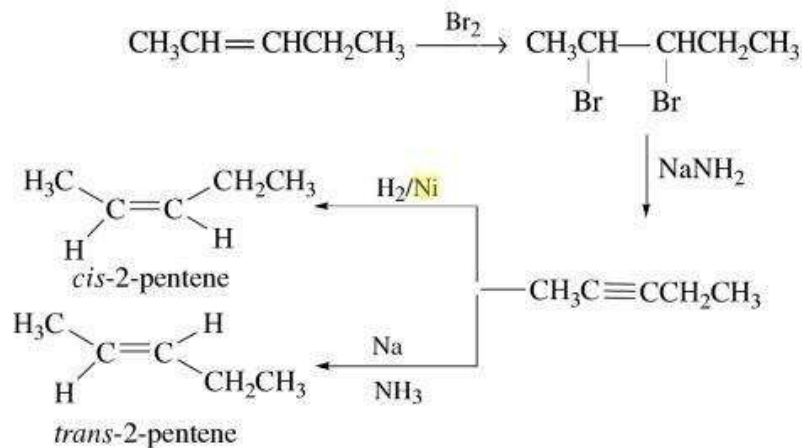
Benzene to 4-amino-2-bromotoluene



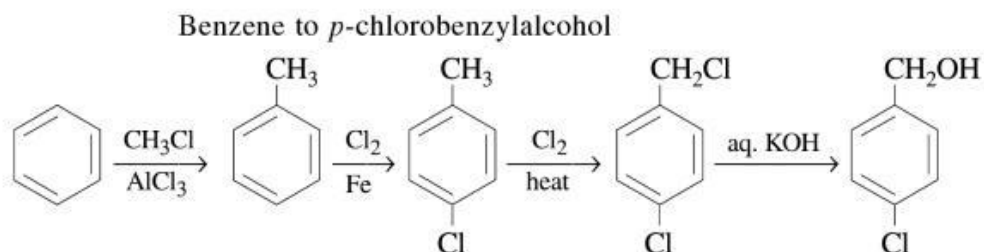
2,4-Dinitrophenol (DNP)

Convert a mixture of *cis*-2-pentene and *trans*-2-pentene into *cis*-2-pentene or *trans*-2-pentene

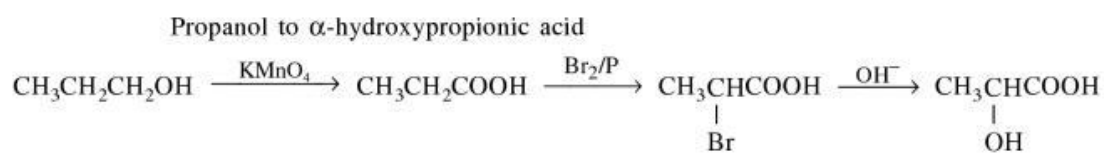
A mixture of *cis*-2-pentene and *trans*-2-pentene into *cis*-2-pentene or *trans*-2-pentene



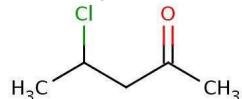
Benzene to *p*-chlorobenzylalcohol



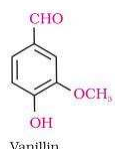
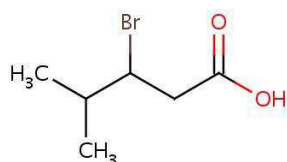
Convert Propanol to α -hydroxypropanoic acid



4-chloropentane-2-one



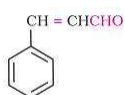
3-Bromo-4-methylpentanoic acid



Vanillin

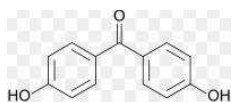


Salicylaldehyde

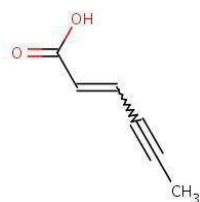


Cinnamaldehyde

p,p'- dihydroxybenzophenone



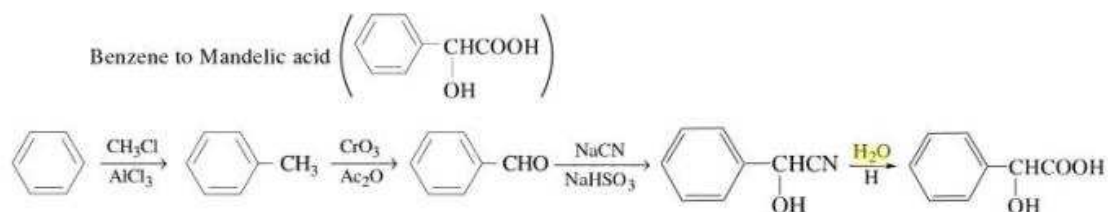
Hex-2-ene-4-ynoic acid



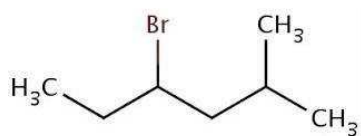
Heptan-2-one



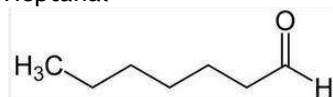
Benzene to Mandelic Acid



4-Bromo-2-methylhexane

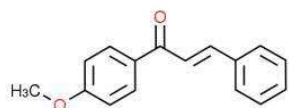


Heptanal

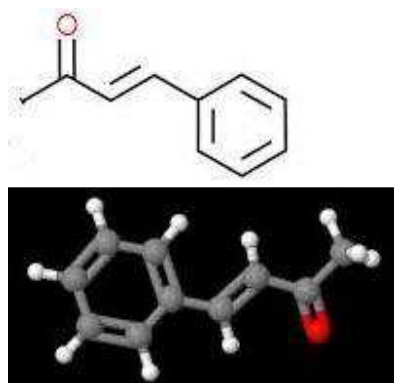


1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one

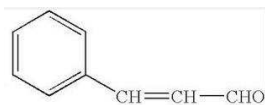
1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one



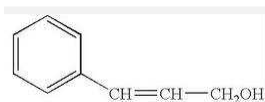
4-phenylprop-3-ene-2-one



3-phenylprop-2-ene-1-al



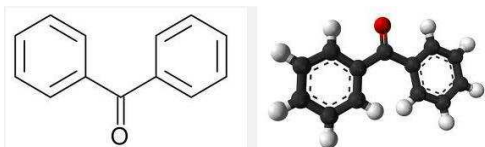
3-phenyl-prop-2-ene-1-ol



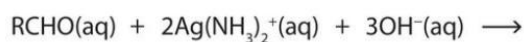
cyclopentancarbaldehyde



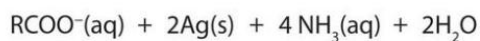
Benzophenone also diphenylmethanone



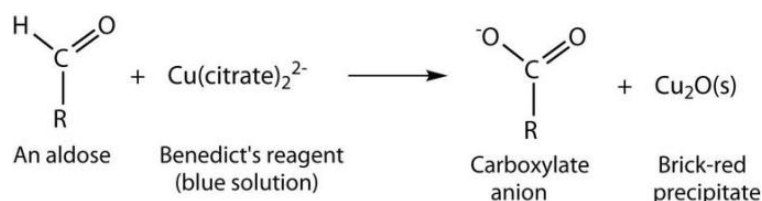
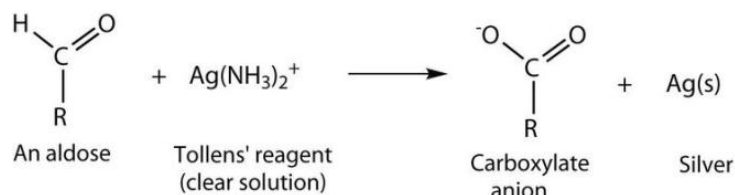
Tollen's Reagent



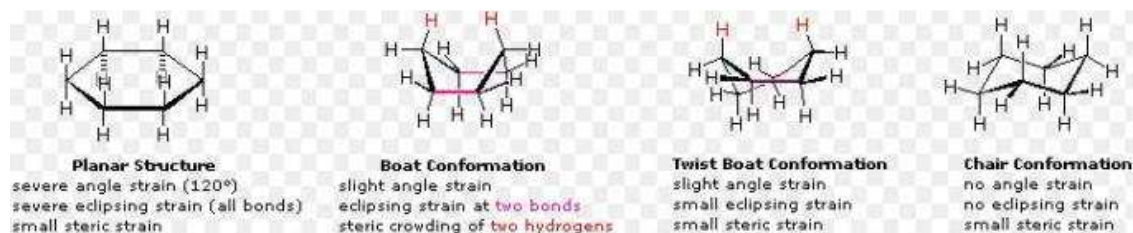
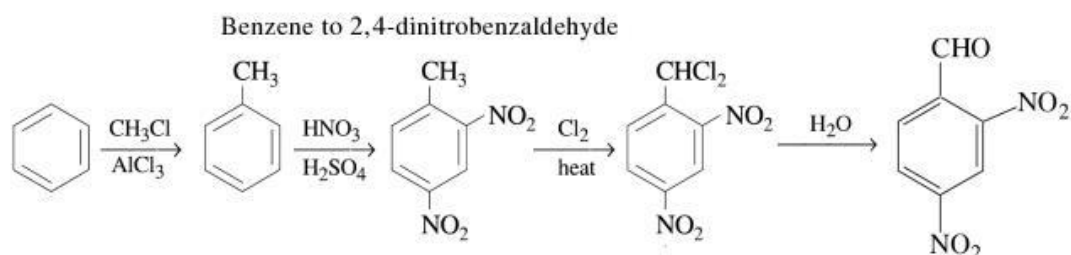
An aldehyde



Free silver

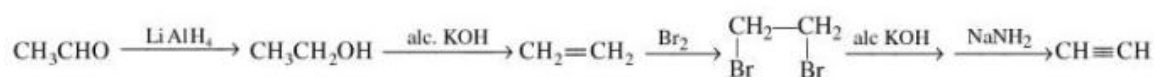


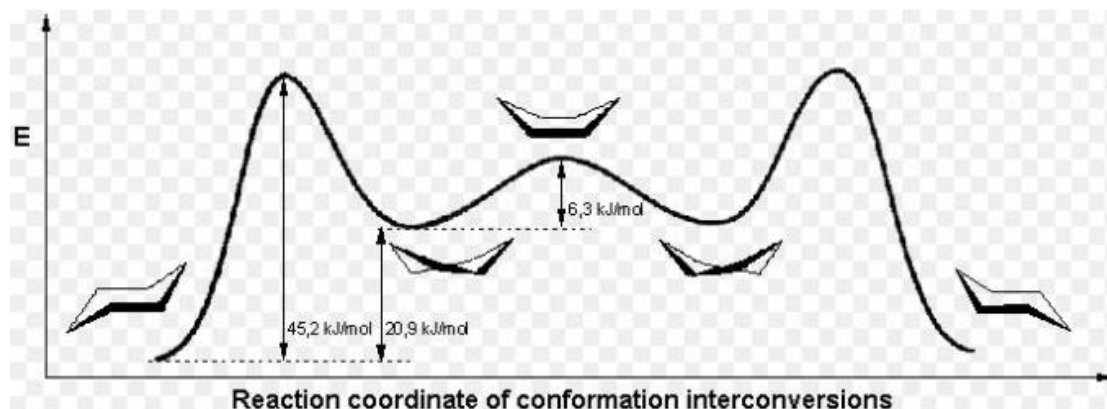
Benzene to 2,4-dinitrobenzaldehyde



Acetaldehyde to Acetylene

Acetaldehyde to acetylene



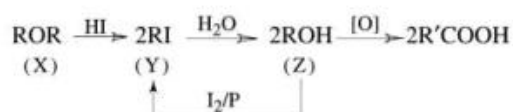


Identify the compounds

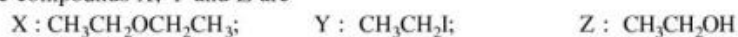
compound contains C, H and O unreactive towards Na (Sodium)

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)

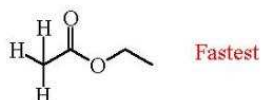
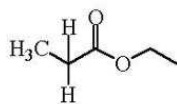
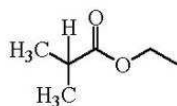
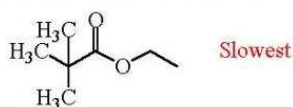
Solution Since the compound is unreactive towards sodium, it is neither alcohol (including phenol) nor carboxylic acid. It is also not an aldehyde. It may be a symmetrical ether because on refluxing with excess of HI, it gives only one product. Thus, we have



Now the equivalent weight of R'COOH is 60. From this, it follows that R' is —CH₃ group and hence R is —CH₂CH₃ group. Thus, the compounds X, Y and Z are



Steric Effects and the Relative Reactivity of Carboxylic Acid Derivatives

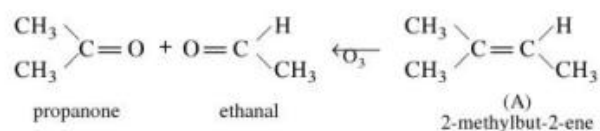


Identify the compound

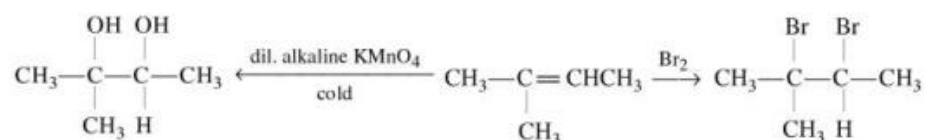
A hydrocarbon reacts with Bromine to give dibromo compound

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



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

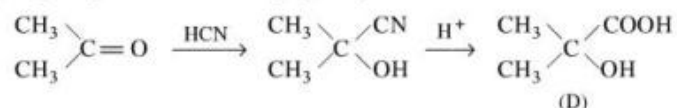


Identify the compound

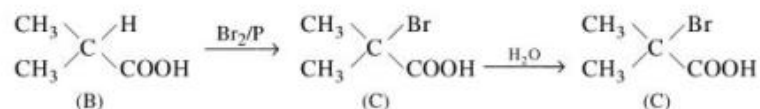
An alkene A on ozonolysis yields acetone and an aldehyde

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.

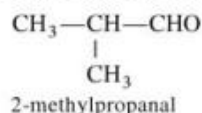
Solution The structure of compound D is easily deduced from the fact that it is obtained by the combination of acetone with hydrogen cyanide followed by hydrolysis.



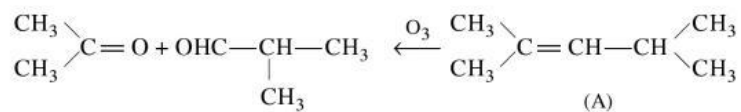
The conversion B to C and then C to D indicates that the reaction B to C is Hell-Volhard-Zelinsky reaction. Thus, we have



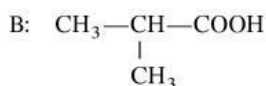
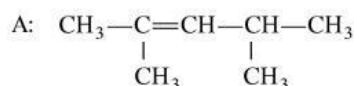
Hence, we conclude that the aldehyde from which compound B is obtained by oxidation has the structure



Now, the ozonolysis of the compound A gives acetone and 2-methyl-propanal, i.e.

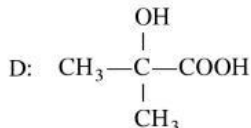
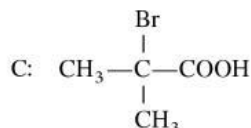


Hence, the compound A, B, C and D are



2, 4-dimethylpent-2-ene

2-methylpropanoic acid



2-bromo-2-methylpropanoic acid

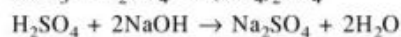
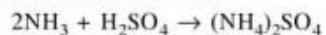
2-hydroxy-2-methylpropanoic acid

Identify the compound

An aromatic compound 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



$$\text{Amount of sodium hydroxide to neutralize excess of sulphuric acid} = (25 \text{ mL}) \left(\frac{0.1 \text{ mol}}{1000 \text{ mL}} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Amount of sulphuric acid neutralized with sodium hydroxide} = \frac{1}{2} \left(\frac{1}{400} \text{ mol} \right) = \frac{1}{800} \text{ mol}$$

$$\text{Amount of sulphuric acid taken to start with} = (50 \text{ mL}) \left(\frac{0.05 \text{ mol}}{1000 \text{ mL}} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Amount of sulphuric acid neutralized by ammonia} = \left(\frac{1}{400} - \frac{1}{800} \right) \text{ mol} = \frac{1}{800} \text{ mol}$$

$$\text{Amount of ammonia evolved} = 2 \left(\frac{1}{800} \text{ mol} \right) = \frac{1}{400} \text{ mol}$$

$$\text{Mass of nitrogen in the evolved ammonia} = \left(\frac{1}{400} \text{ mol} \right) (14 \text{ g mol}^{-1}) = \frac{7}{200} \text{ g}$$

$$\text{Per cent of nitrogen in the given aromatic compound} = \frac{(7/200) \text{ g}}{0.303 \text{ g}} \times 100 = 11.6$$

$$\text{Per cent of oxygen in the given aromatic compound} = 100 - (69.4 + 5.8 + 11.6) = 13.2$$

The ratios of atoms present in the given compound are

$$\text{C} : \text{H} : \text{N} : \text{O} \quad :: \quad \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.6}{14} : \frac{13.2}{16} \quad :: \quad 5.8 : 5.8 : 0.83 : 0.83 \quad :: \quad 7 : 7 : 1 : 1$$

Hence, for the given compound, we have

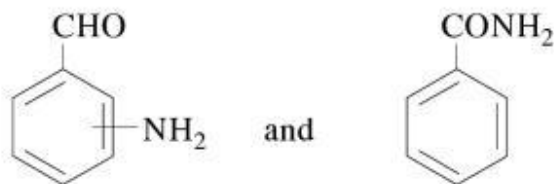
$$\text{Empirical formula} = \text{C}_7\text{H}_7\text{NO}$$

$$\text{Empirical molar mass} = 121 \text{ g mol}^{-1}$$

It is given that 121 g mol^{-1} is also the molar mass. Hence,

$$\text{Molecular formula} = \text{C}_7\text{H}_7\text{NO}$$

Since, the given compound is aromatic, the two possible structures are



Identify the compound

An Organic compound $\text{C}_x\text{H}_2y\text{O}_y$ was burnt with twice the amount of Oxygen

An organic compound $\text{C}_x\text{H}_2y\text{O}_y$ 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 $\text{C}_x\text{H}_2y\text{O}_y + x \text{O}_2 \rightarrow x \text{CO}_2 + y \text{H}_2\text{O}$

To start with, the amount of O_2 taken is $2x$. Hence, after the combustion reaction, we will be left with the following amounts.

$$\text{Amount of oxygen left unreacted} = x; \quad \text{Amount of carbon dioxide} = x; \quad \text{Amount of water} = y$$

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,

$$\text{Amount } x = \frac{(2.24/2) \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.05 \text{ mol}$$

$$\text{Now,} \quad \text{Mass of water collected} = 0.9 \text{ g} \quad \text{Amount of water collected, } y = \frac{0.9 \text{ g}}{18 \text{ g mol}^{-1}} = 0.05 \text{ mol}$$

Thus, the empirical formula of the compound is $\text{C}_{0.05}\text{H}_{2 \times 0.05}\text{O}_{0.05}$, i.e. CH_2O . Now, according to Raoult's law

$$-\frac{\Delta p}{p^*} = x_2 \quad \text{i.e.} \quad \frac{0.104 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{(50 \text{ g}/M)}{(50 \text{ g}/M) + (1000 \text{ g}/18 \text{ g mol}^{-1})}$$

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 Br₂ in CCl₄. Compound A, on oxidation with concentrated KMnO₄, gave compound C (molecular formula C₄H₈O) 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 CH₂.

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.

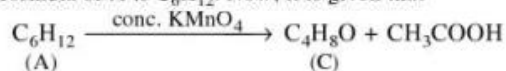
$$\text{Mass of bromine absorbed by 1.0 g of hydrocarbon} = \frac{5}{100} \times 38.05 \text{ g}$$

$$\text{Mass of hydrocarbon absorbing 160 g (= 1 mol) of Br}_2 = \frac{1.0}{(5 \times 38.05/100)} \times 160 \text{ g} = 84.1 \text{ g.}$$

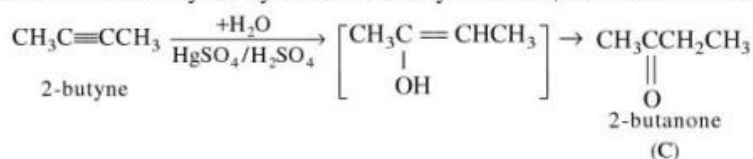
Hence, Molar mass of A is 84.1 g mol⁻¹.

The number of repeating CH₂ group in one molecule of A will be 6 (= 84.1/14). Hence,

Molecular formula of A is C₆H₁₂. Now, it is given that



The compound C is obtained by the hydration of 2-butyne. Hence, its structure obtained from the reaction is



Identify the compound

A liquid X having a molecular formula C₆H₁₂O₂ is hydrolyzed with water

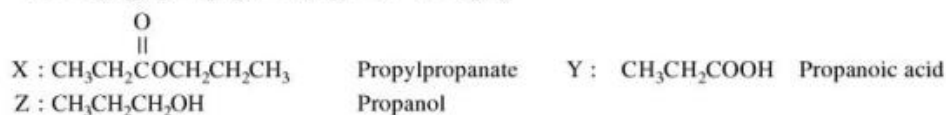
A liquid X, having a molecular formula C₆H₁₂O₂ is hydrolysed with water in the presence of an acid to give a carboxylic acid, Y, and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z?

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



Hence, the given compound X may be written as RCOOCH₂R. From this it follows that

$$2\text{R} = \text{C}_6\text{H}_{12}\text{O}_2 - \text{C}_2\text{H}_4\text{O} = \text{C}_4\text{H}_8 \quad \text{or} \quad \text{R} = \text{C}_2\text{H}_5$$



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.

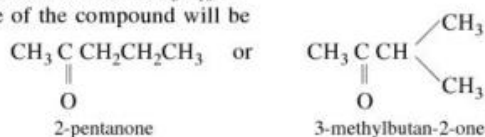
The ratios of atoms in the compound are

$$\text{C} : \text{O} : \text{H} :: \frac{69.77}{12} : \frac{18.60}{16} : \frac{11.63}{1} :: 5.81 : 1.16 : 11.63 :: 5 : 1 : 10$$

Hence Empirical formula is $\text{C}_5\text{H}_{10}\text{O}$.

Thus, Molecular formula is $\text{C}_5\text{H}_{10}\text{O}$.

The structure of the compound will be

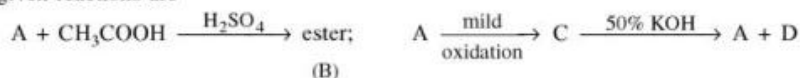


Identify the compound

An organic compound A on treatment with acetic acid in the presence of Sulphuric acid

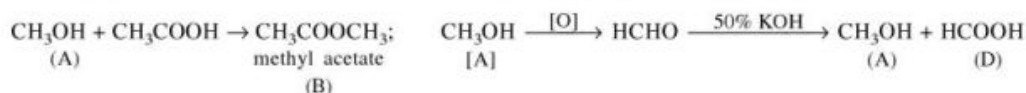
produces an ester B. The compound A on mild oxidation gives C. The compound C with 50% potassium hydroxide followed by acidification with dilute hydrochloric acid generates A and D. The compound D with phosphorus pentachloride followed by reaction with ammonia gives E. The compound E on dehydration produces hydrocyanic acid. Identify the compounds A, B, C, D and E.

Solution The given reactions are

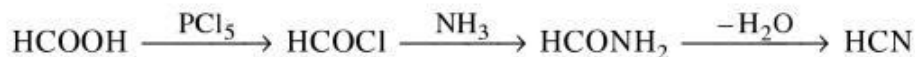


The reaction $\text{C} \xrightarrow{50\% \text{ KOH}} \text{A} + \text{D}$ is a Cannizzaro reaction and thus the compound C is an aldehyde with no α -hydrogen, C must be HCHO. From this it follows that A must be CH_3OH as its mild oxidation gives HCHO.

With this fact, we can write the given reactions as shown below.



