Spoon Feeding Oxidation Methods

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 25th 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.
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.

**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.**
A very polite request:

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

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

Random - 1

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

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

Random - 2

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

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

Random - 3

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

Random - 4

The best Tabla Players are all Men.


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.
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.

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.
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.

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.
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 up to 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.

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 Ethred 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 16 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 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!)

A standardized test of Intelligence will never be possible. It never happened before, nor ever will happen in future; where the IQ test results will be acceptable by all. In the net there are thousands of charts which show that the intelligence scores of girls/women are lesser. Debates of Trillion words, does not improve performance of Girls.
I am not wasting a single second debating or discussing with anyone, on this. I am simply accepting ALL the results. IQ is only one of the variables which is required for success in life. Thousands of books have been written on “Networking Skills”, EQ (Emotional Quotient), Drive, Dedication, Focus, “Tenacity towards the end goal”… etc. In each criteria, and in all together, women (in general) do far worse than men. Bangalore is known as “….. capital of India”. [Fill in the blanks]. The blanks are generally filled as “Software Capital”, “IT Capital”, “Startup Capital”, etc. I am member in several startup eco-systems/groups. I have attended hundreds of meetings, regarding “technology startups”, or “idea startups”. These meetings have very few women. Starting up new companies are all “Men’s Game” / “Men’s business”. Only in Divorce settlements women will take their goodies, due to Biased laws. There is no dedication, towards wealth creation, by women.

Random - 13

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

See http://skmclasses.kinja.com/progressively-daughters-become-monsters-1764484338
See http://skmclasses.kinja.com/vivacious-vixens-1764483974

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

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

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

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

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

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

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

Some Random Examples must be known by all

It is extremely unfortunate that the “woman empowerment” has created. This is the kind of society and women we have now! 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 - Alwayztturnup

‘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.

![Image](https://example.com/image1)

![Image](https://example.com/image2)
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 trying to conclude the trial of a former Shelbyville ISD teacher who had ...

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

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

http://www.thenarivecanadian.com/.../blackmale...
Women are raping boys and young men
Rape advocacy has been reigned and whole into a political agenda controlled by radicalized activists. Tim Patten takes a more keen and well supported look into the manufactured rape culture and...

BRONX WOMAN CONVICTED OF POISONING AND DROWNING HER CHILDREN

Lisette Bannenga researched methods on the internet before she killed her son and daughter in 2012.

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

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 pet dog until he took his last breath. Svetlana Baitkova, 46, battled... Her husband...

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

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

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

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

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.

CBSE Standard 12 Chemistry Survival Guide - Oxidation Methods by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams
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 ...........
HURT FEMINISM BY DOING NOTHING

Don’t help women
Don’t fix things for women
Don’t support women’s issues
Don’t come to women’s defense
Don’t speak for women
Don’t value women’s feelings
Don’t portray women as victims
Don’t protect women

WITHOUT WHITE KNIGHTS FEMINISM WOULD END TODAY

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

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

All chemical reactions happen because of this electrode potential difference. When a Solid is added to a solution of another compound such as a Gold Spoon in CuSO₄ Solution, of a Copper container having AgNO₃ 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.

- The e.m.f of the standard cell Zn | Zn²⁺ | | Ag⁺ | Ag  \( E^\circ_{\text{cell}} = 1.562 \text{ Volts} \)

If the standard electrode potential of Zinc is \(-0.762 \text{ Volts}\), then that of Silver is ?

Solution : \( E^\circ_{\text{cell}} = E^\circ_{\text{Right}} - E^\circ_{\text{Left}} = E_{\text{Ag}^+ | \text{Ag}} - E_{\text{Zn}^{2+} | \text{Zn}} = (E^\circ_{\text{Reduction (Right)}} - E^\circ_{\text{Reduction (Left)}}) \)
So 1.562 = E(Ag⁺ | Ag) - (-0.762) => 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 Fe²⁺/Fe is more negative than that for Cu²⁺/Cu. The iron oxidises first, while copper ions are reduced. Iron will corrode (rust). Or in more simple words it is easier to replace Cu ions by Fe ions from the pot. Any element lower in the series tends to replace the element which is higher up the series.