Hence



A : CH_3OH methanol

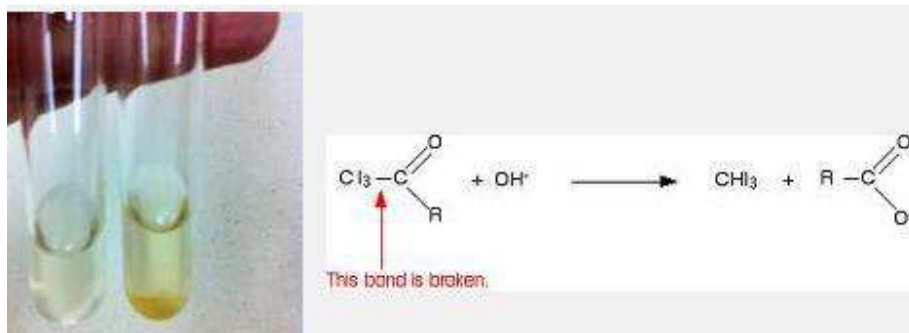
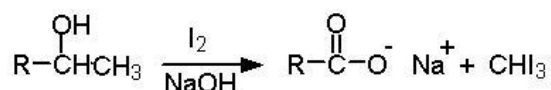
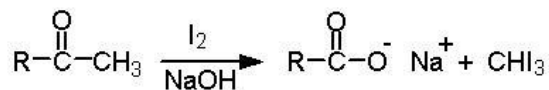
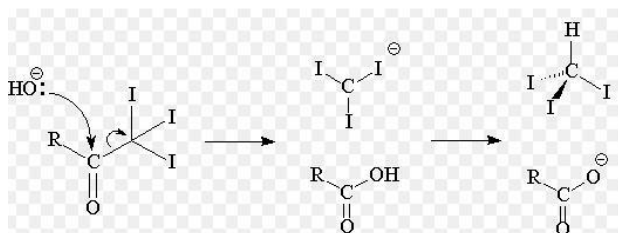
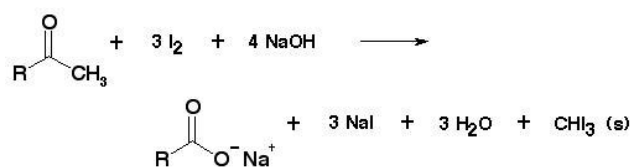
B : $\text{CH}_3\text{COOCH}_3$ methylethionate

C : HCHO methanal

D : HCOOH methanoic acid

E : HCONH_2 methanamide

Iodoform Test



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

$$= \frac{M_{\text{Cl}}}{M_{\text{AgCl}}} \frac{m_{\text{AgCl}}}{m_{\text{compound}}} \times 100 = \frac{35.5}{143.5} \times \frac{2.90}{1.0} \times 100 = 71.21$$

The ratios of atoms in the molecule of X are

$$\text{C} : \text{H} : \text{Cl} :: \frac{24.24}{12} : \frac{4.04}{1} : \frac{71.72}{35.5} :: 2 : 4 : 2 :: 1 : 2 : 1$$

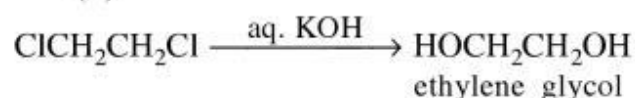
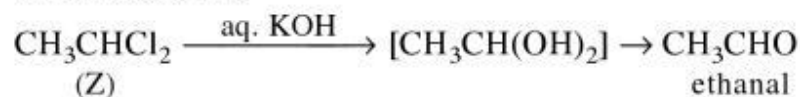
Empirical formula of X is CH_2Cl

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 $\text{C}_2\text{H}_4\text{Cl}_2$.

Its two isomers are CH_3CHCl_2 and $\text{ClCH}_2\text{CH}_2\text{Cl}$.
(Z) (Y)

The reaction are



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)

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Match the entries given on the left with those given on the right.

- | | |
|--|-----------------------------|
| (a) Pyrolysis of alkanes | (p) Elimination reaction |
| (b) Benzene + Chloroethane (+ anhydrous AlCl_3) | (q) Saponification |
| (c) $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{NaOH}$ | (r) Wurtz reaction |
| (d) Preparation of alkanes | (s) Friedel-craft reaction |
| (e) Phenol + CHCl_3 (NaOH) | (t) Reimer-Tiemann reaction |
| (f) $\text{C}_2\text{H}_5\text{Br} + \text{alcKOH}$ | (u) Cracking |

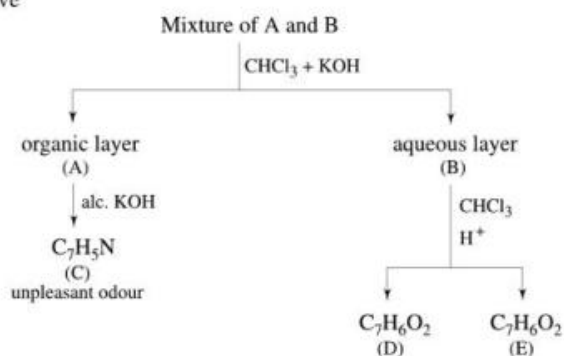
Ans :

- (a) - (u); (b) - (s); (c) - (q); (d) - (r); (e) - (t);
(f) - (p)

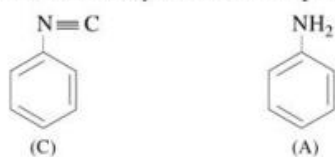
Identify the compound

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 ($\text{C}_7\text{H}_5\text{N}$) 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 $\text{C}_7\text{H}_6\text{O}_2$. Identify the compounds A, B, C, D, and E and write their structures.

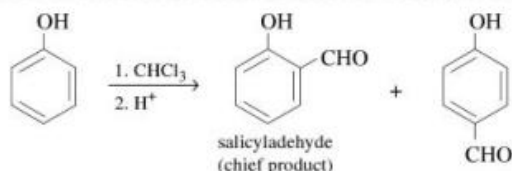
Solution We have



The compound C is an isocyanide which is produced from a primary amine. Hence, the structures of C and A are



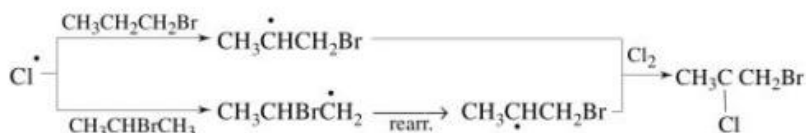
The compound B exhibits Reimer-Tiemann reaction. Thus, the compound B must be phenol. The reaction is



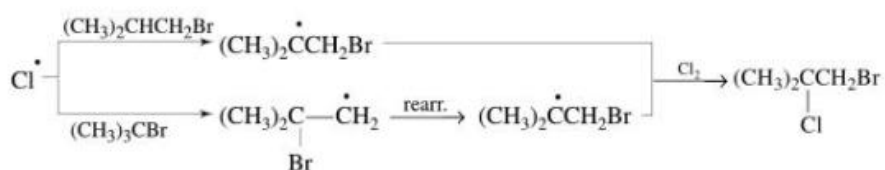
Rearrangement by migration of Bromine

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 CO₂ and 0.072 g of H₂O. A is insoluble in NaOH and NaHCO₃ 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 AgNO₃ solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula, C₇H₅OBr₃. Identify A, B, C, D and E with justification and give their structures.

Solution We have

$$\text{Per cent of carbon in the compound} = \frac{M_C}{M_{\text{CO}_2}} \frac{m_{\text{CO}_2}}{m_{\text{compound}}} \times 100 = \left(\frac{12}{44}\right) \left(\frac{0.308}{0.108}\right) (100) = 77.78$$

$$\text{Per cent of hydrogen in the compound} = \frac{2M_H}{M_{\text{H}_2\text{O}}} \frac{m_{\text{H}_2\text{O}}}{m_{\text{compound}}} \times 100 = \left(\frac{2}{18}\right) \left(\frac{0.072}{0.108}\right) (100) = 7.41$$

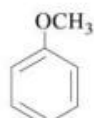
$$\text{Per cent of oxygen in the compound} = 100 - (77.78 + 7.41) = 14.81.$$

The ratios of atoms in the compound are

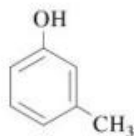
$$\text{C} : \text{H} : \text{O} :: \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} :: 6.48 : 7.41 : 0.926 :: 7 : 8 : 1$$

Hence, Empirical formula of the compound is C₇H₈O.

Since the isomer B on reacting with bromine water gives compound E (C₇H₅OBr₃), 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 NaHCO₃ 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

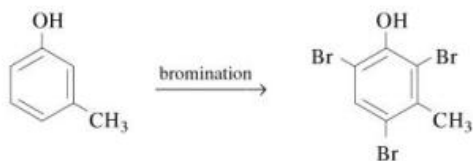


(A)
anisole

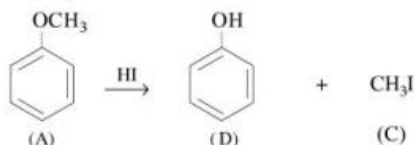


(B)
m-cresol

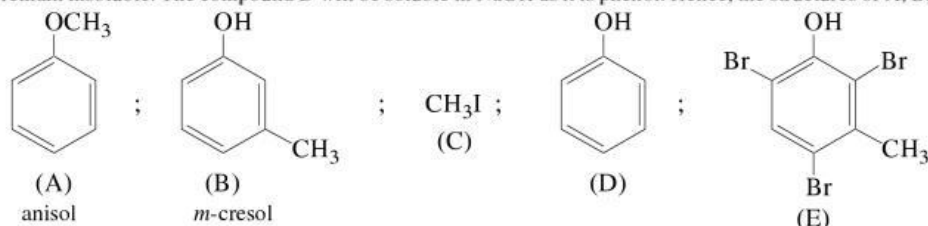
The bromination of B gives



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



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 :

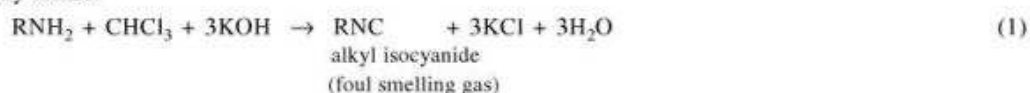
(a) – (q); (b) – (r); (c) – (s); (d) – (p)

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.



Since the compound on treating with NaNO_2/HCl at 0°C produces a colourless gas, the compound must be an aliphatic primary amine.



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

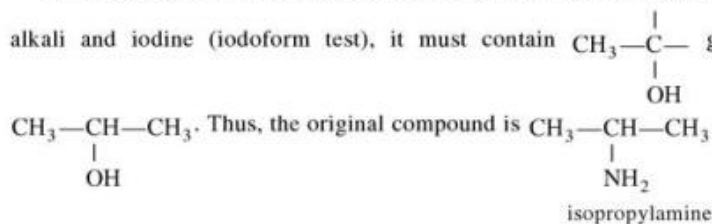
$$\text{Amount of compound RNH}_2 = \frac{1}{200} \text{ mol}$$

If M is the molar mass of RNH_2 , then

$$\frac{2.295 \text{ g}}{M} = \frac{1}{200} \text{ mol} \quad \text{or} \quad M = 0.295 \times 200 \text{ g mol}^{-1} = 59 \text{ g mol}^{-1}.$$

Thus, the molar mass of alkyl group R is $(59 - 16) \text{ g mol}^{-1}$, 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 $\text{CH}_3-\overset{\text{I}}{\underset{\text{OH}}{\text{C}}}-$ group. Hence, it is concluded that ROH is



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 |

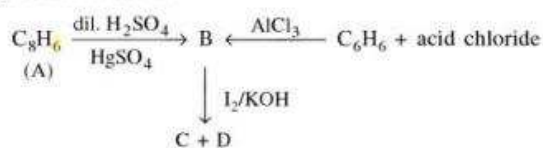
Ans :

(a) - (r); (b) - (p); (c) - (s); (d) - (q)

Identify the compound

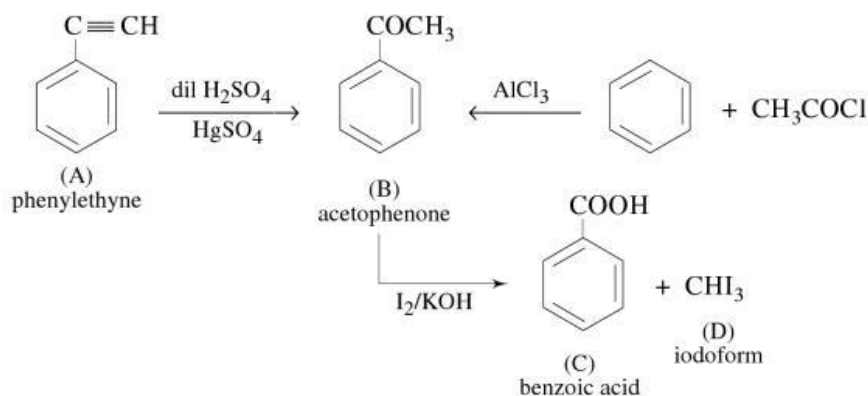
An organic compound A, C_8H_6 , on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH , 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 $-\text{COCH}_3$ group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone ($\text{C}_6\text{H}_5\text{COCH}_3$). The compound C must be an acid.

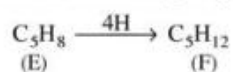
The compound A may be represented as $\text{C}_6\text{H}_5\text{C}_2\text{H}$. Since it gives $\text{C}_6\text{H}_5\text{COCH}_3$ on treating with dilute H_2SO_4 and HgSO_4 , it must contain a triple bond ($-\text{C}\equiv\text{CH}$) in the side chain. Hence, the given reactions may be represented as



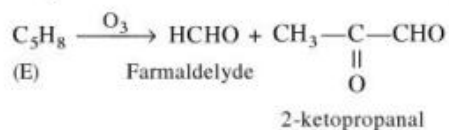
Identify the compound

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

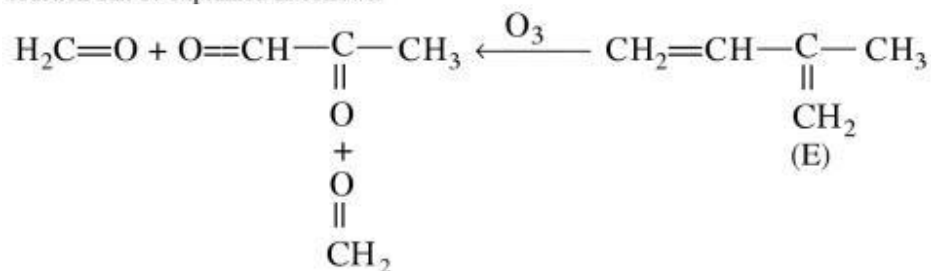


the compound E may contain two double bonds. The ozonolysis reaction is



Since there is no loss of carbon atoms in an ozonolysis reaction, probably 2 molecules of formaldehyde are formed. In 2-ketopropanal, $-\underset{\text{O}}{\underset{\parallel}}{\text{C}}-$ and $-\text{CHO}$ groups must have resulted due to the cleavage of double bonds. Hence, the net

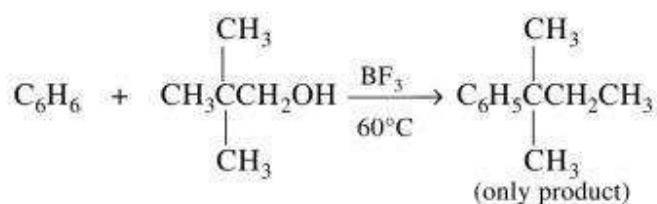
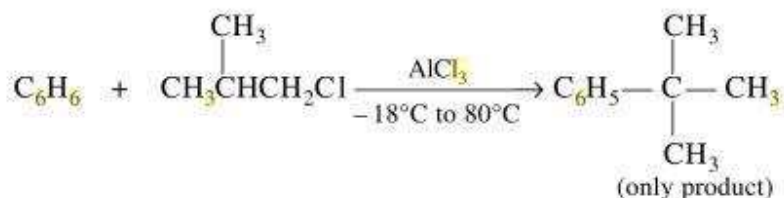
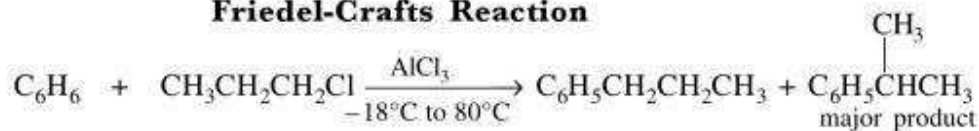
reaction can be explained as follows.



Hence, the compound E is 2-methyl-1, 3-butadiene.

Friedel Crafts Reaction

Friedel-Crafts Reaction



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

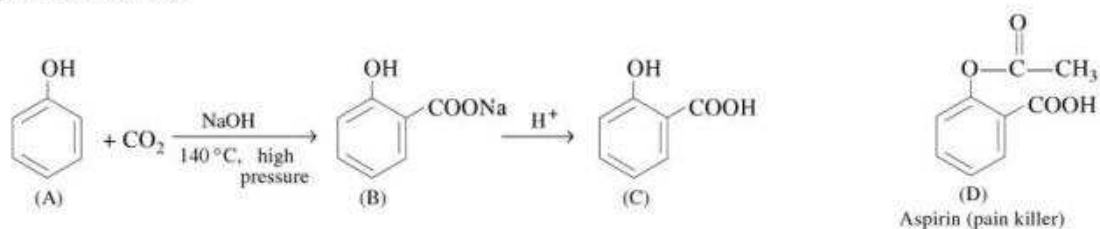
$$\text{C} : \text{H} : \text{O} :: \frac{76.6}{12} : \frac{6.38}{1} : \frac{17.02}{16} :: 6.38 : 6.38 : 1.064 :: 6 : 6 : 1$$

Hence, Empirical formula of A is $\text{C}_6\text{H}_6\text{O}$. Molar empirical formula mass of A = 94 g mol^{-1}

This tallies with the given molar mass ($= 2 \times 47 \text{ g mol}^{-1}$). Thus Molecular formula of A is $\text{C}_6\text{H}_6\text{O}$.

Since, the compound A gives characteristic colour with FeCl_3 , it must be a phenol.

The given reactions are



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, $\text{C}_8\text{H}_{10}\text{O}$. Compound B can be oxidized under mild conditions to compound C, $\text{C}_8\text{H}_8\text{O}$. 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

$$\text{C} : \text{H} : \text{Cl} :: \frac{68.32}{12} : \frac{6.4}{1} : \frac{25.26}{35.5} :: 5.69 : 6.4 : 0.71 :: 8 : 9 : 1$$

Hence, Empirical formula of A is $\text{C}_8\text{H}_9\text{Cl}$. Molar empirical formula mass of A = 140.5 g mol^{-1}

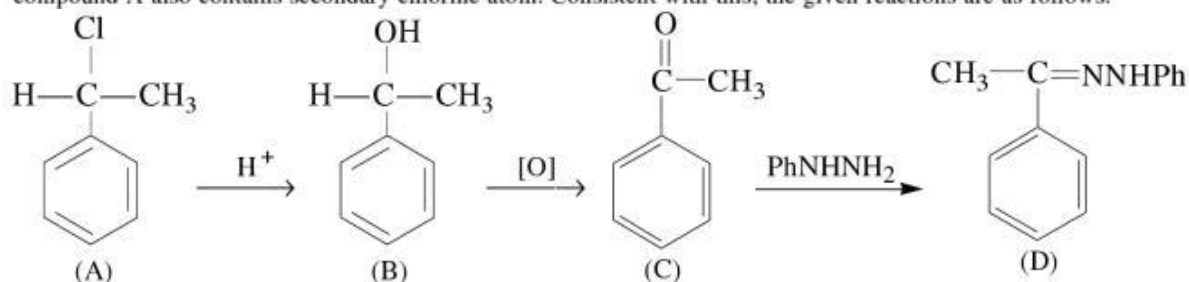
This tallies with the given molar mass. Thus Molecular formula of A is $\text{C}_8\text{H}_9\text{Cl}$.

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 $-\text{COCH}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ was used to reach the end point. The molarity of the household bleach solution is

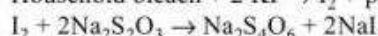
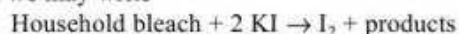
- (a) 0.48 M (b) 0.96 M (c) 0.24 M (d) 0.024 M

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



$$\text{Amount of } \text{Na}_2\text{S}_2\text{O}_3 \text{ used} = VM = (48 \times 10^{-3} \text{ L}) (0.25 \text{ mol L}^{-1}) = 12 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } \text{I}_2 \text{ generated} = \frac{1}{2} (12 \times 10^{-3} \text{ mol}) = 6 \times 10^{-3} \text{ mol}$$

Assuming 1 mol of household bleach produces 1 mol I_2 , we will have

$$\text{Amount of household bleach in 25 mL solution} = 6 \times 10^{-3} \text{ mol}$$

$$\text{Molarity of household bleach} = \frac{n}{V} = \frac{6 \times 10^{-3} \text{ mol}}{25 \times 10^{-3} \text{ L}} = 0.24 \text{ M}$$

For Q 12, we have

Bleaching powder contains $\text{Ca}(\text{OCl})\text{Cl}$.

The oxoacid of this salt is HOCl. The formation of this acid through its anhydride is $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HOCl}$
anhydride oxoacid

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

- (a) $\text{C}_6\text{H}_5\text{CHO}$
 (b) $\text{CH}_3\text{C} \equiv \text{CH}$
 (c) CN^-
 (d) I^-

Column II

- (p) gives precipitate with 2,4-dinitrophenylhydrazine
 (q) gives precipitate with AgNO_3
 (r) is a nucleophile
 (s) is involved in cyanohydrin formation

Ans :

$$(a) - (p), (q), (s); \quad (b) - (q); \quad (c) - (q), (r), (s); \quad (d) - (q)$$

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.



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) $h^2/(4\pi^2ma_0^2)$ (b) $h^2/(16\pi^2ma_0^2)$ (c) $h^2/(32\pi^2ma_0^2)$ (d) $h^2/(64\pi^2ma_0^2)$

Solution :

Bohr model of an atom satisfies the following two requirements.

- Equality of centripetal and centrifugal forces, i.e.
- Quantization of angular momentum, i.e.

$$\frac{(Ze)(e)}{(4\pi\epsilon_0)r^2} = \frac{mv^2}{r} \quad mvr = n\left(\frac{h}{2\pi}\right)$$

Eliminating v in these two expressions, we get

$$r = n^2 \left[\frac{h^2}{4\pi^2 m (Ze^2 / 4\pi\epsilon_0)} \right] = \frac{n^2}{Z} a_0$$

where a_0 is the Bohr radius. The kinetic energy of the electron in Bohr orbit of an atom is

$$\text{KE} = \frac{1}{2}mv^2 = \frac{1}{2}m \left[\frac{n}{mr} \left(\frac{h}{2\pi} \right) \right]^2 = \frac{1}{2}m \left[\frac{n}{m(n^2 a_0 / Z)} \left(\frac{h}{2\pi} \right) \right]^2 = \frac{Z^2}{n^2} \left(\frac{h^2}{8\pi^2 m a_0^2} \right)$$

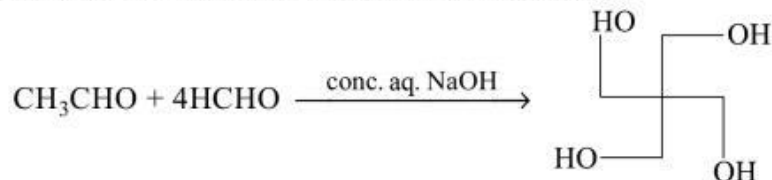
For the second Bohr orbit of hydrogen atom, $Z = 1$, and $n = 2$. Hence

$$\text{KE} = \frac{1}{32} \left(\frac{h^2}{\pi^2 m a_0^2} \right)$$

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

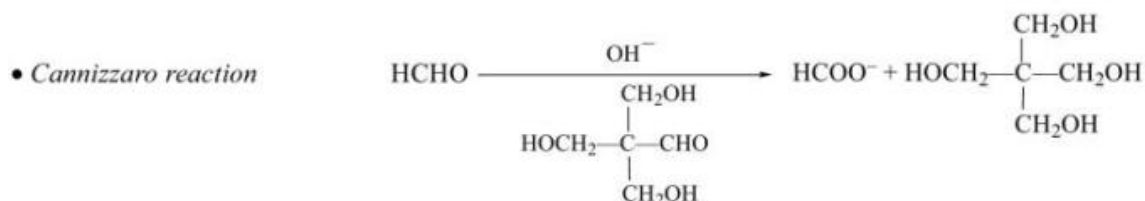
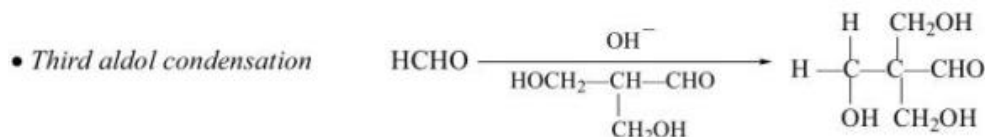
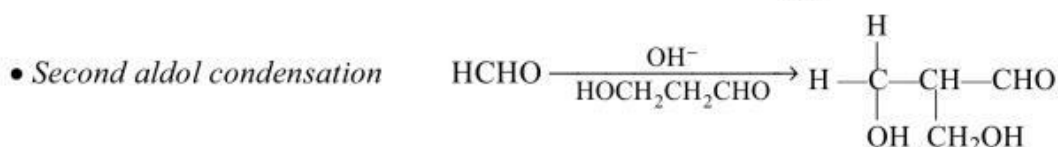
(b) 2

(c) 3

(d) 4

Solution :

The given reaction may be formulated as follows.



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 $(t_{1/8}/t_{1/10}) \times 10$? ($\log 2 = 0.3$.)

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 $\frac{\ln(1/8)}{\ln(1/10)} = \frac{t_{1/8}}{t_{1/10}}$ or $\frac{\log 8}{\log 10} = \frac{t_{1/8}}{t_{1/10}}$

Hence $(t_{1/8}/t_{1/10}) = \log 8 = \log 2^3 = 3 \log 2 = 3 \times 0.3 = 0.9$ or $10(t_{1/8}/t_{1/10}) = 10 \times 0.9 = 9$

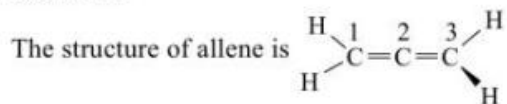
Therefore, the answer is **9**.

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

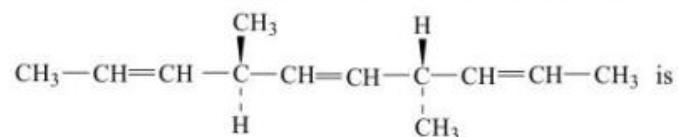
Solution :



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.

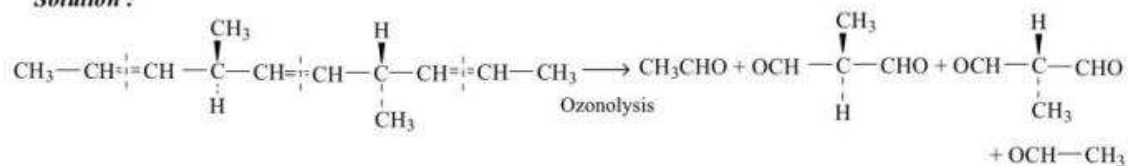
Number of chiral carbon and optically active products

The number of optically active products obtained from the complete ozonolysis of the given compound



- (a) 0 (b) 1 (c) 2 (d) 4

Solution :



None of the products will be optically active. Therefore, the **choice (a)** is correct.

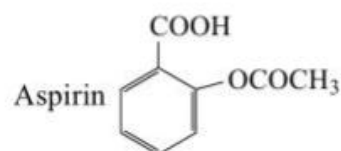
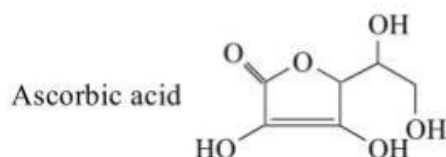
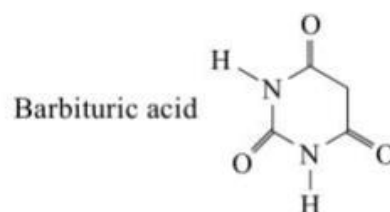
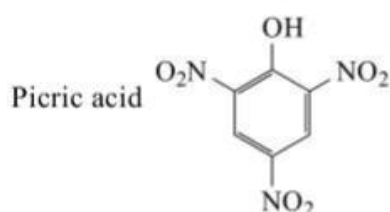
Carboxylic functional group is present in aspirin

The carboxylic functional group (—COOH) is present in

- (a) picric acid (b) barbituric acid (c) ascorbic acid (d) aspirin

Solution :

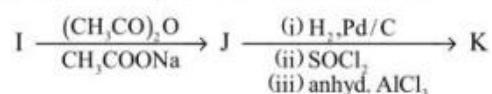
The structures of the given compounds are as follows.



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

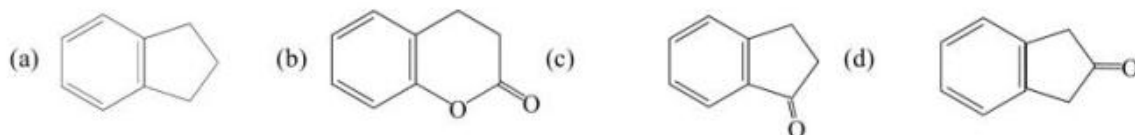
Identify the compound

In the following reaction sequence, the compound J is an intermediate

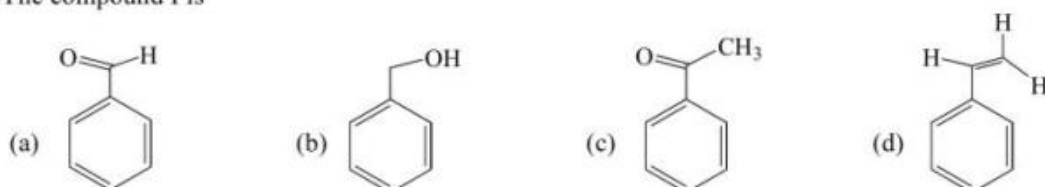


$J(\text{C}_9\text{H}_8\text{O}_2)$ gives effervescence on treatment with NaHCO_3 and positive Baeyer's test.

Q - The compound K is



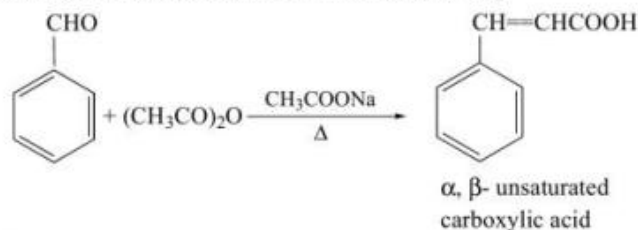
Q - The compound I is



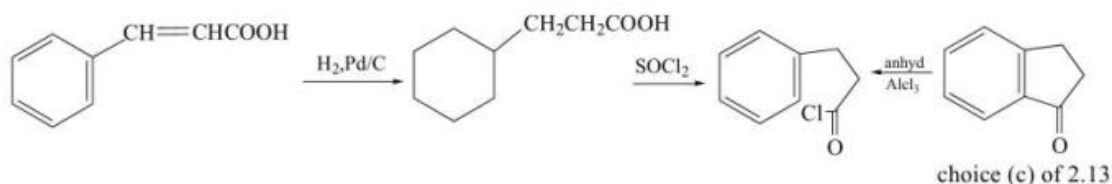
Perkin Condensation

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 $(\text{CH}_3\text{CO})_2\text{O}$ 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



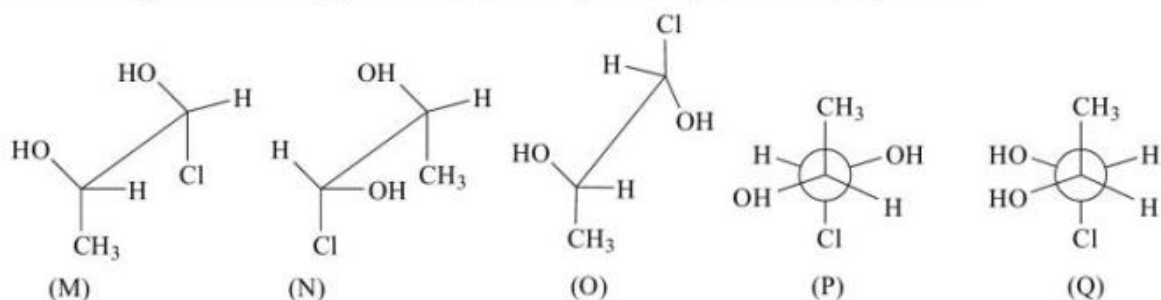
The conversion J to K is as follows.



Hence, we have
The **choice (c)** is correct.
The **choice (a)** is correct.

Question on isomers

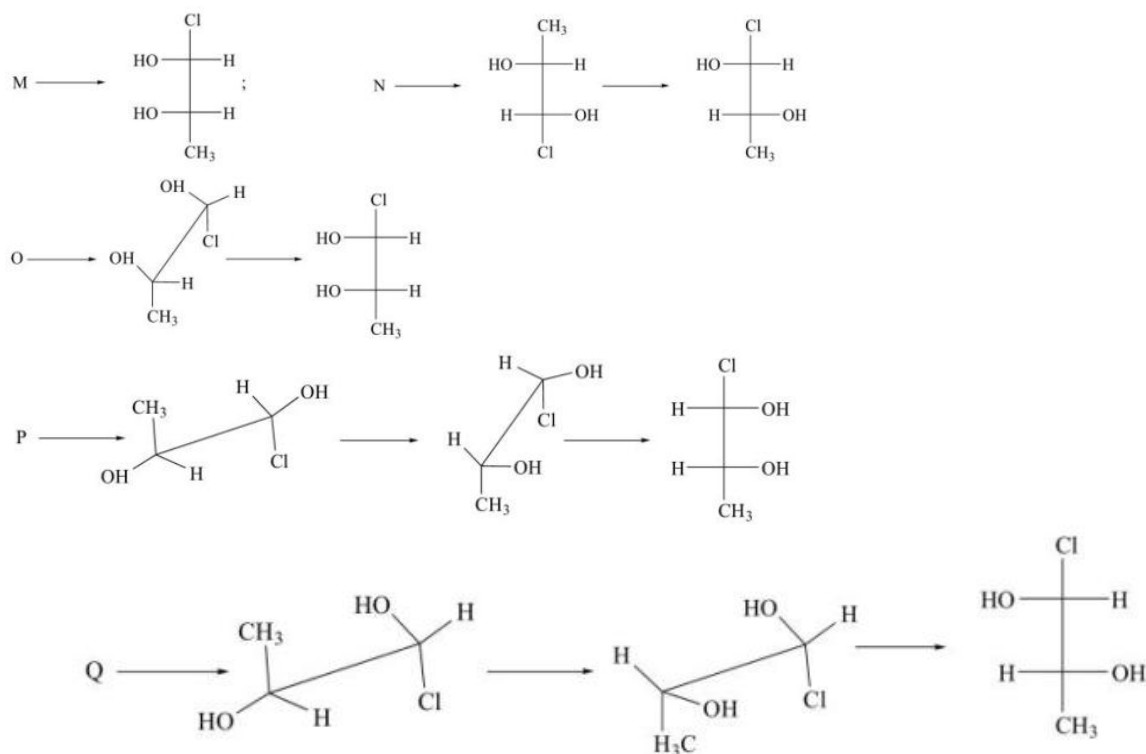
Which of the given statement(s) about N, O, P and Q with respect to M is(are) correct?



- (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



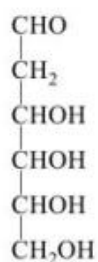
From the Fischer projections, it follows that
M and N are non-mirror images.
M and P are enantiomers.

M and O are identical.
M and Q are not identical.

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

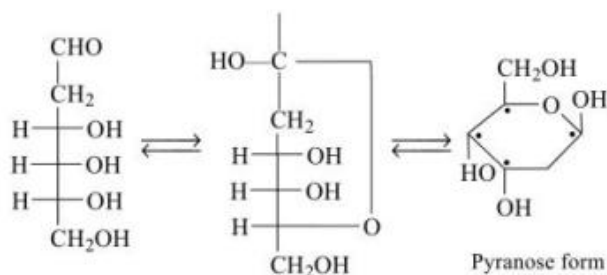
Aldohexose exists in D configuration

When the following aldohexose exists in D-configuration, the total number of stereoisomers in its pyranose form is



Solution:

In D-configuration, the hydroxyl group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right of the straight skeleton. Thus, we will have

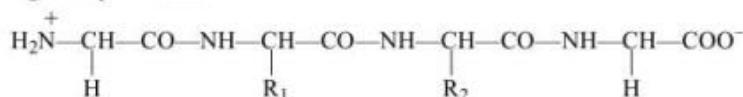


There are four chiral carbon atoms in the pyranose form of the given aldohexose. Thus, there will be $16 (= 2^4)$ stereoisomers, out of which 8 are of D-configurations (CH_2OH group above the ring) and 8 are of L-configurations (CH_2OH group below the ring).

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 $\text{pH} = 7.0$?



| Peptide | R_1 | R_2 |
|---------|------------------------------|------------------------------|
| I | H | H |
| II | H | CH_3 |
| III | CH_2COOH | H |
| IV | CH_2CONH_2 | $(\text{CH}_2)_4\text{NH}_2$ |
| V | CH_2CONH_2 | CH_2CONH_2 |
| VI | $(\text{CH}_2)_4\text{NH}_2$ | $(\text{CH}_2)_4\text{NH}_2$ |
| VII | CH_2COOH | CH_2CONH_2 |
| VIII | CH_2OH | $(\text{CH}_2)_4\text{NH}_2$ |
| IX | $(\text{CH}_2)_4\text{NH}_2$ | 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.

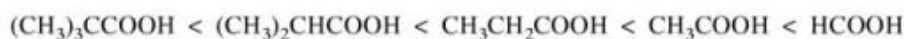
At $\text{pH} = 7$, the acidic side chain (for which isoelectric point < 7) exists as a negatively-charged species (e.g. $-\text{COO}^-$) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g. $-\text{NH}_3^+$). Since peptides IV, VI, VIII and IX contain $-\text{NH}_2$ 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**.

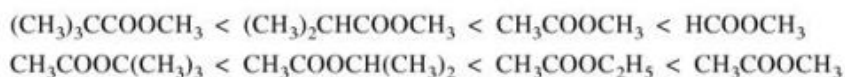
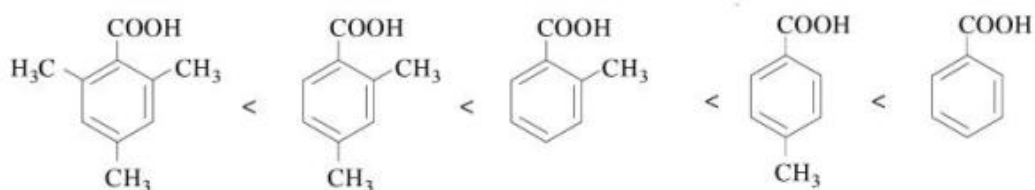
Try to figure out what sequence is depicted

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.

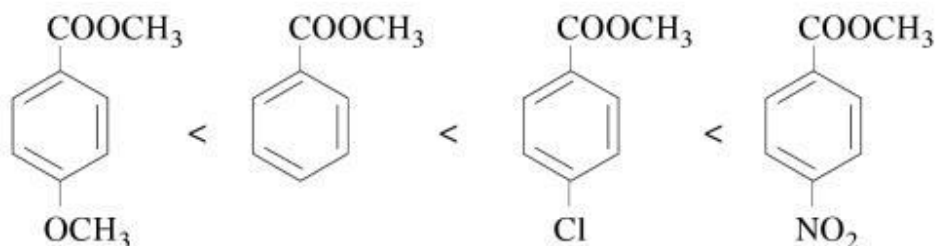
n-butyl alcohol < isobutyl alcohol < *sec*-butyl alcohol < *tert*-butyl alcohol. Polarity of O—H bond increases in the same order.



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).



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 , $\text{C}_2\text{H}_5\text{COCH}_3$

Increasing basicity: *p*-toluidine, *N,N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline.

Increasing ease of hydrolysis: $\text{CH}_3\text{COOC}_2\text{H}_5$, CH_3COCl , $(\text{CH}_3\text{CO})_2\text{O}$, CH_3CONH_2

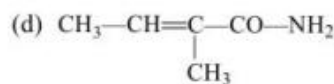
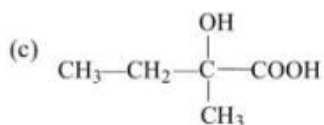
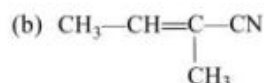
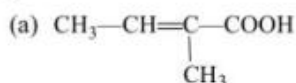
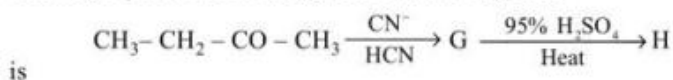
Increasing order of acid strength:

ClCH_2COOH , $\text{CH}_3\text{CH}_2\text{COOH}$, $\text{ClCH}_2\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$, CH_3COOH

Increasing reactivity in nucleophilic substitution reactions: CH_3F , CH_3I , CH_3Br , CH_3Cl

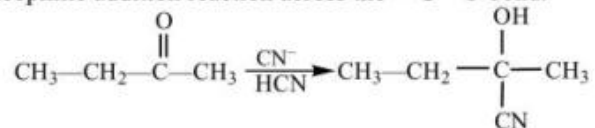
major product H in the given reaction sequence

The major product H in the given reaction sequence

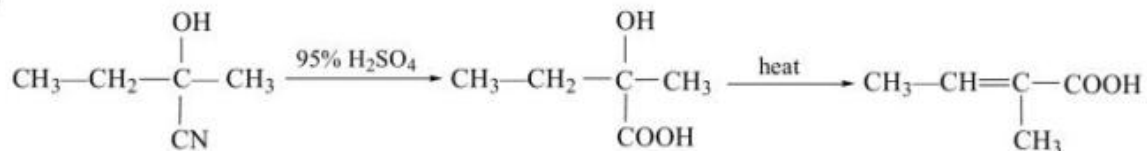


Solution :

The first reaction is nucleophilic addition reaction across the $-\text{C}=\text{O}$ bond.



In the second reaction, $-\text{CN}$ is hydrolysed to $-\text{COOH}$. The resultant molecule undergoes dehydration on heating.



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:

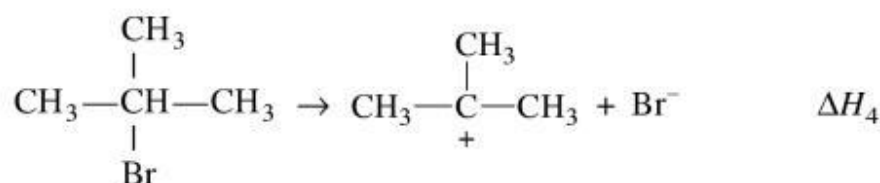
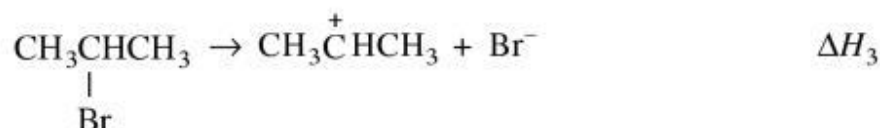
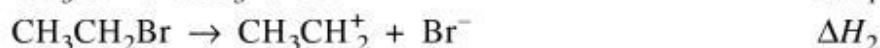
α -phenyl ethyl alcohol, α -(*p*-nitrophenyl) ethyl alcohol, α -(*p*-aminophenyl) ethyl alcohol

Various Increasing Properties

Increasing stability of free radicals: $\bullet\text{CH}_3$, 1° , 2° , 3° , allyl, vinyl

Increasing stability of carbocation: CH_3^+ , 1° , 2° , 3°

Increasing enthalpy of reaction:

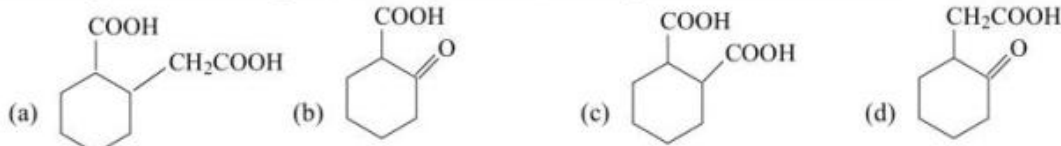


Increasing order of reactivity towards $\text{S}_\text{N}2$ displacement:

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

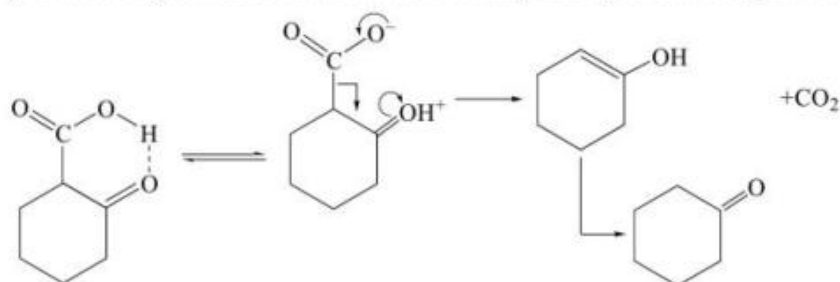
compound undergoes decarboxylation most readily

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

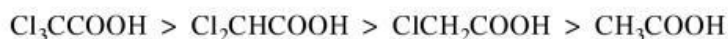
- (a) $\text{C}_3\text{H}_7\text{C}\equiv\text{CH}$ (b) $\text{C}_8\text{H}_9\text{C}\equiv\text{CH}$ (c) $\text{C}_6\text{H}_{11}\text{C}\equiv\text{CH}$ (d) $\text{C}_4\text{H}_7\text{C}\equiv\text{CH}$

Ans :

Empirical formula contains $C : H :: \frac{88.89}{12} : \frac{11.1}{1} :: 7.4 : 11.11 :: 2 : 3$

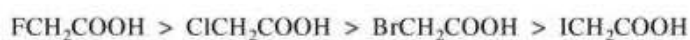
Only the compound $C_6H_{11}C \equiv CH$ has composition 4 times the composition of empirical formula.

More the number of electron withdrawing group stronger is the acid

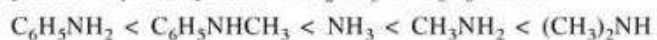
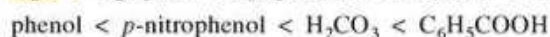
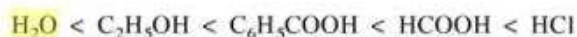
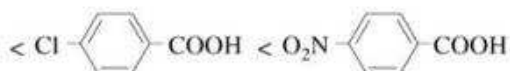
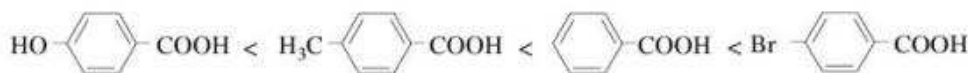


The more the number of electron-withdrawing group, the stronger the acid.

Try to figure out what sequence is depicted



The more the electronegativity of halogen, the stronger the acid.



$(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$. $(CH_3)_3N$ 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 $CH_3OH > 1^\circ > 2^\circ > 3^\circ$.

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 :

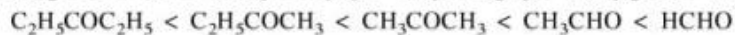
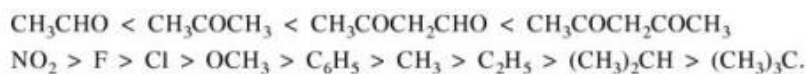
An organic compound A contains 49.32% C, 9.59% H and 19.18% N and rest oxygen. The compound A on boiling with NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67% Ag. The compound A is

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Hence $\frac{108}{M_R + 44 + 108} = 0.5967$. This gives $M = 29$ i.e. $R \equiv C_2H_5$.

Hence, the compound is $C_2H_5CONH_2$.

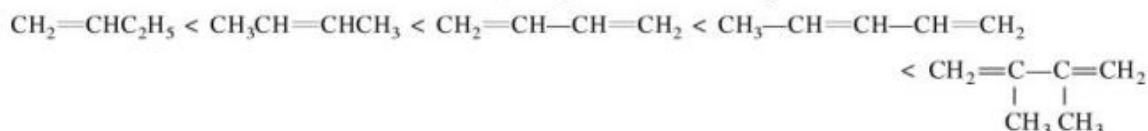
Try to figure out what sequence is depicted



The smaller the alkyl group, the more reactive the carbonyl group.



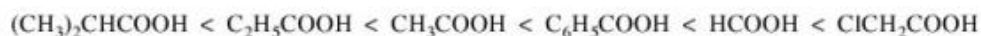
The more stable the intermediate carbocation, the greater the reactivity.



Conjugated dienes form the more stable allyl carbocations and are thus more reactive than alkenes. Alkyl groups on the unsaturated carbon atoms increase reactivity.



tert-butanol < *sec*-butanol < *n*-butanol < CH₃OH. Alkyl group makes an alcohol less acidic. Bigger the alkyl group, the less acidic the alcohol. Methanol is the strongest and tertiary alcohols are the weakest.



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 H₂SO₄. The empirical formula of the compound is

- (a) C₅H₅N₂O (b) C₇H₇NO (c) C₆H₅NO₂ (d) C₆H₈NO

Ans :

$$\text{Amount of H}_2\text{SO}_4 \text{ neutralized} = (25 \times 10^{-3} \text{ L})(0.05 \text{ M}) = 1.25 \times 10^{-3} \text{ mol}$$



$$\text{Amount of NH}_3 \text{ evolved} = 2 \times 1.25 \times 10^{-3} \text{ mol} = 2.5 \times 10^{-3} \text{ mol}$$

$$\text{Mass of N in the compound} = (2.5 \times 10^{-3} \text{ mol})(14 \text{ g mol}^{-1}) = 0.035 \text{ g}$$

$$\text{Per cent of N in the compound} = \frac{0.035}{0.3} \times 100 = 11.67$$

$$\text{Per cent of O in the compound} = 100 - (69.4 + 5.8 + 11.67) = 13.13$$

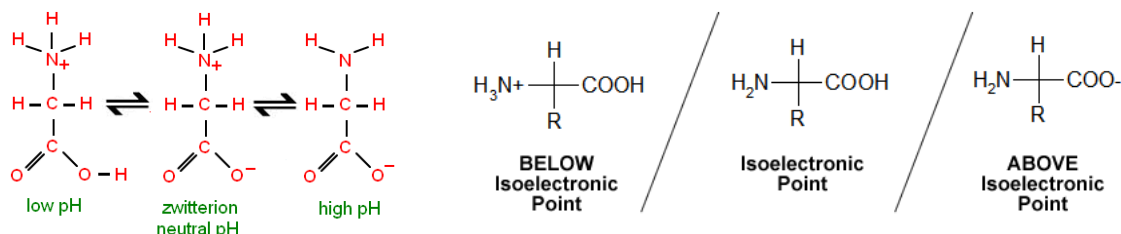
Ratio of atoms in the compound is

$$\text{C} : \text{H} : \text{N} : \text{O} :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.67}{14} : \frac{13.13}{16} :: 5.78 : 5.8 : 0.83 : 0.82 :: 7 : 7 : 1 : 1$$

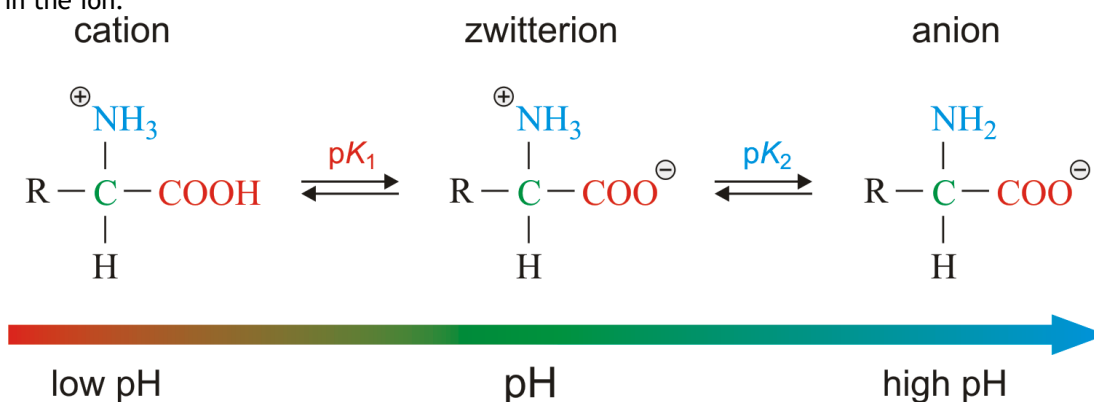
Hence, empirical formula: C₇H₇NO

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)

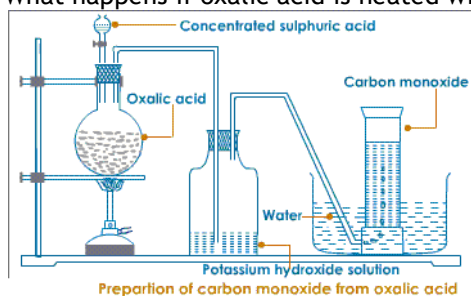


Electrophoresis - is a method to confirm if a positive charge is present or a negative charge is present in the ion.

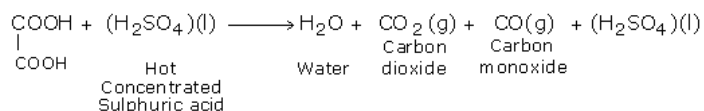


Iso -Electric point - the pH at which the ion (molecule) does not migrate to any electrodes.

What happens if oxalic acid is heated with conc sulphuric acid ?



We get Carbon monoxide

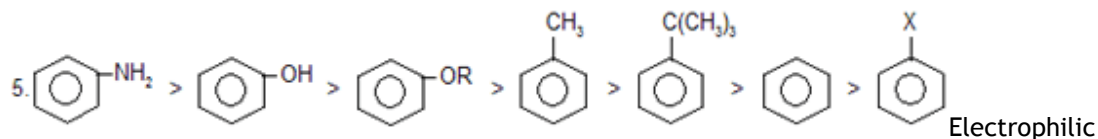


IMPORTANT ORDER AND FACTS OF ORGANIC CHEMISTRY

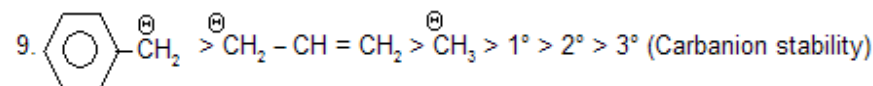
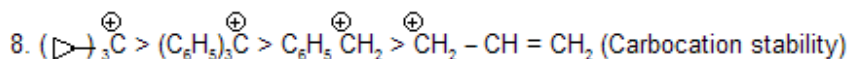
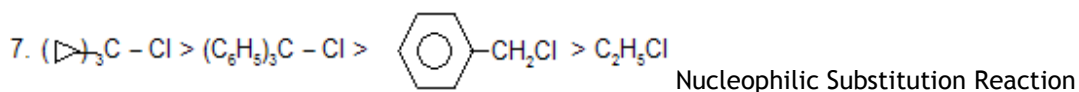
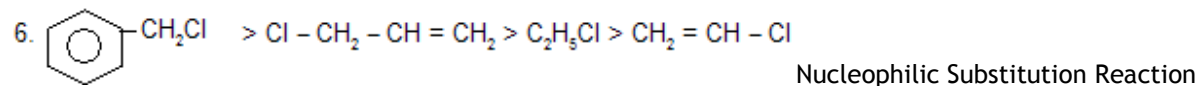
1. $\text{RCOCl} > \text{RCOOCOR} > \text{RCOOR} > \text{RCONH}_2$ Nucleophilic substitution reaction.
2. $\text{HI} > \text{HBr} > \text{HCl} > \text{RCOOH} > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH} \equiv \text{CH} > \text{NH}_3$ (Acidic nature).

3. $\text{CCl}_3\text{CHO} > \text{HCHO} > \text{CH}_3\text{CHO} > \text{CH}_3\text{COCH}_3$ Nucleophilic addition reaction.

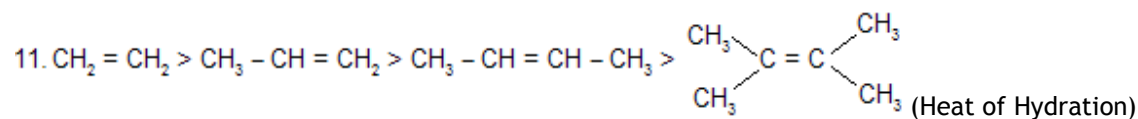
4. $\text{CH}_2 = \text{CH}_2 > \text{CH} \equiv \text{CH} > \text{C}_6\text{H}_6$ Electrophilic addition reaction.



Substitution Reaction



10. $(\text{CH}_3)_2\text{C} = \text{C}(\text{CH}_3)_2 > \text{CH}_3 - \text{CH} = \text{C} - (\text{CH}_3)_2 > \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 > \text{CH}_3 - \text{CH} = \text{CH}_2$ (Stability)



12. $\text{NH}_2^{\ominus} > \text{OH}^{\ominus} > \text{NH}_3 > \text{H}_2\text{O}$ (Basic strength)

13. $\text{NI}_3 > \text{NBr}_3 > \text{NCl}_3 > \text{NF}_3$ (Basic strength)

14. $\text{Br}_2 > \text{Cl}_2 > \text{I}_2$ (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 $:\text{CCl}_2$ 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 $(\text{CH}_3)_2\text{S}$ 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 $\text{Ag}(\text{NH}_3)_2^\ominus$ and $\text{Cu}(\text{NH}_3)_4^+$.

24. Cis-2-butene reacts with Br_2 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 insecticide DDT.

27. NBS is used for free radical allylation.

28. Rate for S_N^1 reaction is $3^\circ > 2^\circ > 1^\circ$ in protic polar solvent.

29. Rate for S_N^2 reaction is $1^\circ > 2^\circ > 3^\circ$ 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 .

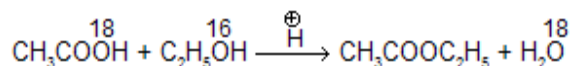
31. If cyclo 1,3-penta diene reacts with CHCl_3 and potassium tert. butoxide to form chlorobenzene.

32. Alkyl halides reacts with AgCN to form isocyanides due to ambident nature of nucleophile, other ambident nucleophiles are NO_2^\ominus 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



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 ziesel's method.

38. If unsym. cyclic ether undergo fission it depends upon medium whether 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 separated by sodium bisulphite 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 α -hydrogen atom in the presence of dil base undergo enolization and form α

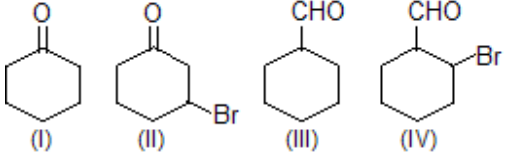
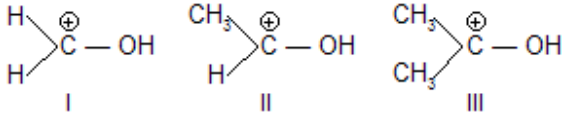
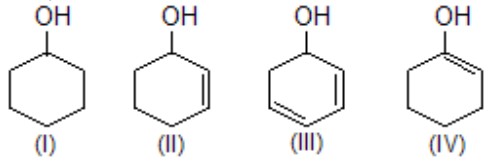
carbonian to give aldol product.

44. If there is two-CHO group with α -hydrogen atom to form cyclic intra aldol product.
45. Aldehydes without α -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 rearrangement 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 H^+ to give polymer nylon-6
53. 2-methyl propanal even contains α -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 reducing 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 α -hydrogen atom when reacts with halogen in the presence of P to form α -haloacid (HVZ).
62. Carboxylic 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 α, β -unsaturated carboxylic acid (perkin reaction)

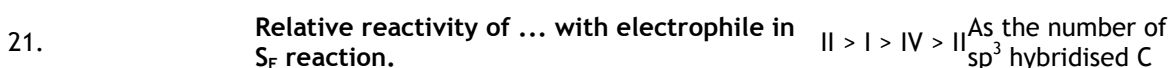
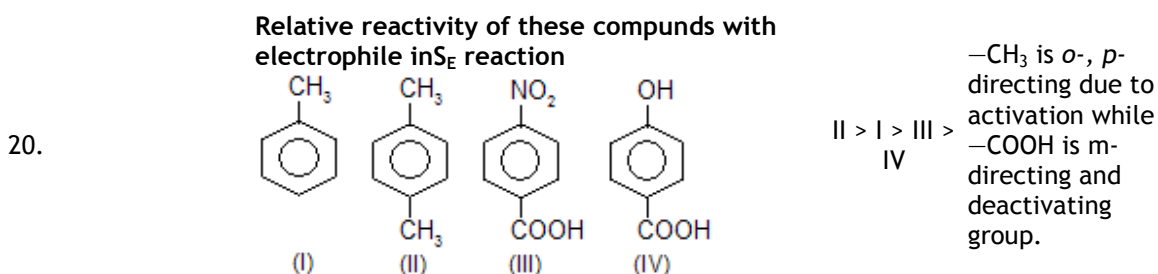
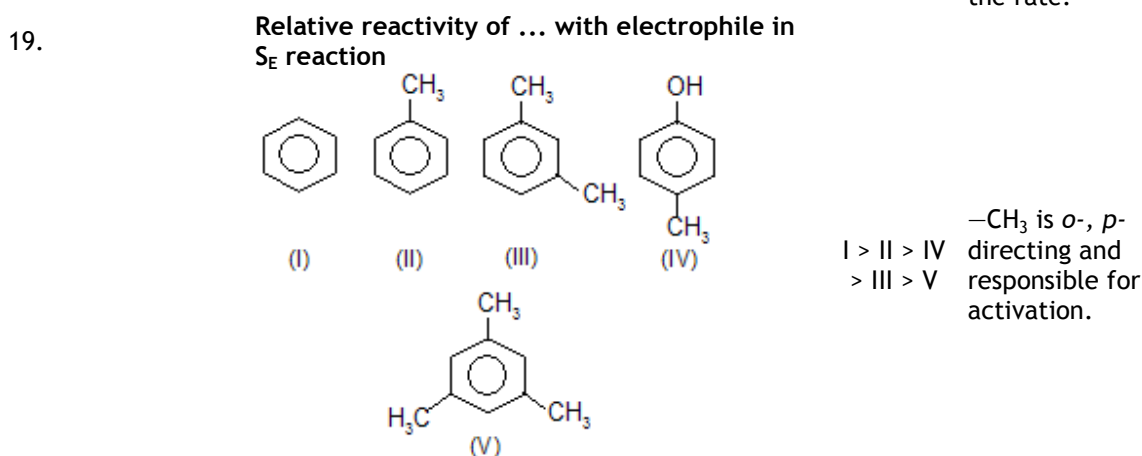
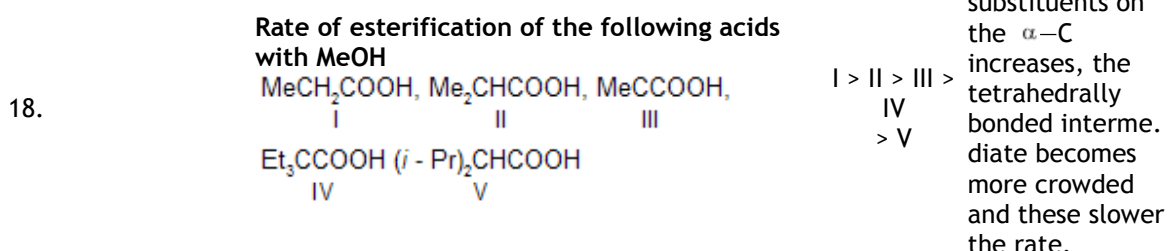
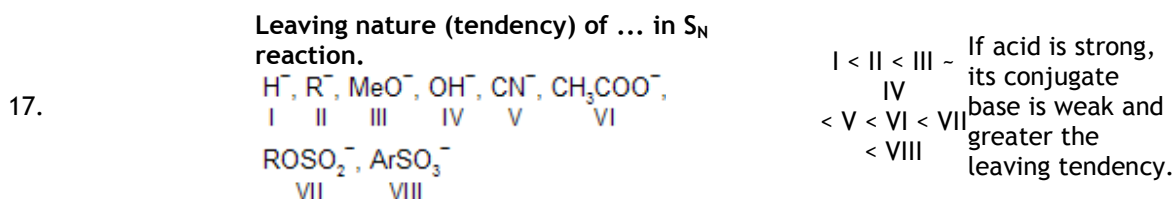
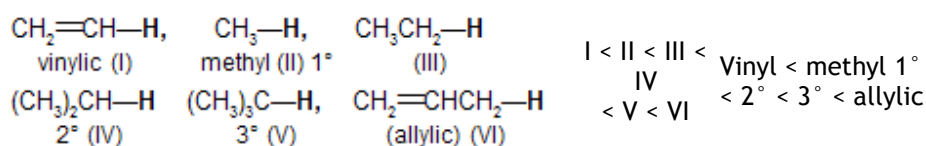
66. Amide on reaction with Br_2 and alkali to form primary amine of lower homologue. Intermediate species is nitrene which undergo intra rearrangement to form RNH_2 .
67. Ester's with α -hydrogen atom in the presence of strong base to form carbanion undergo nucleophilic substitution reaction forms β -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 $(4n + 2)\pi$ 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. $\text{C}_6\text{H}_5\text{NH}_2 > \text{C}_6\text{H}_5\text{OH} > \text{C}_6\text{H}_5\text{OR} > \text{C}_6\text{H}_5\text{Br} > \text{C}_6\text{H}_5\text{NO}_2$ (Reactivity towards electrophilic substitution reaction)

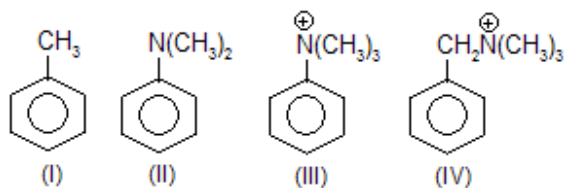
General Series - Chemistry Fact Sheet - 3

| General series | Order | Why ? |
|--|--------------|--|
| 1. B.P. of $\text{CH}_3\text{CH}_2\text{OH}$, CH_3OCH_3 , CH_3CH_3 I II III | I > II > III | There is intermolecular H-bonding I. III has weak force of attraction and is most volatile. Intramolecular H-bonding in o-isomer makes it more volatile. |
| 2. B.P. of o, m, p-nitro phenol | o < m < p | |

3. **Reactivity of ... with Tollen's reagent**
 HCHO , CH_3CHO , CH_3COCH_3 , $\text{C}_6\text{H}_5\text{CHO}$
 I II III IV
 I > II > IV > III
 -CHO group is easily oxidised compared to keto group due to reducing 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)
 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
 I > II > III
 CH₃ group decreases +ve charge on C hence nucleophilic attack.
7. **Reactivity of isomeric 1°, 2°, 3° butyl halide towards elimination (E1 or E2)**
 $3^\circ < 2^\circ < 1^\circ$
 due to stability of intermediate carbocation
8. **Dehydration of**

 (I) (II) (III) (IV)
 IV < I < II < III
 Alcohol leading to increase in conjugation due to dehydration is more easily dehydrated. IV is vinylic, hence least.
9. **Stability of**

- $\text{CH}_2=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CH}_2$, $\text{CH}_3\text{CH}=\text{CHCH}_3$
 I II III
- Substituted alkenes are more stable. More the alkyl groups are attached to the doubly bonded carbon atom more is the stability.
- I < II < III < IV < V < VI
10. **Stability of**
- II is more substituted than III (More hyperconjugation more stability)
- I < III < II
11. **Stability of**
- IV is vinylic while in conjugative, II allylic.
- III > II > I > IV
12. **Stability of**
- III is 3° allylic and II is 1° allylic
- I < IV < II < III
13. **Dehydration of**
 1°, 2°, 3° isomeric butyl alcohol
- More the stability of intermediate, greater the reactivity of chemical reaction.
- 3° < 2° < 1°
14. **Boiling points of**
n-butyl amine, *n*-butyl alcohol, *n*-pentane
 I II III
- I, II have H-bonding but electronegativity of O > N hence H-bonding in II > I
- II > I > III
15. **Formation of**
- greater the stability, easier the formation of particular species.
- I > II > III > IV (easiest I)
16. **Reactivity of C—H bond (abstraction of H)**

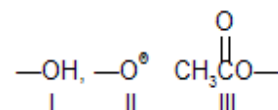




atoms separating the ring from the positively charged substituent increases, deactivating effect decreases due to less electronegativity.

$-\text{O}^\ominus$ is best able to donate electrons there by giving a very stable uncharged intermediate. In

22.



II > I > III

$\text{CH}_3\text{CO}-$ cross conjugation diminished its ability to donate electrons to an arenium ion. Intermediates are benzylic cations. So CH_3O (electron repelling) gives greater stability through delocalisation while NO_2 (electron attracting) decreases stability.

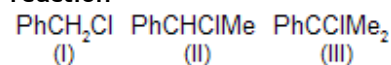
23.

Relative reactivity of ... towards $\text{S}_{\text{N}}1$ reaction
benzyl chloride, *p*-methoxy benzyl chloride
and *p*-nitro benzyl chloride

I II III

II > I > III

Relative reactivity of ... towards $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reaction



(Ph stands for phenyl, C_6H_5)

$\text{S}_{\text{N}}1$:
III > II > I

$\text{S}_{\text{N}}2$:
II < II < I

$\text{S}_{\text{N}}1$: $1^\circ < 2^\circ < 3^\circ$
alkyl halide

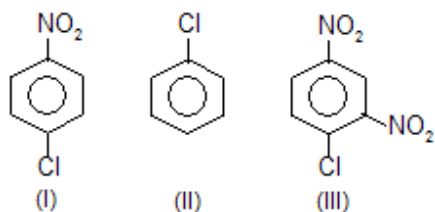
$\text{S}_{\text{N}}2$: $3^\circ < 2^\circ < 1^\circ$
alkyl halide

25.

Relative reactivity of ... with E^+ (electrophile) in S_{E} reaction.

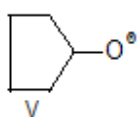
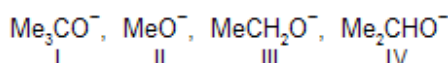
II > I > III

$-\text{NO}_2$ deactivates benzene ring for S_{E}



26.

Order of S_N2 reactivity of alkoxide nucleophiles

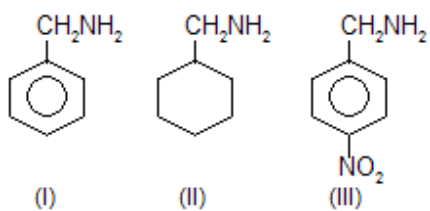
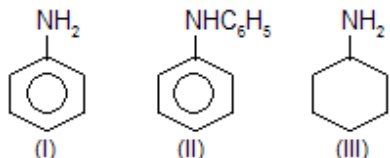
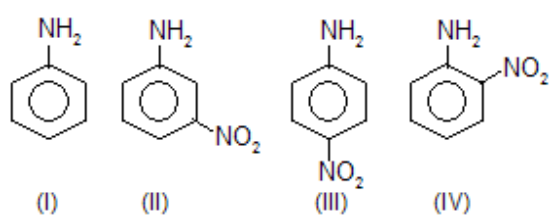
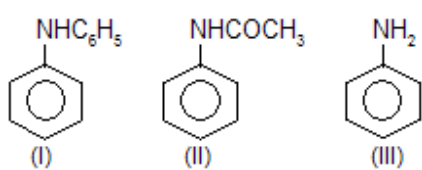
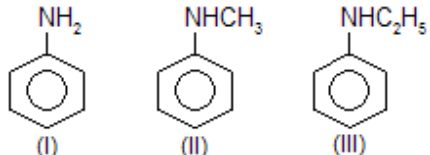


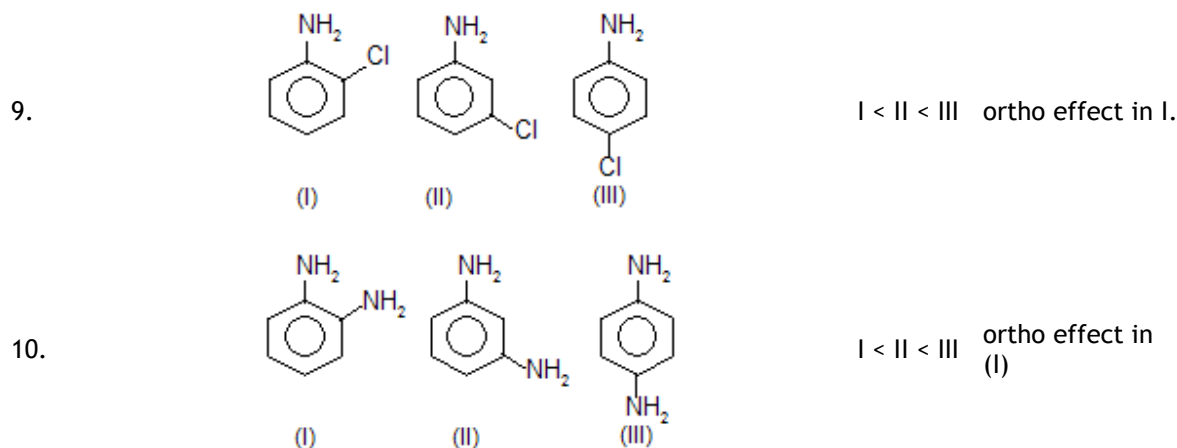
$I < IV < V < III < II$

S_N2 reactivity is susceptible to steric hindrance by the nucleophile as well as by the size of alkyl group.

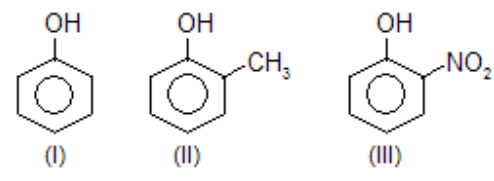
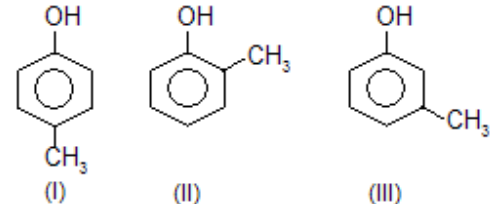
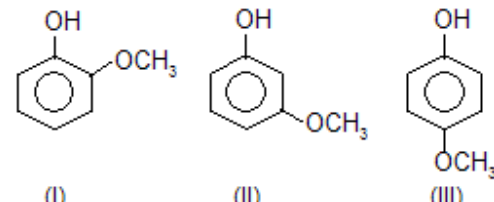
Basic power - Chemistry Fact Sheet - 2

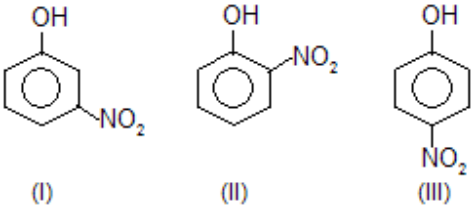
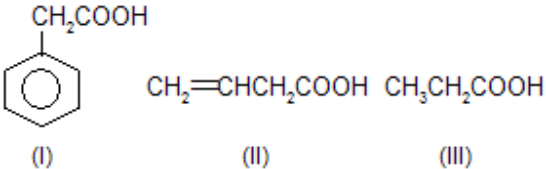
| | Basic power | Order | Why ? |
|----|-------------|-------------------|--|
| 1. | | I > III > II | lone pair on N is not used in resonance of π -electrons in I. In II lone pair of the ring is itself used in delocalisation while that of outside ring in III. |
| 2. | | I > II > III > IV | $-\text{OCH}_3$ is strong electron donating group. This is due to ortho effect , all the aniline are less basic than <i>p</i> -substituted aniline due to steric hindrance . |
| 3. | | I > II > III > IV | I (hyper conjugation and induction) II (induction) IV (ortho effect), ortho effect normally decreases basic nature. |

4.  II > I > III
- In II there is sp^3 hybridised C, In I, sp^2 . NO_2 is electron withdrawing.
5.  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. NO_2 is electron-withdrawing, thus nitro-anilines are less basic than aniline. IV is less basic than III because $-\text{NO}_2$ is closer and exerts a stronger inductive effect.
6.  I > II > III > IV
7.  III > I > II
- phenyl and $-\text{COCH}_3$ are electronwithdrawing and $-\text{C}_6\text{H}_5 < \text{COCH}_3$
8.  I < II < III
- Electron donating nature of $\text{C}_2\text{H}_5 > \text{CH}_3$ So more basic strength.



Acidic Powers & Their Orders - Chemistry Fact Sheet

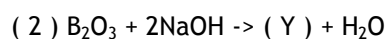
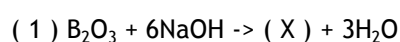
| Acidic power | Order | Why ? |
|--------------|---|---|
| 1. | 1-, 2-, 3- chlorobutanoic acid I II III | Farther the (-I) group (Cl), lesser the acidic strength III < II < I |
| 2. | 1-, 2-, 3- methyl pentanoic acid I II III | Farther the (+I) group, greater the acidic power I < II < III |
| 3. |  | -CH ₃ is electron donating and -NO ₂ is electron attracting II < I < III |
| 4. |  | -CH ₃ is electron repelling; decreases acidic strength of phenol II < I < III |
| 5. |  | -OCH ₃ group contains +M effect and decreases acidic power. III < I < II |

6.  (I) (II) (III) $I < II < III$
7.  (I) (II) (III) $I > II > III$
8.
 oxalic acid, succinic acid, malonic acid, adipic acid
 I II III
 adipic acid (all dibasic) IV $I > II > III > IV$
9.
o- *m*- *p*- nitrobenzoic acid
 I II III $II < III < I$
10.
o- *m*- *p*- hydroxy benzoic acid
 I II III $III < II < I$
- NO₂ is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative. sp² hybridised carbon of I, II are more electronegative hence acid strength is increased. Benzylic (C₆H₅CH₂) is more stabilised than allylic (CH₂=CHCH₂). Effect of one –COOH on the other decreases as its distance between them increases, (COOH)₂ is maximum acidic. –NO₂ is electron attracting (-I effect) –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. $\begin{matrix} o- \\ | \\ \text{I} \end{matrix}$ $\begin{matrix} m- \\ || \\ \text{II} \end{matrix}$ $\begin{matrix} p- \\ ||| \\ \text{III} \end{matrix}$ methoxy benzoic acid III < II < I –do–
12. $\begin{matrix} o- \\ | \\ \text{I} \end{matrix}$ $\begin{matrix} m- \\ || \\ \text{II} \end{matrix}$ $\begin{matrix} p- \\ ||| \\ \text{III} \end{matrix}$ amino benzoic acid I < III < II –NH₂ is electron donating.

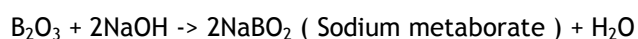
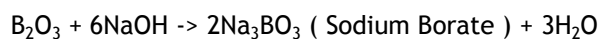
Topic wise grouping of information kind of Dictionary of Inorganic Chemistry

Given two Equations



What are (X) and (Y)?

Ans : X is Sodium Borate and Y is Sodium meta borate



Silica is soluble in which of the following acids ?

(1) HF (2) HCl (3) HBr (4) HI

Solution : $\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ and again $\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6$ (Hydroflurosilicic acid)

-

$\text{K}_3\text{Co}(\text{NO}_2)_6$ is Fischer's Salt

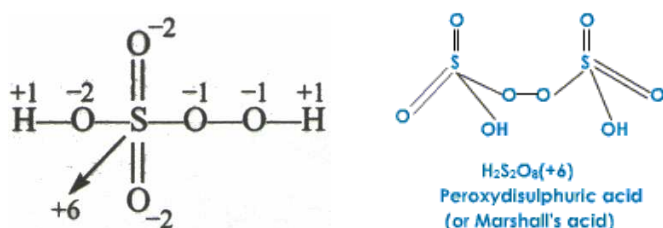
The brown ring test for NO_3^- is due to formation of the complex $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$

Merck's perhydrol is 30.4% H_2O_2

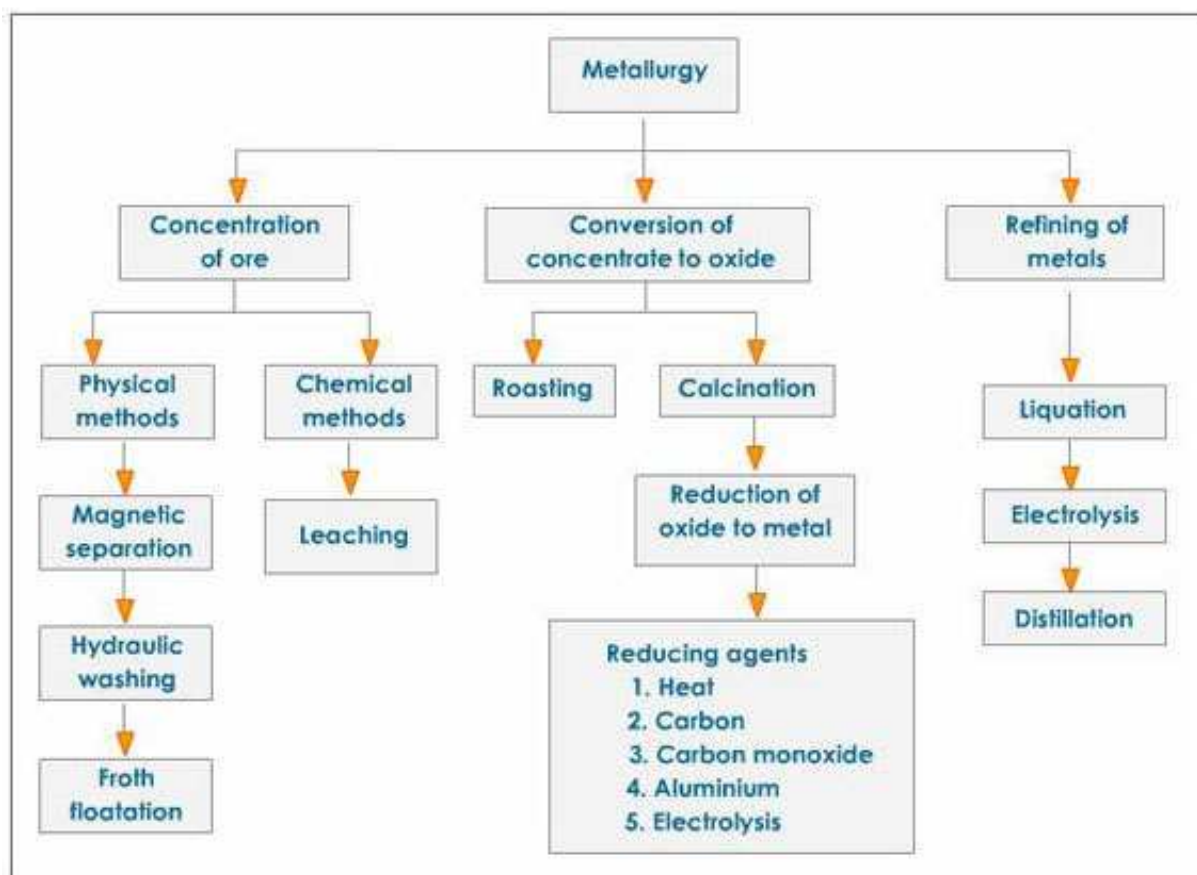
Elements having one or more solvated ions in water

| | | | | | | | | | | III A | | | | | IV A | | | | | V A | | | | | VI A | | | | | VII A | | | | | VIII 18 | | | | |
|----|----|-----|----|----|----|----|----|----|----|-------|----|----|----|----|------|----|----|---------|----|-----|----|----|--------|----|------|----|----|----|----|-------|----|----|----|--|---------|--|--|--|--|
| | | | | | | | | | | 13 | | | | | 14 | | | | | 15 | | | | | 16 | | | | | 17 | | | | | 18 | | | | |
| H | | | | | | | | | | | | | | | | | | He | | | | | | | | | | | | | | | | | | | | | |
| Li | Be | | | | | | | | | | | | | | | | | | Ne | | | | | | | | | | | | | | | | | | | | |
| Na | Mg | Al | Si | P | S | Cl | Ar | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | | | | | | | | | | | |
| K | Ca | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | |
| Cs | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | |
| Rb | Ba | lan | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | | | |
| Fr | Ra | act | Rf | Db | Sg | Bh | Hs | Mt | Ds | | | | | | | | | cations | | | | | anions | | | | | | | | | | | | | | | | |

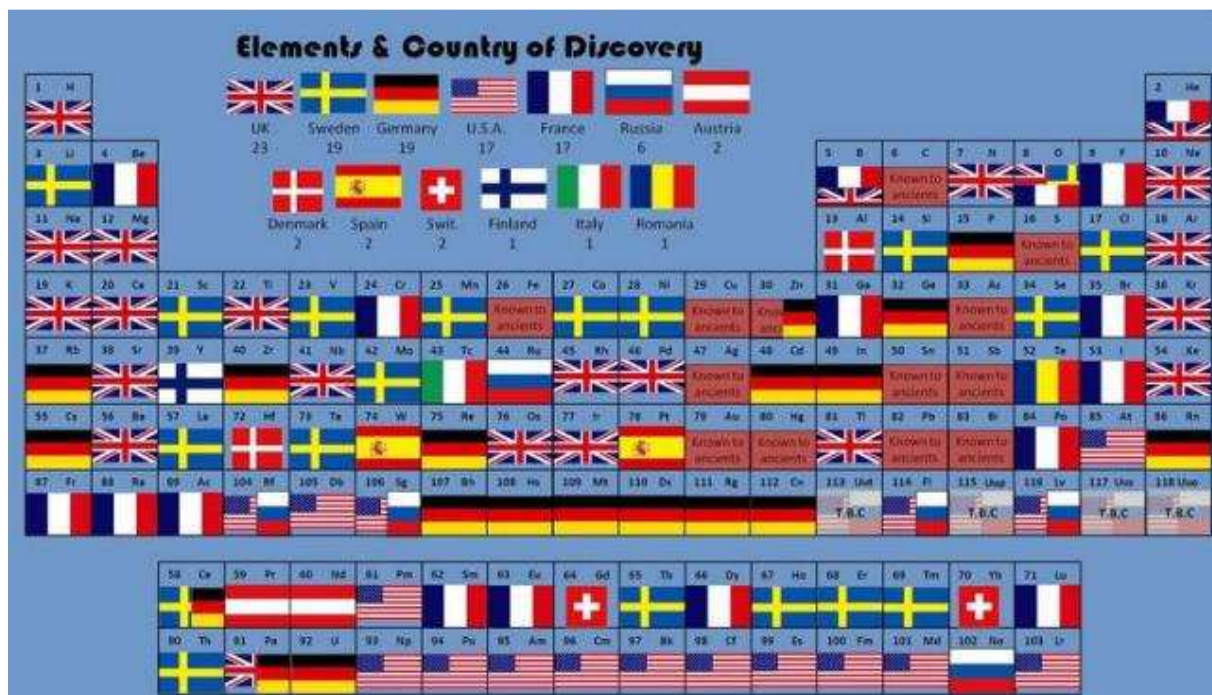
H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$ have peroxide linkages



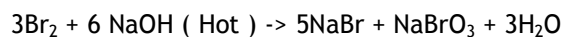
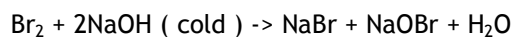
| | | | | | | | | | | | | | | | | | | |
|----|----|--|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|--|
| 1 | | | | | | | | | | | | | | | | | 2 | |
| H | | | | | | | | | | | | | | | | | He | |
| | | <input checked="" type="checkbox"/> Ferromagnetic <input checked="" type="checkbox"/> Antiferromagnetic <input type="checkbox"/> Paramagnetic <input checked="" type="checkbox"/> Diamagnetic | | | | | | | | | | | | | | | | |
| 3 | 4 | | | | | | | | | | | 5 | 6 | 7 | 8 | 9 | 10 | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | |
| 11 | 12 | | | | | | | | | | | 13 | 14 | 15 | 16 | 17 | 18 | |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 | 51 | 52 | 53 | 54 | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| 55 | 56 | 57 | 72 | 73 | 74 | 75 | 76 | 77 | 78 | 79 | 80 | 81 | 82 | 83 | 84 | 85 | 86 | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| 87 | 88 | 89 | | | | | | | | | | | | | | | | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |
| | | | 58 | 59 | 60 | 61 | 62 | 63 | 64 | 65 | 66 | 67 | 68 | 69 | 70 | 71 | | |
| | | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | |



| | |
|--|---|
| KNO_2 Potassium Nitrite | BaSO_3 Barium Sulfite |
| $\text{Mg}(\text{NO}_3)_2$ Magnesium Nitrate | Na_2SO_4 Sodium Sulfate |
| LiClO_4 Lithium Perchlorate | $\text{Ca}(\text{BrO})_2$ Calcium Hypobromite |
| NaClO_3 Sodium Chlorate | $\text{Al}(\text{IO}_2)_3$ Aluminum Iodite |
| RbClO_2 Rubidium Chlorite | KBrO_3 Potassium Bromate |
| CsClO Cesium Hypochlorite | LiIO_4 Lithium Periodate |
| Calcium Nitrate $\text{Ca}(\text{NO}_3)_2$ | Ammonium Sulfite $(\text{NH}_4)_2\text{SO}_3$ |
| Strontium Sulfate SrSO_4 | Lithium Nitrite LiNO_2 |
| Potassium Hypochlorite KClO | Lithium Perbromate LiBrO_4 |
| Rubidium Chlorate RbClO_3 | Calcium Iodite $\text{Ca}(\text{IO}_2)_2$ |
| Ammonium Chlorite NH_4ClO_2 | Boron Bromate $\text{B}(\text{BrO}_3)_3$ |
| Sodium Perchlorate NaClO_4 | Magnesium Hypoiodite $\text{Mg}(\text{IO})_2$ |

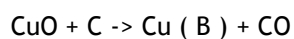
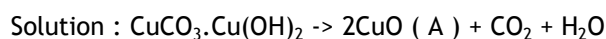


Bromine reacting with NaOH in cold and hot give different mix of products. Specify



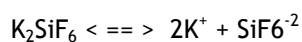
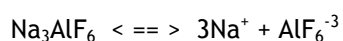
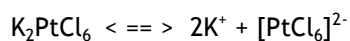
Malachite decomposes to give A + CO₂ + H₂O and compound A on reduction with Carbon gives CO + B

Identify A and B

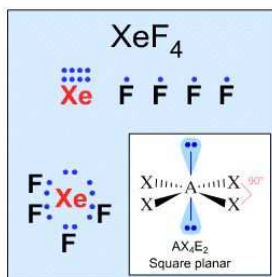
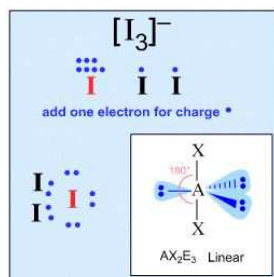


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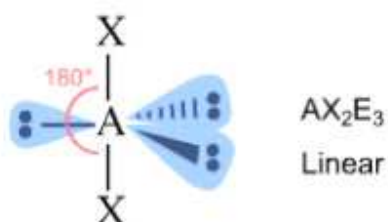
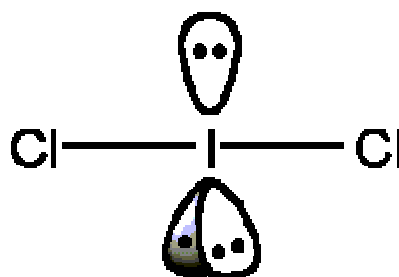
Some examples of Complex Anions



| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|-----------|------------|-----------|------------|------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|---------|----------|----------|----------|----------|----------|----------|----------|-----------|-----------|-----------|-----------|
| 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 | -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 | -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 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <table border="1"> <tr> <td>57 La</td> <td>58 Ce</td> <td>59 Pr</td> <td>60 Nd</td> <td>61 Pm</td> <td>62 Sm</td> <td>63 Eu</td> <td>64 Gd</td> <td>65 Tb</td> <td>66 Dy</td> <td>67 Ho</td> <td>68 Er</td> <td>69 Tm</td> <td>70 Yb</td> <td>71 Lu</td> </tr> <tr> <td>89 Ac</td> <td>90 Th</td> <td>91 Pa</td> <td>92 U</td> <td>93 Np</td> <td>94 Pu</td> <td>95 Am</td> <td>96 Cm</td> <td>97 Bk</td> <td>98 Cf</td> <td>99 Es</td> <td>100 Fm</td> <td>101 Md</td> <td>102 No</td> <td>103 Lr</td> </tr> </table> | | | | | | | | | | | | | | | | | | 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 |
| 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 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <p> ■ Known in antiquity ■ also known when (akw) Lavoisier 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 </p> | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |



and ICl_2^-



sp^3d 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 — | | | | |
| Lr 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 $\text{Na}(\text{NH}_4)\text{HPO}_4$ Sodium ammonium hydrogen phosphate

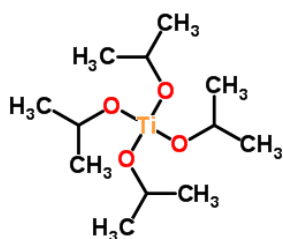
Which of the following electrolyte will be most effective in coagulation of gold sol ?

- (1) NaNO_3 (2) $\text{K}_4\text{Fe}(\text{CN})_6$ (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 $\text{Ti}(\text{OC}_3\text{H}_7)_4$ is not an organometallic compound.



| Periodic table of electronegativity using the Pauling scale | | | | | | | | | | | | | | | | | | | |
|---|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|--|
| → Atomic radius decreases → Ionization energy increases → Electronegativity increases → | | | | | | | | | | | | | | | | | | | |
| Group → | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | |
| ↓ Period | | | | | | | | | | | | | | | | | | | |
| 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 $[\text{Co}(\text{H}_2\text{O})_4(\text{NH}_3)_2] \text{Cl}_3$ is

- (a) Tetraaquadiammincobalt(III) chloride (b) Tetraaquadiammincobalt(III) chloride
(c) Diamminetetraaquacobalt(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.

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|----|----|----------------------|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|---|---|---|---|----|
| Li | Be | Covalent Hydride | | | | | | | | | | | | | | H | He | | | | | | | | | | | | | | |
| Na | Mg | Metallic Hydride | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| K | Ca | Intermediate Hydride | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Rb | Sr | Ionic Hydride | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Cs | Ba | Hydride Gap | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Fr | Ra | La | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | B | C | N | O | F | Ne |
| | | Ac | Th | Pa | U | Np | Pu | Am | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | Al | Si | P | S | Cl | Ar | | | | | | | |
| | | | | | | | | | Lu | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Ga | Ge | As | Se | Br | Kr | | | | | | | |
| | | | | | | | | | | | | | | | | | | In | Sn | Sb | Te | I | Xe | | | | | | | | |
| | | | | | | | | | | | | | | | | | | Tl | Pb | Bi | Po | At | Rn | | | | | | | | |

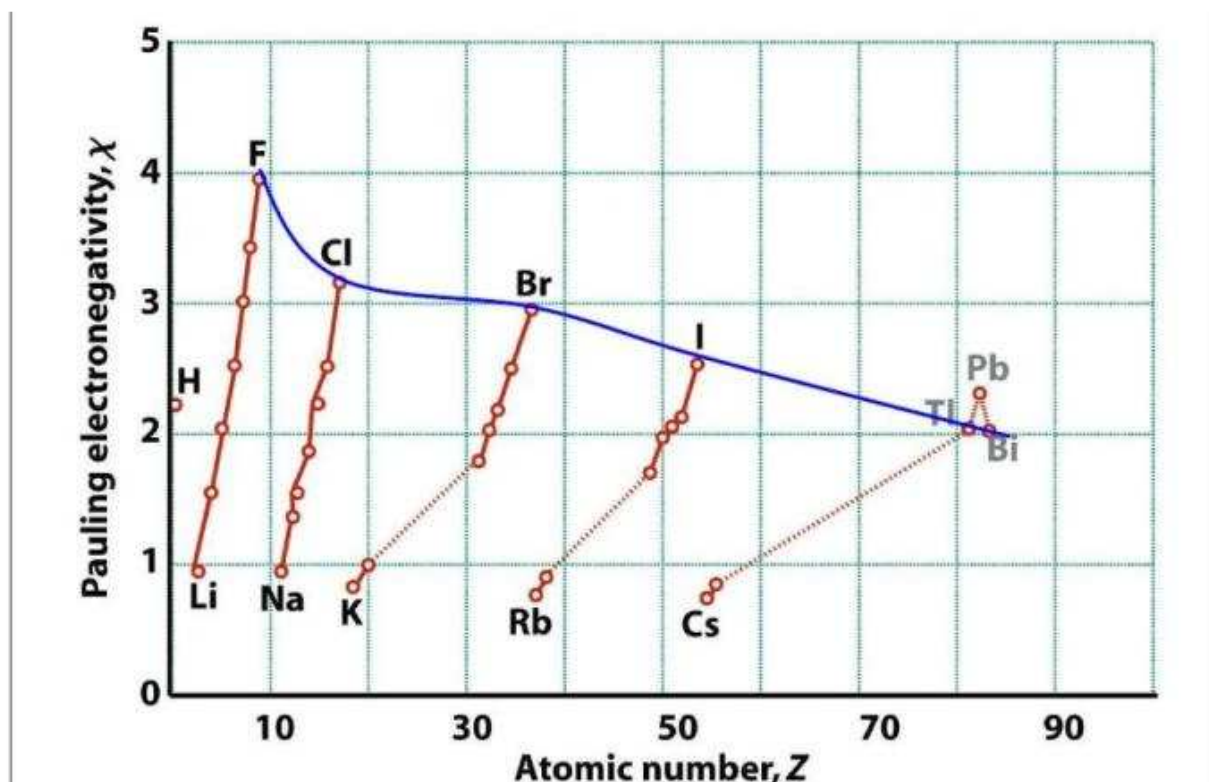
Color of light absorbed by aqueous solution of CuSO_4

- 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

| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
|--------------|--|--|--|--|--|--|--|--|--|----------------------|--|--|--|--|--|--|--|--|--|---------------------|--|--|--|--|--|--|--|--|--|---------------------|--|--|--|--|--|--|--|--|--|---------------|--|--|--|--|--|--|--|--|--|------------|--|--|--|--|--|--|--|--|--|----------|--|--|--|--|--|--|--|--|--|-------|--|--|--|--|--|--|--|--|--|-------|--|--|--|--|--|--|--|--|--|-------|--|--|--|--|--|--|--|--|--|-------|--|--|--|--|--|--|--|--|--|-------|--|--|--|--|--|--|--|--|--|--------|--|--|--|--|--|--|--|--|--|--------|--|--|--|--|--|--|--|--|--|--------|--|--|--|--|--|--|--|--|--|--------|--|--|--|--|--|--|--|--|--|-----|--|--|--|--|--|--|--|--|--|-----|--|--|--|--|--|--|--|--|--|
| 1A | | | | | | | | | | 2A | | | | | | | | | | 3A | | | | | | | | | | 4A | | | | | | | | | | 5A | | | | | | | | | | 6A | | | | | | | | | | 7A | | | | | | | | | | 8A | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| H | | | | | | | | | | 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 | | | | | | | | | | 57-71 | | | | | | | | | | Hf | | | | | | | | | | Ta | | | | | | | | | | W | | | | | | | | | | Re | | | | | | | | | | Os | | | | | | | | | | Ir | | | | | | | | | | Pt | | | | | | | | | | Au | | | | | | | | | | Hg | | | | | | | | | | Tl | | | | | | | | | | Pb | | | | | | | | | | Bi | | | | | | | | | | Po | | | | | | | | | | At | | | | | | | | | | Rn | | | | | | | | | |
| Fr | | | | | | | | | | Ra | | | | | | | | | | 89-103 | | | | | | | | | | Rf | | | | | | | | | | Db | | | | | | | | | | Sg | | | | | | | | | | Bh | | | | | | | | | | Hs | | | | | | | | | | Mt | | | | | | | | | | Ds | | | | | | | | | | Rg | | | | | | | | | | Cn | | | | | | | | | | Uut | | | | | | | | | | Fl | | | | | | | | | | Uup | | | | | | | | | | Lv | | | | | | | | | | Uus | | | | | | | | | | 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 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| $< 10^{-12}$ | | | | | | | | | | $10^{-12} - 10^{-9}$ | | | | | | | | | | $10^{-9} - 10^{-6}$ | | | | | | | | | | $10^{-6} - 10^{-3}$ | | | | | | | | | | $10^{-3} - 1$ | | | | | | | | | | $1 - 10^3$ | | | | | | | | | | $> 10^3$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |

BaCl₂ · 5 H₂O 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 ClO₄⁻ anion, therefore we need two perchlorate anions for each Mg cation therefore the formula is: **Mg(ClO₄)₂**

(NH₄)₂SO₃ NH₄⁺ is the ammonium ion, and SO₃⁻² is the sulfite anion, therefore the name is:
Ammonium Sulfite

Calcium Nitrate Calcium is the Ca⁺² cation, and nitrate is the NO₃⁻ anion, therefore the formula is:
Ca(NO₃)₂

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|------------------|---|---|-----------------|-----------------|-----------------|-----------------|--------------|-----------------|---------------|------------------|-----------------|------------------|-----------------|----------------|-----------------|-----------------|----------------|
| 1 | H 1.00794 | Alkali Metals, Alkaline Earth Metals, Lanthanoids, Actinoids, Transition Metals | | | | | | | | | | He 4.002602 | | | | | | |
| 2 | Li 6.941 | Be 9.012182 | Post-transition Metals, Metalloids, Other Non-metals, Halogens, Noble gases | | | | | | | | | | B 10.811 | C 12.0107 | N 14.0067 | O 15.9994 | F 18.9984032 | Ne 20.1797 |
| 3 | Na 22.9897692 | Mg 24.305 | Solid, Liquid, Gas, Unknown | | | | | | | | | | Al 26.9815386 | Si 28.0855 | P 30.973762 | S 32.065 | Cl 35.453 | Ar 39.948 |
| 4 | K 39.0983 | Ca 40.078 | Sc 44.9559 | Ti 47.887 | V 50.9415 | Cr 51.9961 | Mn 54.938045 | Fe 55.845 | Co 58.933195 | Ni 58.6934 | Cu 63.546 | Zn 65.38 | Ga 69.723 | Ge 72.63 | As 74.9216 | Se 78.96 | Br 79.904 | Kr 83.798 |
| 5 | Rb 85.4678 | Sr 87.62 | Y 88.90585 | Zr 91.224 | Nb 92.90638 | Mo 95.94 | Tc 98 | Ru 101.07 | Rh 102.9055 | Pd 106.42 | Ag 107.8682 | Cd 112.411 | In 114.818 | Sn 118.71 | Sb 121.76 | Te 127.6 | I 126.90447 | Xe 131.293 |
| 6 | Cs 132.905451 | Ba 137.327 | | Hf 178.49 | Ta 180.94788 | W 183.84 | Re 186.207 | Os 190.23 | Ir 192.22 | Pt 195.084 | Au 196.966569 | Hg 200.59 | Tl 204.3833 | Pb 207.2 | Bi 208.9804 | Po 209 | At 210 | Rn 222 |
| 7 | Fr 223 | Ra 226 | | Rf 267 | Db 268 | Sg 271 | Bh 272 | Hs 270 | Mt 278 | Ds 281 | Rg 280 | Cn 285 | Uut 284 | Fl 289 | Uup 288 | Lv 293 | Uus 294 | Uuo 294 |
| | | | | La 138.90547 | Ce 140.116 | Pr 140.90765 | Nd 144.242 | Pm 145 | Sm 150.36 | Eu 151.964 | Gd 157.25 | Tb 158.92535 | Dy 162.5 | Ho 164.93032 | Er 167.259 | Tm 168.93421 | Yb 173.054 | Lu 174.9668 |
| | | | | Ac 227 | Th 238.02891 | Pa 231.03688 | U 238.02891 | Np 237 | Pu 244 | Am 243 | Cm 247 | Bk 247 | Cf 251 | Es 252 | Fm 257 | Md 258 | No 259 | Lr 262 |

KBr Potassium hypobromite Structure



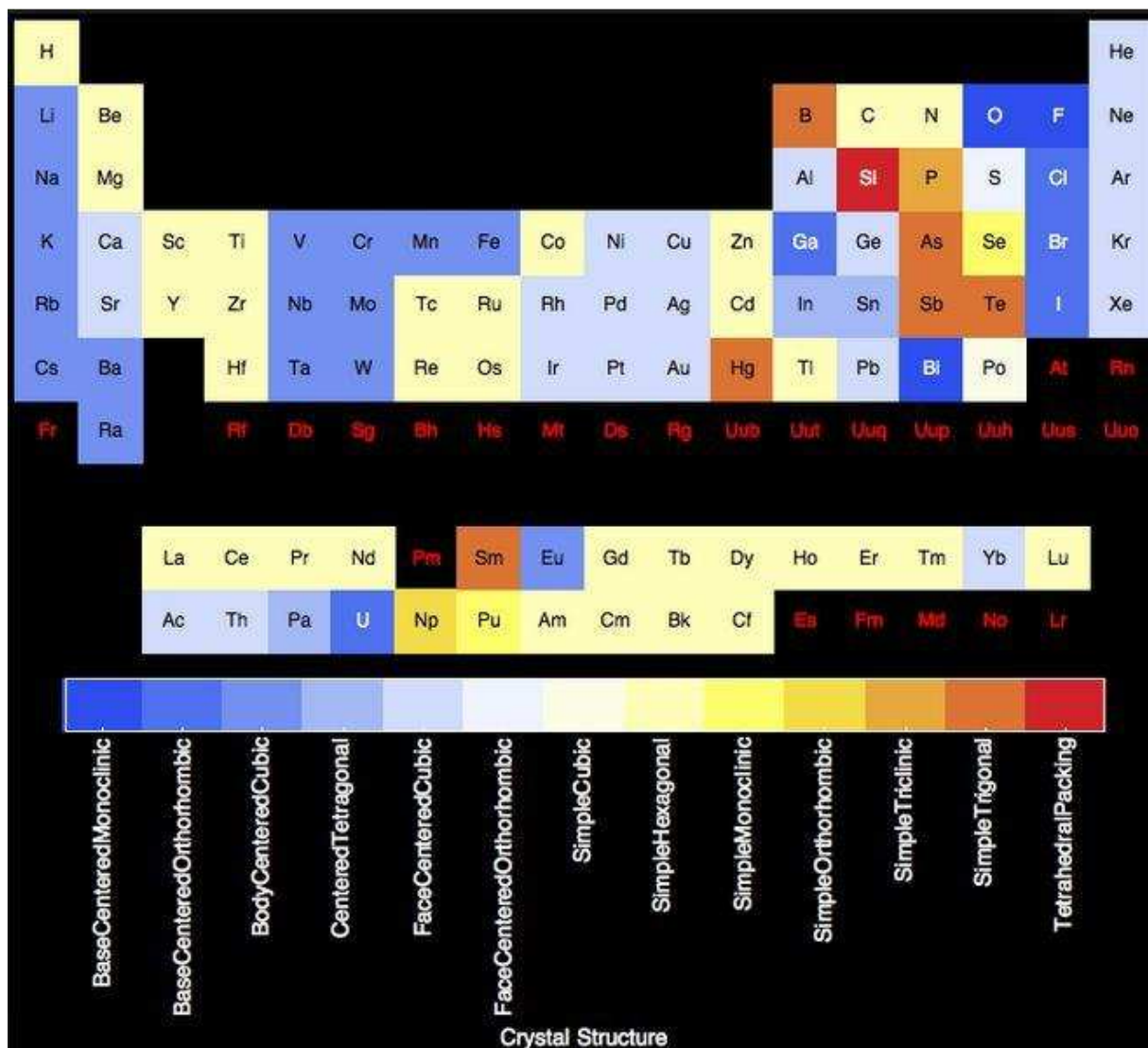
Group 2 Elements—Alkaline Earth Metals

Group 2 contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

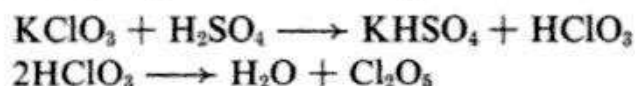
All alkaline earth metals contain two electrons in their outermost orbitals. These are soft. But compared to alkali metals, they are harder and have higher cohesive energy. Their melting points are higher than those of Group 1 elements and vary irregularly because of different structures. The atomic 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.



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 :



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:



The molecule has a triangular structure, with $\text{O}-\text{Cl}-\text{O}$ angle 118° and

bond lengths 1.49 \AA . We assign it the structure $\begin{array}{c} \text{:}\ddot{\text{O}} \\ \parallel \\ \text{Cl} \cdots \ddot{\text{O}}\text{:} \\ \vdots \end{array}$, with interchange of the two kinds of bonds (resonance).

| Rare Earth Elements | | | | | | | | | | | | | | | | | | | | | |
|--|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|---|---|----|----|
| 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 | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | | | |
| Fr | Ra | Ac | Rf | Db | Sg | Bh | Hs | Mt | | | | | | | | | | | | | |
| Lanthanides | | | | | | | | | | | | | | | | | | | | | |
| La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu | | | | | | | | | | | | | | | | | | | | | |
| Actinides | | | | | | | | | | | | | | | | | | | | | |
| Ac Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr | | | | | | | | | | | | | | | | | | | | | |

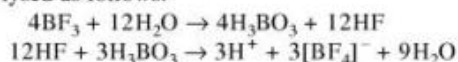
Atomic radii of fluorine and neon in Angstrom units are respectively given by

- (a) 0.72, 1.60 (b) 1.60, 1.60 (c) 0.72, 0.72 (d) none of these values

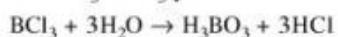
Ans : (a)

Atomic radius of Neon will be larger than Fluorine

BF_3 is hydrolysed as follows.



Hydrolysis of BCl_3 or BI_3 produces boric acid.

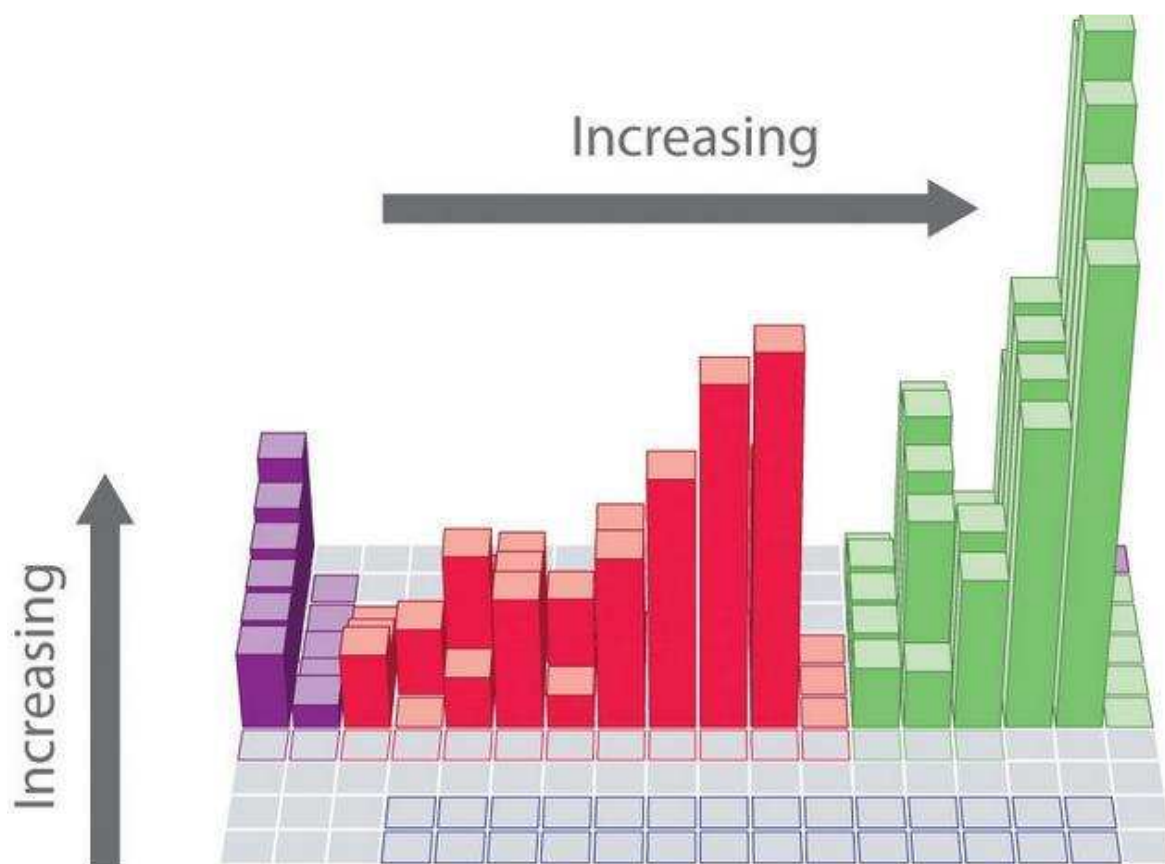


The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Due to back bonding, the electron density on boron is increased. The tendency to form $p\pi-p\pi$ 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 $\text{BF}_3 < \text{BCl}_3 < \text{BBr}_3$.

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 (Blue 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 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| <table border="1"> <tbody> <tr> <td>58 Ce</td> <td>59 Pr</td> <td>60 Nd</td> <td>61 Pm</td> <td>62 Sm</td> <td>63 Eu</td> <td>64 Gd</td> <td>65 Tb</td> <td>66 Dy</td> <td>67 Ho</td> <td>68 Er</td> <td>69 Tm</td> <td>70 Yb</td> <td>71 Lu</td> </tr> <tr> <td>90 Th</td> <td>91 Pa</td> <td>92 U</td> <td>93 Np</td> <td>94 Pu</td> <td>95 Am</td> <td>96 Cm</td> <td>97 Bk</td> <td>98 Cf</td> <td>99 Es</td> <td>100 Fm</td> <td>101 Md</td> <td>102 No</td> <td>103 Lr</td> </tr> </tbody> </table> | | | | | | | | | | | | | | | | | | 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 |
| 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 | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |



Magnitude of electron affinity (kJ/mol), *s*-, *p*-, and *d*-block elements

■ *s* block
 ■ *p* block
 ■ *d* block
 ■ *f* block

Common Name

acetone

acid potassium sulfate

acid of sugar

ackey

alcali volatil

alcohol, grain

alcohol sulfuris

Chemical Name

dimethyl ketone; 2-propanone (usually known as acetone)

potassium bisulfate

oxalic acid

nitric acid

ammonium hydroxide

ethyl alcohol

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 verdigris | 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 cyanide |
| 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 | sulfurated 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 |
| methyated 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

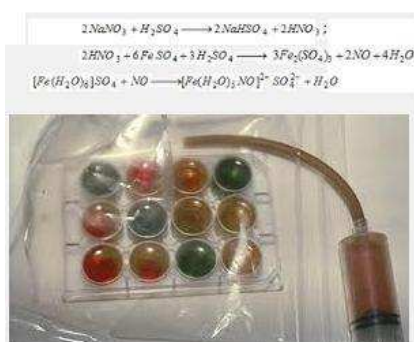
Cr₂(SO₄)₃ - green



PbS - Black



[Fe(H₂O)₅NO]SO₄ - brown



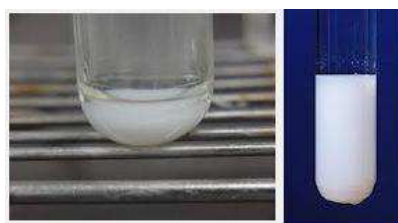
(CH₃COO)₃Fe - blood red



NH₄Cl - white fumes

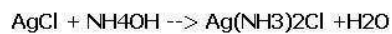
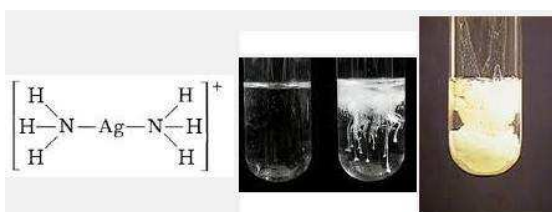


AgCl - curdy white precipitate



AgCl - curdy white precipitate

AgCl + NH₄OH → Ag(NH₃)₂Cl + H₂O



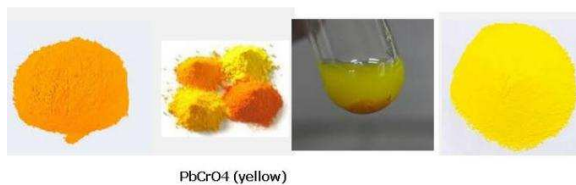
CrO₃ + HCl → CrO₂Cl₂ (deep red fumes) + H₂O



CrO₂Cl₂ (deep red fumes)



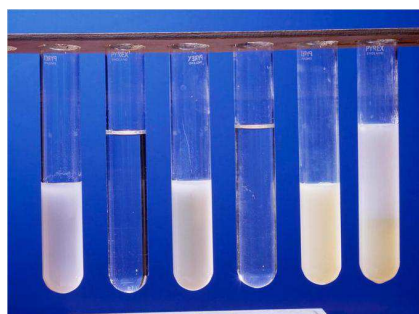
Na_2CrO_4 (yellow)



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.



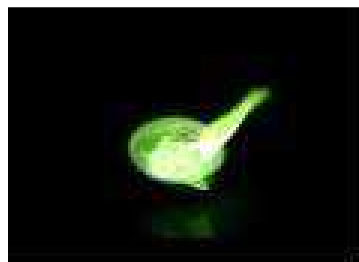
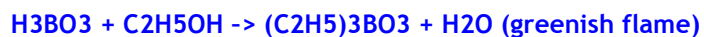
BrCl - pale yellow



$\text{NaI} + \text{AgNO}_3 \rightarrow \text{AgI (yellow ppt)} + \text{NaNO}_3$



CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams



In the presence of Arsenic, we get yellow precipitate of $(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3$ (ammonium arsenomolybdate)

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Mo3O8.xH2O - molybdenum blue



SiF4 + H2O -> H4SiO4 (silicic acid - white) + H2SiO4



Na2S + Na2[Fe(CN)5NO] -> Na4[Fe(CN)5NOS] - violet colour

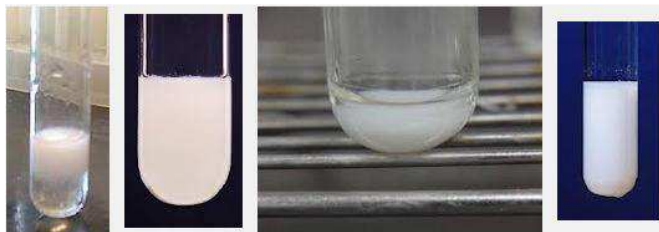
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Cadmium Sulfide



K₃[Co(NO₂)₆] (potassium cobaltnitrate - yellow ppt)



AgCl White

PbCl₂ is white



Hg₂Cl₂ is white

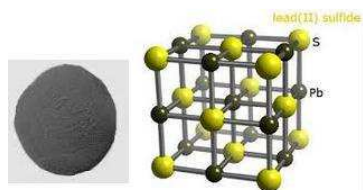


H₂S, PbS, Bi₂S₃, CuS - black

H₂S is Black



PbS is Black



PbS Lead Sulfide is Black

Bi₂S₃ is Black



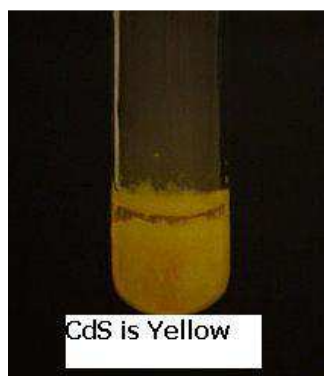
CuS - black



Copper Sulfide Powder

CdS, As₂S₃, SnS₂ - Yellow

CdS is Yellow



As₂S₃ is Yellow



SnS₂ is Yellow



Sb₂S₃ is orange

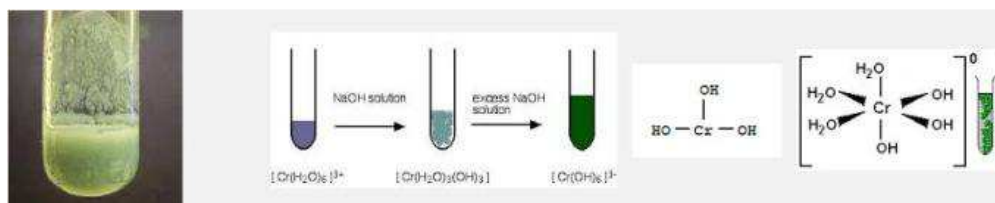


SnS is Brown



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

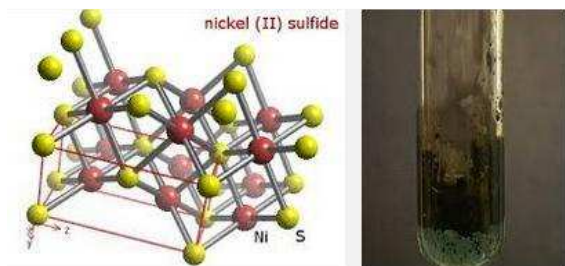


CoS, NiS - black

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



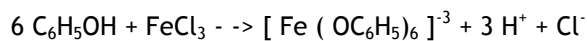
Cobalt Acetate is deep Brown



Azulene - Deep Blue

Iodoform - CHI_3 Yellow

Iron Phenol complex - Violet - $[\text{Fe}(\text{OC}_6\text{H}_5)_6]^{-3}$



Ammonium Phosphomolybdate - Yellow - $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ (Yellow)

Prussian Blue - $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$

$[\text{Fe}(\text{CN})_3\text{NOS}]^{-4}$ - Violet

$[\text{Fe}(\text{SCN})]^{2+}$ Blood Red

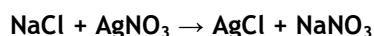
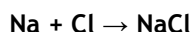
$[\text{Co}(\text{NH}_3)_5\text{Br}]^{+2} \text{SO}_4^{-2}$ - Violet - Pentaaminebromocobalt(III)sulphate

$[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+ \text{Br}^- \rightarrow \text{Red}$

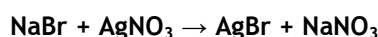
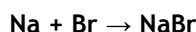
Test for Halogen:

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 .

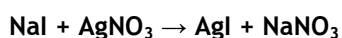
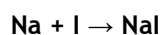
If chlorine is present, a white curdy precipitate soluble in ammonium hydroxide solution is formed.



If bromine is present, an yellowish white precipitate sparingly soluble in ammonium hydroxide solution is formed.



If iodine is present, an yellow precipitate insoluble in ammonium hydroxide solution is formed.

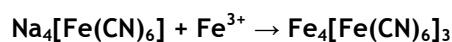


Test for Nitrogen:

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.



Sodium ferrocyanide

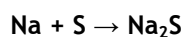


Ferric ferrocyanide



Test for Sulphur:

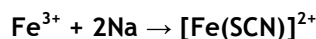
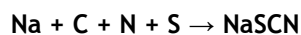
If sulphur is present in the organic compound, sodium fusion will convert it into sodium sulphide. Sulphide ions are readily identified using sodium nitroprusside.



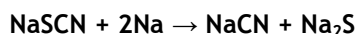
Sodium nitroprusside violet colour

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 $[\text{Fe}(\text{SCN})]^{2+}$



Note: If the Lassaigne's extract containing excess of sodium metal, sodium cyanide and sulphides are formed instead of sodium thiocyanate.



Here in this type of cases, both sulphur and nitrogen are to be identified in separate tests.

BaCO_3 , SrCO_3 , CaCO_3 , $\text{Mg}(\text{NH}_4)\text{PO}_4$ - white

BaCO_3 is white



BaCO_3 powder

SrCO_3 is white



CaCO_3 powder is white



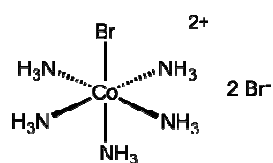
CaCO_3 Calcium Carbonate Powder

Mg(NH₄)PO₄ is white



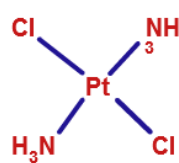
Pentaamminechlorocobalt(III)Bromide

[Co(NH₃)₅Cl] Cl₂ Pentaamminechlorocobalt(III)chloride



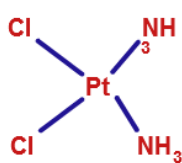
Pentaamminesulphatocobalt(III)Bromide

Dark Yellow

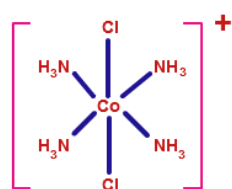


trans- Pt(NH₃)₂Cl₂

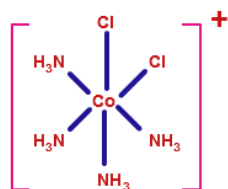
Pale Yellow



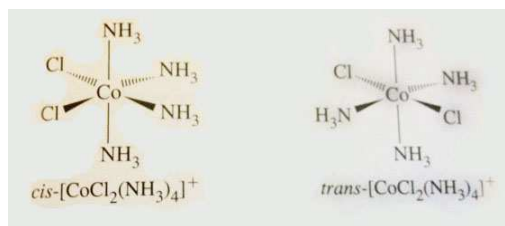
cis- Pt(NH₃)₂Cl₂



Trans - [Co(NH₃)₄Cl₂]⁺

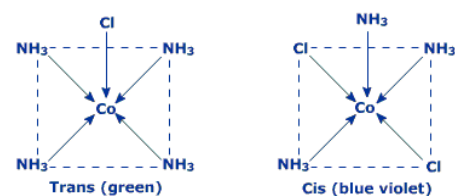
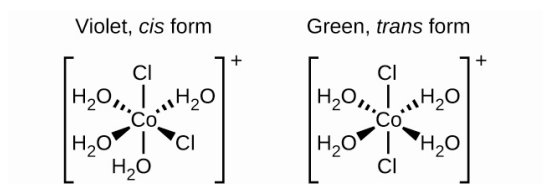


Cis - [Co(NH₃)₄Cl₂]⁺



Cis is Blue Violet

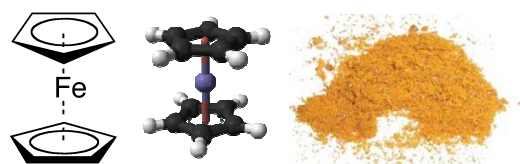
trans is green



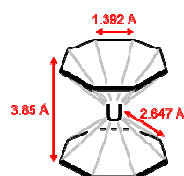
Eta bonds - Also known as **Hapticity** - Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms.

The hapticity of a ligand is described with the Greek letter η ('eta'). For example, η^2 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(η^5 -cyclopentadienyl)iron



Uranocene - bis(η^8 -1,3,5,7-cyclooctatetraene)uranium



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$W(CO)_3(PPr_3)_2(\eta^2-H_2)$ - the first compound to be synthesized with a dihydrogen ligand (also known as Dihydrogen Complexes)

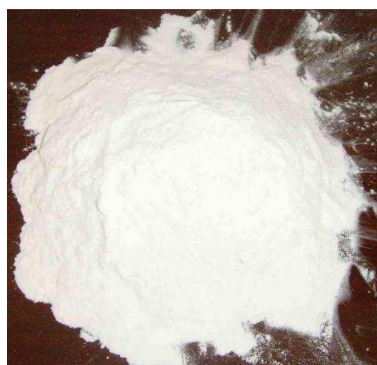
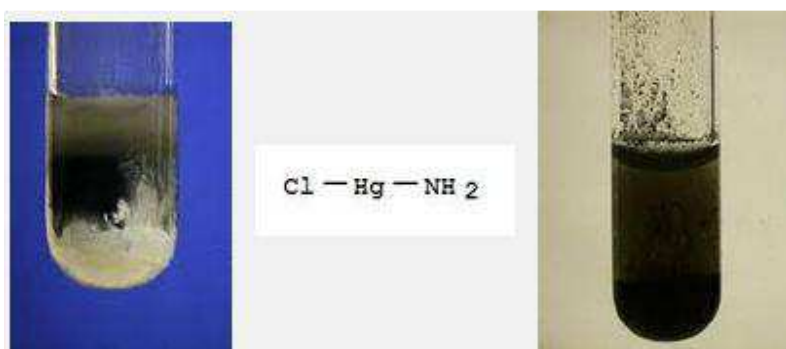
$IrCl(CO)[P(C_6H_5)_3]_2(\eta^2-O_2)$ - the dioxygen derivative which forms reversibly upon oxygenation of Vaska's complex.

-

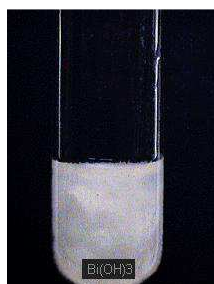
Chromium (III) chloride is purple



black ppt



$Bi(OH)_3$ Bismuth Hydroxide is white

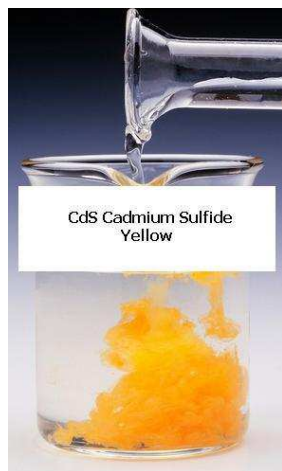
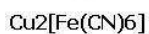
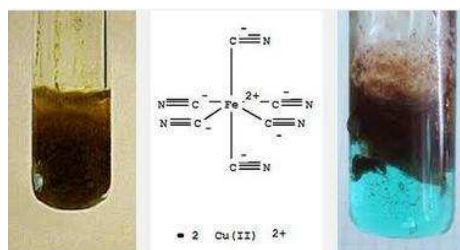
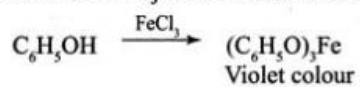


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Oxidation of Phenol

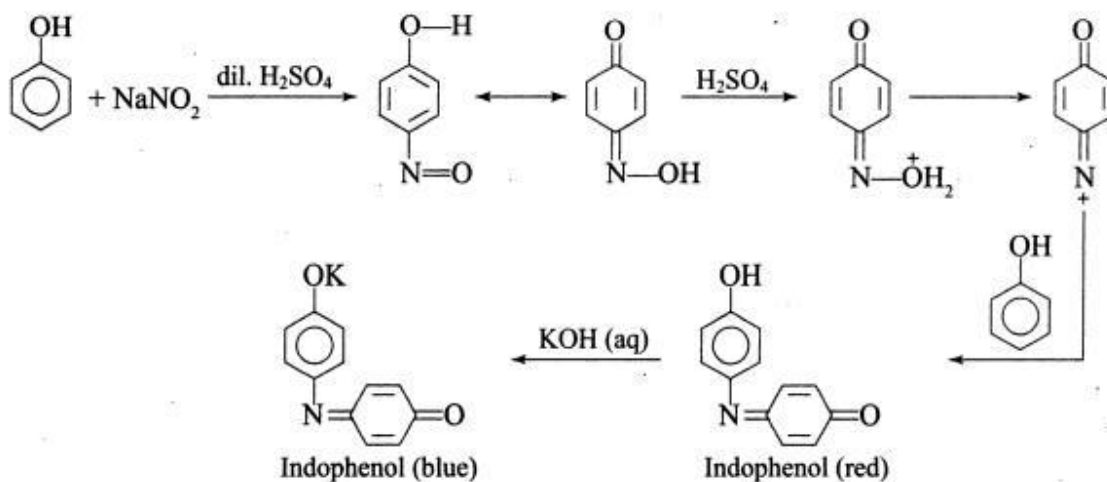
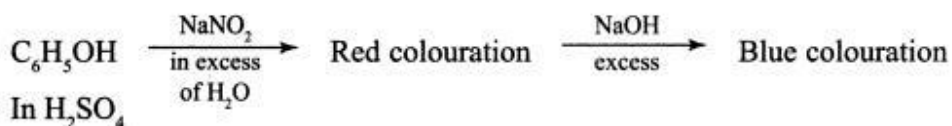
Test of Phenol

With Neutral $FeCl_3$, Phenol on reaction with neutral ferric chloride gives violet colour of ferric phenoxide

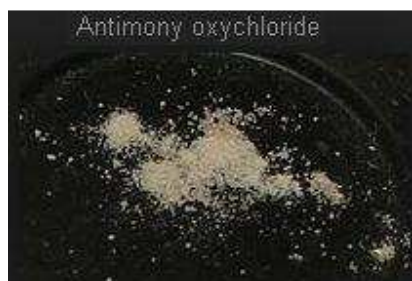




Liebermann's Nitroso Reaction



SbOCl Antimony oxychloride



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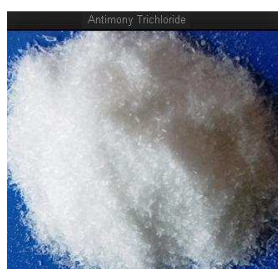
Antimony Trioxide is white



Antimony Pentoxide is gray

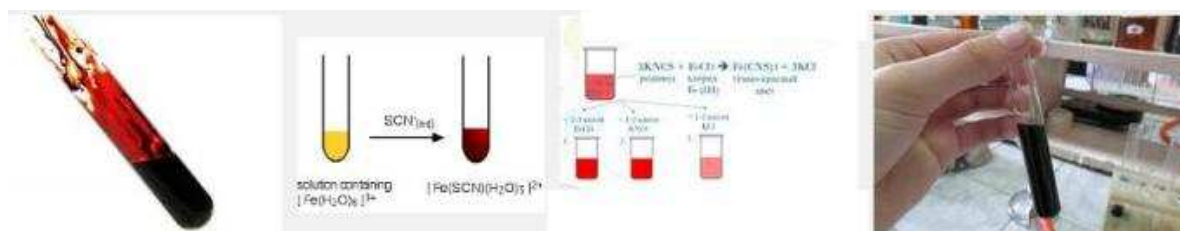


Antimony Trichloride is white



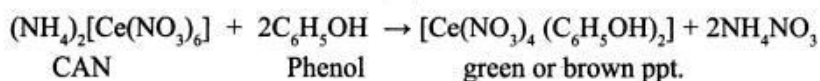
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Potassium antimonate white

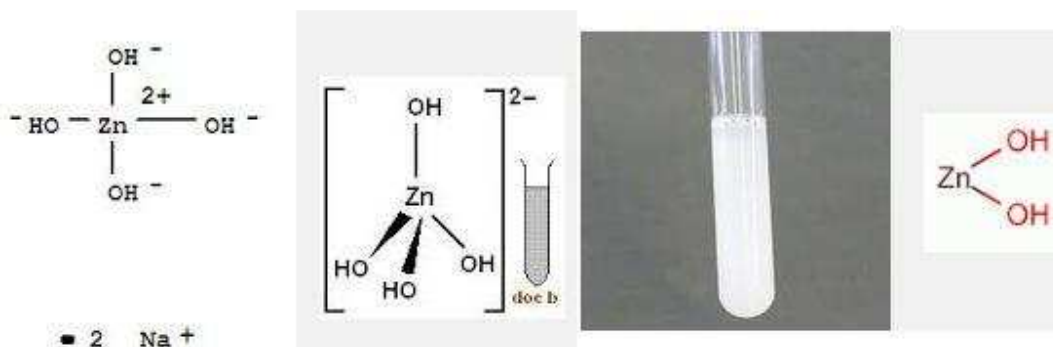


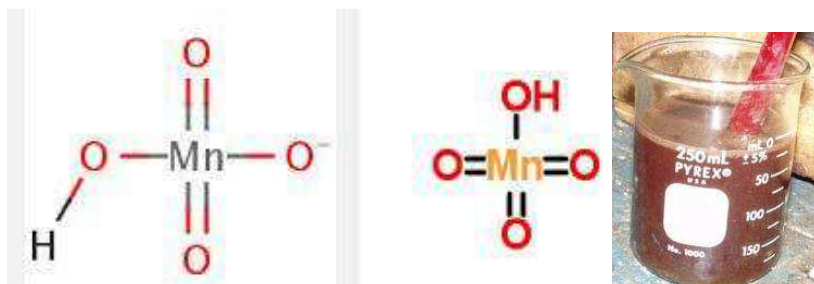
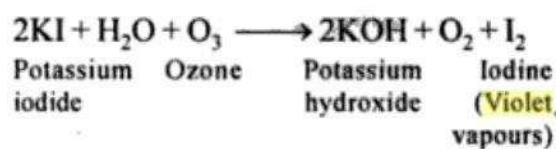
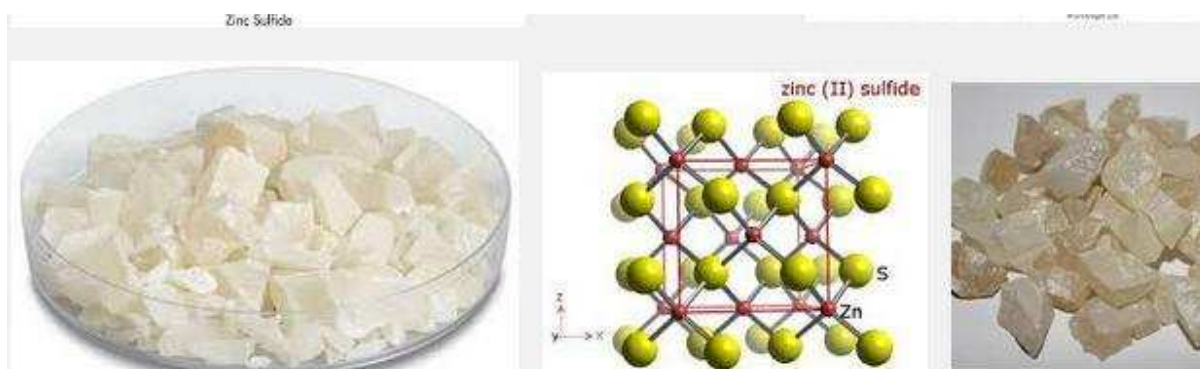
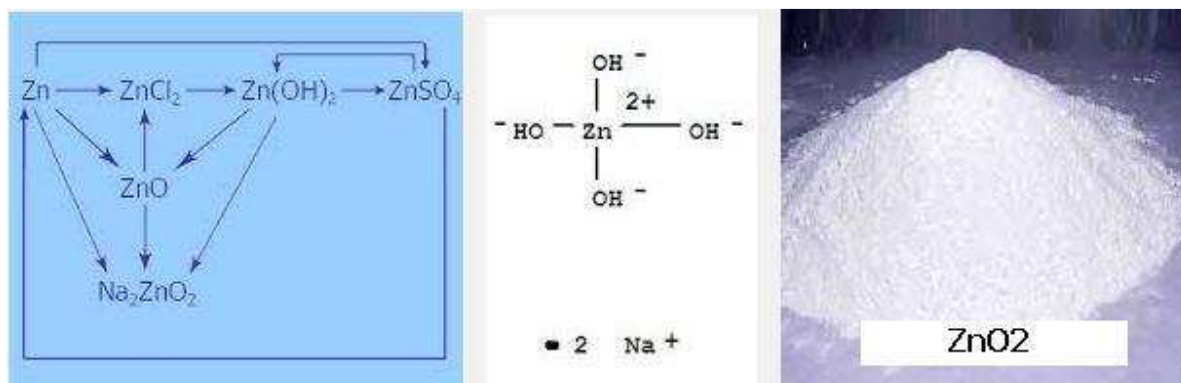
Can Test

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.



Phenol gives blue colour with ammonia and sodium hypochlorite.









magnesium ammonium phosphate



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Chromium oxide powder is green



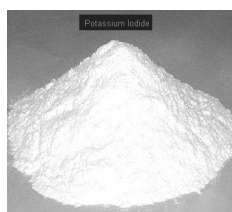
Chromium Oxide
Powder

Bismuth oxide is Yellow



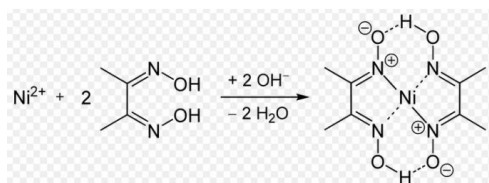
Bismuth Oxide
Powder

KI Potassium Iodide is white



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Add NH_4OH excess and dimethylglyoxime to NiCl_2 then a rosy red ppt of nickel appears



A sample of $\text{Ni}(\text{dmgH})_2$

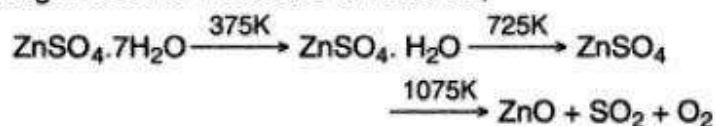
$\text{CuO} + \text{B}_2\text{O}_3$ (Glassy bead) \rightarrow $\text{Cu}(\text{BO}_2)_2$ (Copper metaborate - blue)



Compounds of zinc

Zinc oxide ZnO : Zincite (ZnO) is also called Philosopher'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), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$: 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,



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



$2Hg + O_2 \rightarrow 2HgO$ (red) or by heating mercuric nitrate alone or in the presence of Hg

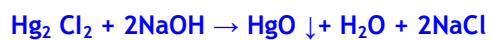
Heat



red



When NaOH is added to a solution of HgCl_2 , yellow precipitate of HgO are obtained.



(yellow)



Red and yellow forms of HgO differ only in their particle size. On heating to 673 K , yellow form changes to red form.



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



MnO_2

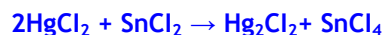




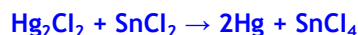
HgCl_2 is a white crystalline solid and is commonly known as corrosive sublimate. It is a covalent compound since it dissolves in organic solvents like ethanol and ether.

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).



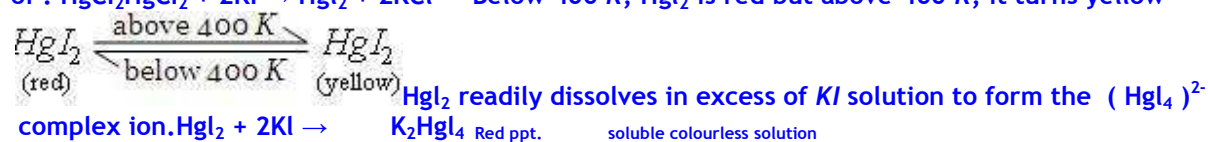
white ppt.



grey

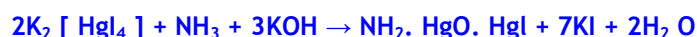
With ammonia it gives a white ppt. known as infusible white ppt.

$\text{HgCl}_2 + 2\text{NH}_3 \rightarrow \text{Hg}(\text{NH}_2)\text{Cl} + \text{NH}_4\text{Cl}$ 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 . $\text{HgCl}_2 + 2\text{KI} \rightarrow \text{HgI}_2 + 2\text{KCl}$ (red) Below 400 K, HgI_2 is red but above 400 K, it turns yellow



An alkaline solution of $\text{K}_2[\text{HgI}_4]$ is called Nessler's reagent and is used to test NH_4^+ ions.

It gives a brown ppt. of $\text{NH}_2 - \text{Hg} - \text{O} - \text{Hg} - \text{I}$ (Iodide of Millon's base) with NH_4^+ ions.



It is used in ointments for treating skin infections.

(4) Mercurous chloride, Hg_2Cl_2 : It is obtained as under:



white ppt.

Heat in an iron retort



It is purified by sublimation.

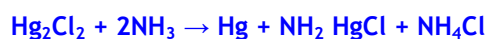
Mercurous chloride is also called calomel. It is a white powder insoluble in H_2O . On heating, it decomposes to give HgCl_2 and Hg .



It dissolves in chlorine water forming mercuric chloride.



With ammonia, it turns black due to the formation of a mixture of finely divided black Hg and mercuric amino chloride.



(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.



It is insoluble in water and HCl but dissolves in aqua regia (1 part conc. HNO_3 + 3 parts conc. HCl)



Aqua regia Nitrosyl chloride Nascent chlorine



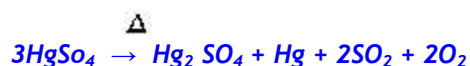
(Soluble)

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 .



It is a white solid which decomposes on heating to give mercurous sulphate.



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.

XXXXXXXXXXXXXXXXXXXXXXXXXX

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($\text{S}_2\text{O}_3^{2-}$)

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 ($\text{B}_4\text{O}_7^{2-}$)

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 NH₄ 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, SO₂, 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 HCl, HBr, H₂S, the compound is said to be a binary (i.e. composed of two elements) acid, or an hydric acid. 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 : H₂SO₄ sulphuric, and H₂SO₃ 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 : AgNO₃, Cu(NO₃)₂, AsCl₃, Fe₂Cl₆, Co(NO₃)₂, Ba(NO₃)₂, NaCl.

Take about 2 c.c. of each solution, and add HCl.*

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 :

HCl was added to the seven solutions with the following results :

Typical of Gr. I AgNO₃ + HCl = AgCl w. pp. + I IN () 8 .

Typical of Gr. II A Cu(NO₃)₂ + HCl = No change.

Typical of Gr. II B AsCl₃ + HCl = No change.

Typical of Gr. III Fe₂Cl₆ + HCl = No change.

Typical of Gr. IV Co(NO₃)₂ + HCl = No change.

Typical of Gr. V $\text{Ba}(\text{NO}_3)_2 + \text{HCl} = \text{No change.}$

Typical of Gr. VI $\text{NaCl} + \text{HCl} = \text{No change.}$

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 difficultly 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), $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ | Effervescence and a colourless odourless gas is evolved, Carbon dioxide (CO_2), $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$ | 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. $\text{NaNO}_2 + \text{HCl} \rightarrow \text{NaCl} + \text{HNO}_2$ $3\text{HNO}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO}$ $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ |

| | 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 $\text{Na}_2\text{CO}_3 + \text{MgSO}_4 \rightarrow \text{MgCO}_3 \downarrow + \text{Na}_2\text{SO}_4$ | No ppt. in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt. of magnesium carbonate is obtained: $2\text{NaHCO}_3 + \text{MgSO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{Mg}(\text{HCO}_3)_2$ soluble in water $\text{Mg}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{MgCO}_3 \downarrow + \text{CO}_2 + \text{H}_2\text{O}$ ppt | 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 $(\text{FeNO})\text{SO}_4$. 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 see the ring). |
| 2) Salt solution + mercuric chloride solution | Reddish brown precipitate of mercuric carbonate $\text{Na}_2\text{CO}_3 + \text{HgCl}_2 \rightarrow \text{HgCO}_3 \downarrow + 2\text{NaCl}$ | No ppt. in the cold, but on heating a reddish-brown ppt. of mercuric carbonate is obtained: $2\text{NaHCO}_3 + \text{HgCl}_2 \rightarrow 2\text{NaCl} + \text{Hg}(\text{HCO}_3)_2$ soluble in water $\text{Hg}(\text{HCO}_3)_2 \xrightarrow{\Delta} \text{HgCO}_3 \downarrow + \text{CO}_2 + \text{H}_2\text{O}$ ppt | 2) solution of nitrite + potassium iodide solution (KI) + dilute sulfuric acid: a pale brown colour appears, due to the liberation of iodine. (The nitrite solution is an oxidizing agent.) $2\text{KNO}_2 + 2\text{KI} + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{I}_2 + 2\text{NO}$ Iodide Iodine 3) Solution of nitrite + acidified solution of potassium permanganate KMnO_4 (i.e. $\text{KMnO}_4 + \text{dil. H}_2\text{SO}_4$): the purple colour of the permanganate disappears. (the nitrite solution is an reducing agent.) $5\text{KNO}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 5\text{KNO}_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}$ |





Is HgCO_3 reddish Brown ?



| | Sulphites (SO_3^{2-}) | Thiosulphates ($\text{S}_2\text{O}_3^{2-}$) | 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 | <p>Sulphur dioxide gas (SO_2), is evolved, which is recognizable by its pungent smell:</p> $\text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2$ <p><u>Test for sulphur dioxide:</u> 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.</p> $3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ <p>Orange colour Green colour</p> | <p>Colourless gas with pungent odour, which turns an acidified potassium dichromate paper green, is evolved (SO_2), and a yellow precipitate of sulphur (S) appears:</p> $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 + \text{S} \downarrow$ $3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ <p>Orange colour Green colour</p> | <p>Colourless gas, hydrogen sulphide (H_2S), is evolved which is recognizable by its bad smell.</p> $\text{Na}_2\text{S} + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{S}$ <p><u>Test for hydrogen sulphide:</u> 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.</p> $\text{H}_2\text{S} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbS} + 2\text{CH}_3\text{COOH}$ <p>Black</p> |



K_2SO_4 is white



$\text{Cr}_2(\text{SO}_4)_3$ is green

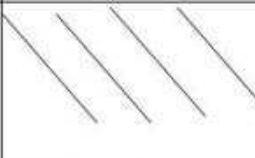
| | Sulphites | Thiosulphates | Sulphides |
|---|--|---|--|
| Confirmatory tests: 1) Salt solution + silver nitrate solution (AgNO ₃) | A white precipitate forms (silver sulphite Ag ₂ SO ₃), which dissolves in excess of sulphite due to the formation of soluble complex. $\text{Na}_2\text{SO}_3 + 2 \text{AgNO}_3 \rightarrow \text{Ag}_2\text{SO}_3 \downarrow + 2 \text{NaNO}_3$ ppt $\text{Ag}_2\text{SO}_3 + \text{Na}_2\text{SO}_3 \rightarrow 2 \text{Na}[\text{AgSO}_3]$ Soluble complex | A white precipitate forms (silver thiosulphate Ag ₂ S ₂ O 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 ₂ S). $\text{Na}_2\text{S}_2\text{O}_3 + 2 \text{AgNO}_3 \rightarrow \text{Ag}_2\text{S}_2\text{O}_3 \downarrow + 2 \text{NaNO}_3$ White ppt | A black precipitate of silver sulphide (Ag ₂ S) is formed. $\text{Na}_2\text{S} + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{S} \downarrow + 2\text{NaNO}_3$ ppt |
| 2) Salt solution + lead acetate solution Pb(CH ₃ COO) ₂ | A white ppt. of lead sulphite (PbSO ₃) is formed. $\text{Na}_2\text{SO}_3 + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbSO}_3 \downarrow + 2 \text{CH}_3\text{COONa}$ ppt | A white ppt. of lead thiosulphate (PbS ₂ O ₃) is formed, the ppt. turns black (PbS) on boiling. $\text{Na}_2\text{S}_2\text{O}_3 + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbS}_2\text{O}_3 \downarrow + 2 \text{CH}_3\text{COONa}$ White ppt $\text{PbS}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{PbS} \downarrow + \text{H}_2\text{SO}_4$ Black ppt | A black ppt. of lead sulphide (PbS) is formed. $\text{Na}_2\text{S} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbS} \downarrow + 2 \text{CH}_3\text{COONa}$ 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. $5\text{Na}_2\text{SO}_3 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 5\text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O}$ | | * Salt solution + Sodium nitroprusside solution: A violet colour is formed. |

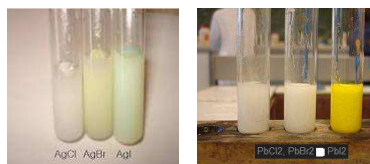
| | Sulphites | Thiosulphates |
|--|---|---|
| | Salt solution + 2 drops of dil. H₂SO₄ + Iodine solution(I₂) | |
| | The brown colour of the iodine solution disappears. $\text{Na}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HI}$ | The brown colour of the 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: $2\text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2 \text{NaI}$ |

2) Anions which react with concentrated sulphuric acid

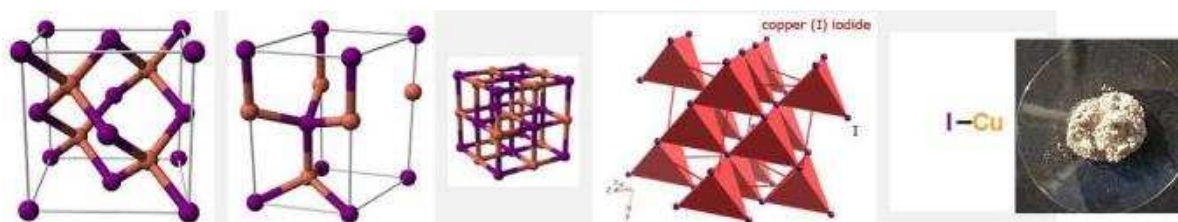
Note: Do these tests in fuming cuper because the gases which are given off in these tests are extremely irritating, and can cause damage to the sensitive mucous membranes of nose and throat.

| | 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. H₂SO₄: | Effervescence with evolution of colourless gas, Hydrogen chloride (HCl). $2\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ 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: $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$ | Reddish fumes evolve and the solution turns orange due to liberation of bromine (Br ₂). $2\text{NaBr} + \text{H}_2\text{SO}_4 \rightarrow 2\text{HBr} + \text{Na}_2\text{SO}_4$ $2\text{HBr} + \text{H}_2\text{SO}_4 \rightarrow 2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2$ | Violet fumes are evolved, (Iodine gas I ₂) and a brown or black precipitate is formed in the test tube. $2\text{KI} + 2\text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2$ | ⁻³⁸ 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. $2\text{KNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{HNO}_3$ $4\text{HNO}_3 + \text{Cu} \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$ |

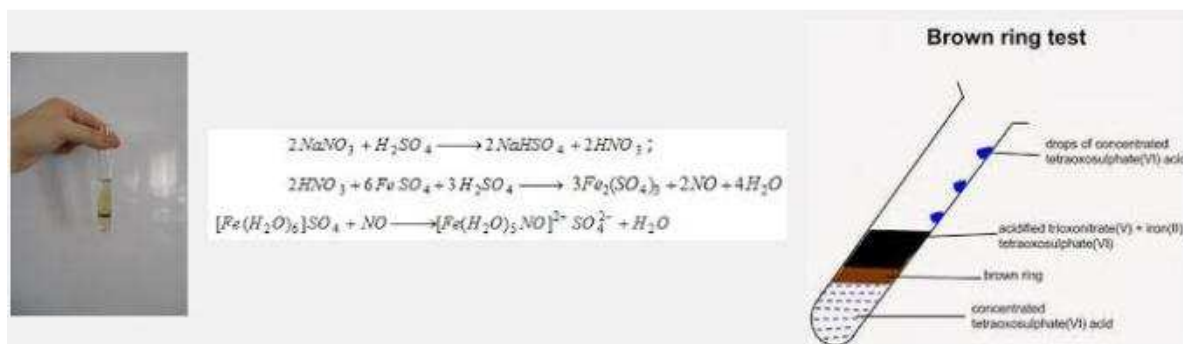
| | Chlorides | Bromides | Iodides | Nitrates |
|--|--|--|--|--|
| Confirmatory tests: 1) Salt solution + silver nitrate (AgNO ₃) | A dense white ppt. of silver chloride (AgCl) slowly turns a violet colour when exposed to bright sunlight. $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} \downarrow + \text{NaNO}_3$ ppt | A yellowish white precipitate of silver bromide (AgBr) is formed. $\text{NaBr} + \text{AgNO}_3 \rightarrow \text{AgBr} \downarrow + \text{NaNO}_3$ ppt | A yellow precipitate of silver iodide (AgI) is formed. $\text{KI} + \text{AgNO}_3 \rightarrow \text{AgI} \downarrow + \text{KNO}_3$ ppt | ⁻³⁸ |
| 2) Salt solution + lead acetate Pb(CH ₃ COO) ₂ | A white precipitate of lead chloride (PbCl ₂) is formed which is soluble in hot water, and reprecipitates on cooling. $2\text{NaCl} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbCl}_2 \downarrow + 2\text{CH}_3\text{COONa}$ | A white precipitate of lead bromide (PbBr ₂) appears which is soluble in boiling water and reprecipitates on cooling. $2\text{NaBr} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbBr}_2 \downarrow + 2\text{CH}_3\text{COONa}$ | A yellow precipitate of lead iodide (PbI ₂) is formed which dissolves in boiling water and recrystallises on cooling. $2\text{KI} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbI}_2 \downarrow + 2\text{CH}_3\text{COOK}$ |  |
| | | | ³⁹ Salt solution + Mercuric chloride (HgCl ₂): A reddish precipitate of mercuric iodide is formed which dissolves in excess of KI. $\text{HgCl}_2 + 2\text{KI} \rightarrow \text{HgI}_2 \downarrow + 2\text{KCl}$ ppt $\text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2[\text{HgI}_4]$ soluble | ⁴⁰ Brown ring test: The nitrate solution is mixed with freshly prepared FeSO ₄ solution, then conc. H ₂ SO ₄ is added and allowed to flow cautiously on the side of the test tube. A brown ring (Fe(NO) ₂ SO ₄) is formed at the interface of the two layers. The brown ring disappears on shaking the solution. |
| | | | ⁴¹ Salt solution + copper sulphate (CuSO ₄): A brown ppt. of cuprous iodide CuI and iodine I ₂ . $4\text{KI} + 2\text{CuSO}_4 \rightarrow 2\text{CuI} \downarrow + 2\text{K}_2\text{SO}_4 + \text{I}_2$ | |



CuI Cuprous iodide



Brown Ring Test



3) Anions which do not react with acids:

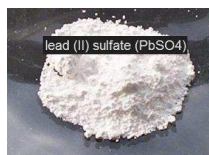
| | Phosphates (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) | Borates (BO_2^- , BO_3^{3-} , $\text{B}_4\text{O}_7^{2-}$) | Sulphates (SO_4^{2-}) |
|---|---|---|---|
| | Most phosphates are insoluble in water except those of ammonium and alkali metals. | Ammonium and alkali metal borates are water soluble while 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. $\text{Na}_2\text{HPO}_4 + \text{BaCl}_2 \rightarrow \text{BaHPO}_4 \downarrow + 2\text{NaCl}$ | A white ppt. of barium borate from concentrated solutions $\text{Ba}(\text{BO}_2)_2$ is produced, soluble in dilute acids and in excess of barium chloride. $\text{Na}_2\text{B}_4\text{O}_7 + 3\text{H}_2\text{O} + \text{BaCl}_2 \rightarrow \text{Ba}(\text{BO}_2)_2 + 2\text{H}_3\text{BO}_3 + 2\text{NaCl}$ | A white precipitate of barium sulphate (BaSO_4) is formed which is insoluble in dilute acids and in excess of barium chloride. $\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 \downarrow + 2\text{NaCl}$ |
| 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) $\text{Na}_2\text{B}_4\text{O}_7 + 3\text{H}_2\text{O} + 2\text{AgNO}_3 \rightarrow 2\text{AgBO}_2 + 2\text{H}_3\text{BO}_3 + 2\text{NaNO}_3$ $2\text{AgBO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2\text{H}_3\text{BO}_3$ | A white ppt. of silver sulphate (Ag_2SO_4) is formed with concentrated solution. $\text{Na}_2\text{SO}_4 + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{SO}_4 \downarrow + 2\text{NaNO}_3$ |



BaSO₄ is white



| | | |
|--|--|---|
| <p>For phosphates:</p> <p><u>0.5 ml of salt solution + 4 ml of ammonium molybdate solution + 0.5 ml of conc. HNO₃:</u></p> <p>Form a canary yellow precipitate of ammonium phosphomolybdate (NH₄)₃PO₄ · 12MoO₃ · H₂O in the cold or by gentle warming. (note the volume needed in this test).</p> | | <p>For sulphates:</p> <p><u>Salt solution + lead acetate:</u></p> <p>A white precipitate of lead sulphate is formed, which is readily soluble in hot concentrated ammonium acetate or conc. H₂SO₄</p> <p>$K_2SO_4 + Pb(CH_3COO)_2 \rightarrow PbSO_4 \downarrow + 2CH_3COOK$</p> <p>$PbSO_4 + H_2SO_4 \rightarrow Pb(HSO_4)_2$</p> |
|--|--|---|



Scheme for the identification of acid radicals

1) Solid salt + dil. HCl:

| | | | | | | |
|--------------------|--|---|---|--|---|--|
| Observation | Effervescence and a colourless odourless 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 dichromate 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 $\text{Cr}_2(\text{SO}_4)_3$. The anion is sulphite. | The gas is SO_2 , the ppt. is S and the green colour is $\text{Cr}_2(\text{SO}_4)_3$. 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. <u>(Go to step 2).</u> |

To differentiate between carbonate and bicarbonate:

| | |
|---|---|
| <p>1) Salt solution + magnesium sulphate solution: <u>For carbonate:</u> White precipitate of magnesium carbonate (MgCO_3). <u>For bicarbonate:</u> No ppt. in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained.</p> | <p>2) Salt solution + mercuric chloride solution: <u>For carbonate:</u> Reddish brown precipitate of mercuric carbonate (HgCO_3). <u>For bicarbonate:</u> No ppt. in the cold, but on heating a reddish-brown ppt. of mercuric carbonate is obtained.</p> |
|---|---|

2) Solid salt + conc. H_2SO_4 :

| | | | | | |
|--------------------|--|---|--|--|---|
| Observation | Effervescence with the evolution of a colourless gas which forms white fumes with NH_4OH . | Reddish 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 . The anion is Nitrate. | The anion is not from group 2. <u>(Go to step 3).</u> |

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 $\text{Ba}(\text{BO}_2)$. 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 + AgNO₃ (silver nitrate): | | | |
| | phosphate | borate | Sulphate |
| Observation | A yellow precipitate is formed, which is readily 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 ₃ PO ₄). The anion is phosphate. | The white ppt. is silver borate (AgBO ₂). The anion is borate. | The white ppt. is silver sulphate (Ag ₂ SO ₄). The anion is sulphate. |

Which one of the following is the smallest in size?

- (a) N³⁻ (b) O²⁻ (c) F⁻ (d) Na⁺

Ans : (d)

Na⁺ will have the smallest size

Group 14 Elements—Carbon Family

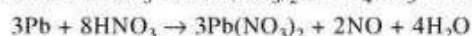
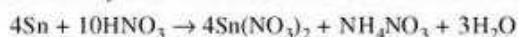
Group 14 contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is $(ns)^2 (np)^2$, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is a nonmetal but also has some metallic 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(SiH₃)₃.

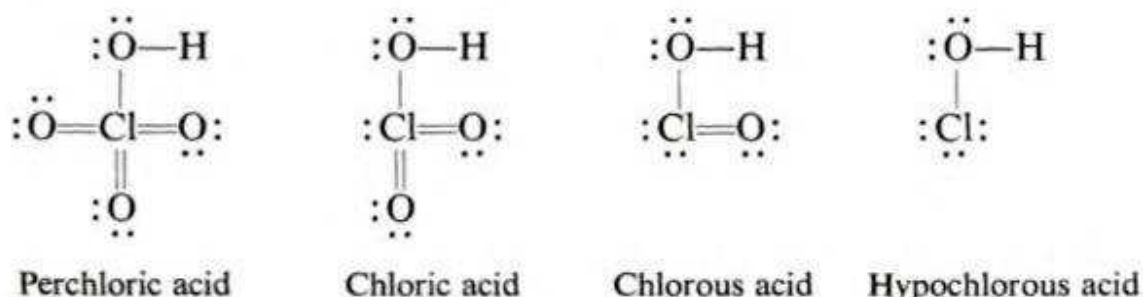
The chemical reactivity of elements decreases down the group. The inert pair effect becomes increasingly effective on descending the group.

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.



C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannate, $[\text{Sn}(\text{OH})_6]^{2-}$, and plumbate, $[\text{Pb}(\text{OH})_6]^{2-}$, respectively.

The size of Nb is very similar to Tantalum (Ta) due to Lanthanide contraction



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 polonium 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 alkalis it forms a hypobromite in cold dilute solution and a bromate in a hot solution



Cold and dilute

Potassium hypobromite



hot and concentrated

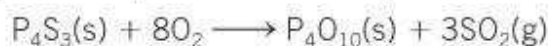
Potassium bromate

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, $(\text{NH}_4)_2\text{CO}_3$, 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.



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 $\epsilon(\text{X}-\text{X})$ —*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 $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

Halogens with the exception of F form a number of oxoacids—hypohalous acids (HOX), halous acids (HXO₂), halic acid (HXO₃) and perhalic acid (HXO₄). The acid strength follows the order HXO₄ > HXO₃ > HXO₂ > HXO. Fluorine forms only hypofluorous acid (HOF).

Halogens also form interhalgoen compounds AX, AX₃, AX₅ and AX₇. The compounds AX and AX₃ are formed where the electronegativity is not very large. The compounds AX₅ and AX₇ are formed by large Br and I atoms surrounded by small atom F. The molecule AX₃ 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 AX₅ acquire octahedral orientation. The seven pairs of electrons around atom A in AX₇ 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 Cl₂O, ClO₂, Cl₂O₆ and Cl₂O₇. All these oxides are highly reactive and very unstable.

Dichloro Oxide (Cl₂O)

Preparation

- It can be prepared by passing dry chlorine over a fresh precipitate of yellow mercuric oxide as follows:



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:



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 $[\text{XeO}_6]^{4+}$

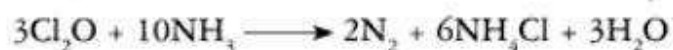
4. **With Water:** It dissolves in water forming a golden yellow solution of hypochlorous acid (HClO) i.e., it is an anhydride of hypochlorous acid.



5. **Oxidizing Action:** Being a strong oxidizing agent, it oxidizes HCl to Cl_2 as follows:



6. **With Ammonia:** It reacts with ammonia with an explosion as follows:



Structure It has angular or V-shaped structure. Here oxygen atom is sp^3 hybridized. Cl – O – Cl bond angle is 110.9° and O – Cl bond length is 1.71 \AA

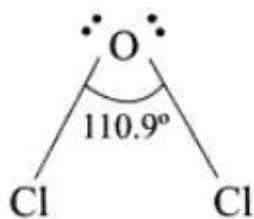
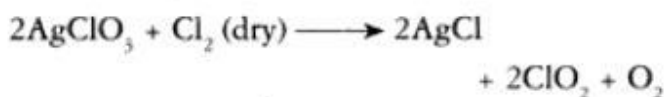


Fig. 6.12

Chlorine Dioxide (ClO₂)

Preparation

1. Pure ClO₂ can be obtained by passing dry Cl₂ over AgClO₃ heated to 363 K as follows:



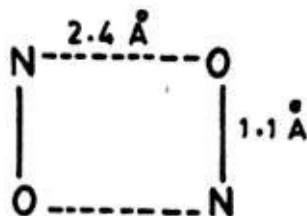
2. It can also be prepared by the action of Cl₂ on sodium chlorite as follows:



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 Cl₂ and O₂ by an electric spark.
4. With H₂O: 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

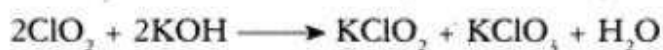


Structure of $(NO)_2$

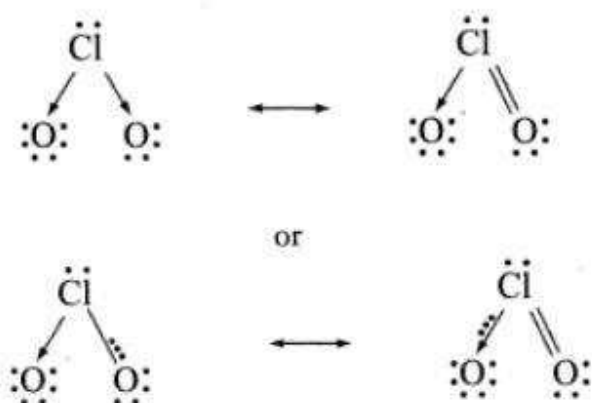
Group 12-Electrode potential of Mercury is +ve, 1st ionisation Energy higher than Cd



5. **With Alkalies:** It gives a mixture of chlorite and chlorate with alkalies as follows:



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 \AA .



Dichlorine Hexoxide (Cl_2O_6)

Preparation

1. It can be prepared by mixing chlorine dioxide with ozonized air at 273 K.



Physiochemical Properties

1. It is a dark 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.



5. With HF: It gives HClO_4 and chloryl fluoride with HF as follows:



6. With Alkalies: It reacts with alkalies to give chlorates and perchlorates.

5. With HF: It gives HClO_4 and chloryl fluoride with HF as follows:



6. With Alkalies: It reacts with alkalies to give chlorates and perchlorates.



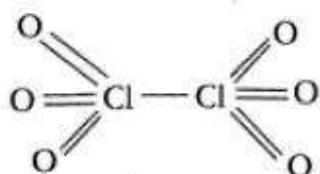
Structure: In liquid state it is a diamagnetic molecule with uncertain structure which is not known so far.



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 (Cl₂O₇)

Preparation

It can be formed by the dehydration of perchloric acid with P_2O_5 at 263 K



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.



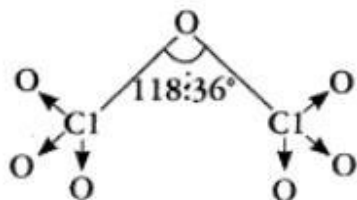
Structure: In it two ClO_3 units are joint through oxygen at an angle of 118.5° or $118^\circ 36'$ giving tetrahedral look. Here Cl – O_b bond length is 1.72 \AA while Cl – O_c is 1.42 \AA .

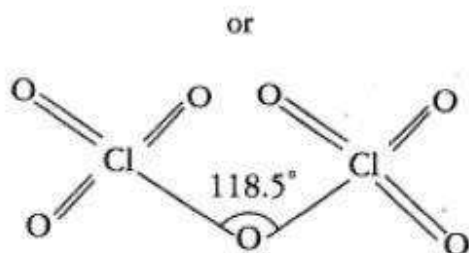
(1) Oxoacids of Nitrogen

| | | |
|------------------------|----------------------------------|----|
| (i) Hyponitrous acid | $\text{H}_2\text{N}_2\text{O}_2$ | +1 |
| (ii) Hydronitrous acid | H_2NO_2 | +2 |
| (iii) Nitrous acid | HNO_2 | +3 |
| (iv) Hyponitric acid | $\text{H}_2\text{N}_2\text{O}_3$ | +5 |
| (v) Nitric acid | HNO_3 | +5 |
| (vi) Pernitric acid | HNO_4 | +7 |

(2) Oxoacids of Phosphorous

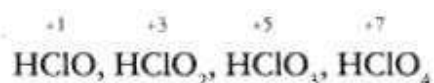
| | | |
|--------------------------------|---|----------|
| (i) Hypophosphorous acid | H_3PO_2 | +1 |
| (ii) Phosphorous acid | H_3PO_3 | +3 |
| (iii) Hypophosphoric acid | $\text{H}_4\text{P}_2\text{O}_6$ | +4 |
| (iv) Orthophosphoric acid | H_3PO_4 | +5 |
| (v) Pyrophosphoric acid | $\text{H}_4\text{P}_2\text{O}_7$ | +5 |
| (vi) Metaphosphoric acid | HPO_3 | +5 |
| (vii) Peroxophosphoric acid | H_3PO_5 or $\text{H}_4\text{P}_2\text{O}_8$ | +7 or +6 |
| (viii) Tripolyphosphoric acid | $\text{H}_5\text{P}_3\text{O}_{10}$ | +5 |
| (ix) Tetra polyphosphoric acid | $\text{H}_6\text{P}_4\text{O}_{13}$ | +5 |



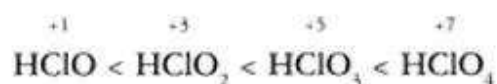


Oxy-acids of Chlorine

Chlorine forms all the four oxy-acids, which are hypochlorous acid ($\text{HCl}^{\text{+1}}\text{O}$), chlorous acid ($\text{HCl}^{\text{+3}}\text{O}_2$), chloric acid ($\text{HCl}^{\text{+5}}\text{O}_3$) and perchloric acid ($\text{HCl}^{\text{+7}}\text{O}_4$). It may be noted that Cl-atom is in +1, +3, +5 and +7 oxidation state respectively in these acids.



The acidic strength of these acids increases as follows:



Hypochlorous Acid (HClO)

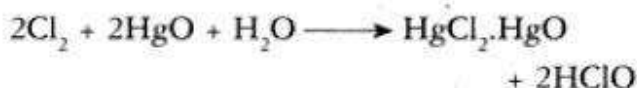
Preparation

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)



- (ii) It can be prepared by shaking Cl_2 water with freshly precipitated HgO .



The insoluble $\text{HgCl}_2 \cdot \text{HgO}$ 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.

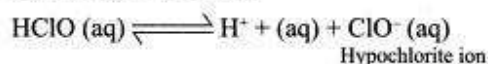


3. *From bleaching powder* Hypochlorous acid can be prepared by distilling the aqueous solution of bleaching powder (CaOCl_2) with a calculated quantity of 5 per cent HNO_3 or by passing CO_2 into aqueous solution of CaOCl_2 and then distilling it.



Physiochemical properties

- The dilute solution of hypochlorous acid is colourless while its concentrated solution is yellow in colour.
- It is a weak acid, even weaker than H_2CO_3 with a dissociation constant of 3×10^{-8} at 20°C .
- Acidic nature:* (Monobasic nature) HClO is a monobasic acid as its aqueous solution on ionization gives only one H^+ ion.



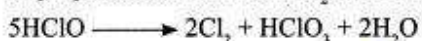
The monobasic nature shows that this molecule has one $-\text{OH}$ group attached directly with the central Cl atom.

Being an acid it reacts with alkalis to give salts which are called hypochlorites.

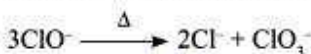
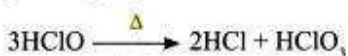


4. *Disproportionation*

- (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 .



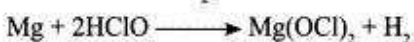
- (ii) When aqueous solution of HClO is heated, it undergoes disproportionation into HCl and HClO_3 .



- (iii) On distillation it decomposes into H_2O and Cl_2O .



5. *Reaction with metals:* HClO reacts with Mg with the evolution of H_2 .

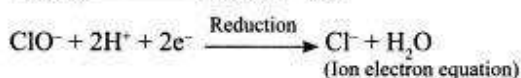
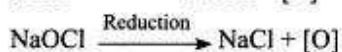
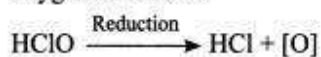


It reacts with Fe and Al with the evolution of H_2 and Cl_2 while with Co , Ni and Cu , Cl_2 and O_2 are evolved.

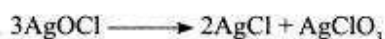
6. **Reaction with mercury:** When it is shaken with Hg, a light brown precipitate of basic mercuric chloride, $\text{HgCl}(\text{OH})$ is formed which is soluble in HCl.



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.



8. **Action of AgNO_3 :** It reacts with AgNO_3 to give silver hypochlorite (AgOCl) which is unstable and undergoes disproportionation into AgCl and AgClO_3 .



Uses

- (i) Hypochlorous acid is used for bleaching paper pulp etc.

Structure It is a linear molecule in which chlorine atom is sp^3 hybridized.

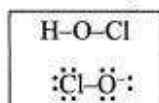


Figure 16.38 Structure of Hypochlorous Acid

Chlorous acid (HClO_2)

Preparation

1. *From Barium hypochlorite* It is prepared in the aqueous solution by treating a suspension of barium hypochlorite, $\text{Ba}(\text{ClO}_2)_2$ with dil. H_2SO_4 and filtering off the precipitate of BaSO_4 .

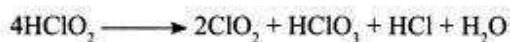


2. *From ClO_2* It can also be obtained by the action of ClO_2 on H_2O_2 .

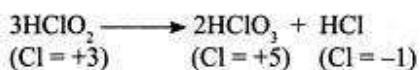


Physicochemical properties

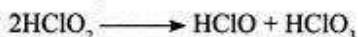
1. The freshly prepared solution of chlorous acid is colourless but it soon decomposes to ClO_2 which colours the solution yellow.
2. It gives a violet colour with FeSO_4 .
3. *Decomposition:* In acid solution, HClO_2 rapidly decomposes as shown.



4. *Disproportionation:* HClO_2 and its salts undergo disproportionation on heating in an alkaline solution as shown.



It undergoes auto-oxidation.



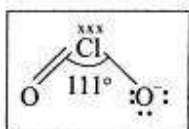
5. *Oxidizing properties:* Both HClO_2 and its salts show oxidizing properties due to nascent oxygen.



HClO_2 and its salts liberate I_2 from KI solution.



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 Cl_2 from HCl passed on hot saturated slag Chemistry

$\text{Cu}_2\text{Fe}(\text{CN})_6$ Chocolate Brown Precipitate

$\text{Cd}(\text{CN})_2$, K_2SO_4 , KCN are all white - $\text{Cd}(\text{CN})_2$ white precipitate

$\text{Ag}_2\text{S}_2\text{O}_3$ White Precipitate

$2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4$ green vitriol, ZnSO_4 White Vitriol, CuSO_4 Blue Vitriol

Ti+3 Violet, V+3 Grey, Fe+3 yellow, Co+2 Pink - ion colours

Silver nitrate (Lunar caustic) AgNO_3

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 ($\text{Cr}_2\text{O}_7^{2-}$) | |
| Mn | | Pale pink | | Brown | | Dark green (MnO_4^{2-}) | Intense purple (MnO_4^-) |
| Fe | | Pale green | Yellow or brown | | | | |
| Co | | Pink | Orange/y ellow | | | | |
| Ni | | Green | | | | | |
| Cu | | Blue | | | | | |
| Zn | | colorless | | | | | |

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