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

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

<table>
<thead>
<tr>
<th>Half-Reaction</th>
<th>E (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₂(g) + 2e⁻</td>
<td>2F⁻(aq)</td>
</tr>
<tr>
<td>Cl₂(g) + 2e⁻</td>
<td>2Cl⁻(aq)</td>
</tr>
<tr>
<td>MnO₂(g) + 4H⁺(aq) + 2e⁻</td>
<td>Mn²⁺(aq) + 2H₂O(l)</td>
</tr>
<tr>
<td>NO₃⁻(aq) + 4H⁺(aq) + 3e⁻</td>
<td>NO(g) + 2H₂O(l)</td>
</tr>
<tr>
<td>Ag⁺(aq) + e⁻</td>
<td>Ag(s)</td>
</tr>
<tr>
<td>Fe³⁺(g) + e⁻</td>
<td>Fe²⁺(aq)</td>
</tr>
<tr>
<td>O₂(g) + 2H₂O(l) + 4e⁻</td>
<td>4OH⁻(aq)</td>
</tr>
<tr>
<td>Cu²⁺(aq) + 2e⁻</td>
<td>Cu(s)</td>
</tr>
<tr>
<td>2H⁺(aq) + 2e⁻</td>
<td>H₂(g)</td>
</tr>
<tr>
<td>N₂(g) + 5H⁺(aq) + 4e⁻</td>
<td>N₂H₅⁺(aq)</td>
</tr>
<tr>
<td>Fe²⁺(aq) + 2e⁻</td>
<td>Fe(s)</td>
</tr>
<tr>
<td>2H₂O(l) + 2e⁻</td>
<td>H₂(g) + 2OH⁻(aq)</td>
</tr>
<tr>
<td>Na⁺(aq) + e⁻</td>
<td>Na(s)</td>
</tr>
<tr>
<td>Li⁺(aq) + e⁻</td>
<td>Li(s)</td>
</tr>
</tbody>
</table>
A more detailed table

| Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions |
|---|---|---|---|---|
| Half-Reaction | $E^\circ$ (V) | Half-Reaction | $E^\circ$ (V) |
| $F_2 + 2e^- \rightarrow 2F^-$ | 2.87 | $O_3 + 2H_2O + 4e^- \rightarrow 4OH^-$ | -0.40 |
| $\text{Ag}^{2+} + e^- \rightarrow \text{Ag}^+$ | 1.99 | $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$ | 0.34 |
| $\text{Co}^{2+} + e^- \rightarrow \text{Co}^{3+}$ | 1.02 | $\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$ | -0.27 |
| $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$ | 1.78 | $\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$ | 0.22 |
| $\text{Cd}^{2+} + e^- \rightarrow \text{Cd}^+$ | 1.70 | $\text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$ | 0.20 |
| $\text{Pb}^4+ + 4\text{H}^+ + 2e^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$ | 1.69 | $\text{Ca}^{2+} + e^- \rightarrow \text{Ca}^+$ | -0.16 |
| $\text{MnO}_4^- + 4\text{H}^+ + 3e^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}$ | 1.68 | $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$ | 0.00 |
| $2e^- + \text{Pb}^{2+} + \text{Cu}^{2+} \rightarrow \text{Pb} + \text{Cu}$ | 1.60 | $\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$ | -0.036 |
| $\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$ | 1.51 | $\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$ | -0.13 |
| $\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$ | 1.50 | $\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$ | -0.14 |
| $\text{PbSO}_4 + 4\text{H}^+ + 2e^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$ | 1.46 | $\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$ | -0.23 |
| $\text{Cu}_2 + 2e^- \rightarrow 2\text{Cu}^+$ | 1.36 | $\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$ | -0.35 |
| $\text{CeO}_2^{2+} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Ce}^{3+} + 7\text{H}_2\text{O}$ | 1.33 | $\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$ | -0.40 |
| $\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$ | 1.23 | $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$ | -0.44 |
| $\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$ | 1.21 | $\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^{+}$ | -0.59 |
| $\text{IO}_3^- + 6\text{H}^+ + 5e^- \rightarrow 3\text{H}_2\text{O} + \text{I}_2$ | 1.20 | $\text{Cu}^{2+} + 3e^- \rightarrow \text{Cu}$ | -0.73 |
| $\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$ | 1.09 | $\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$ | -0.76 |
| $\text{VO}_4^{3-} + 2\text{H}^+ + e^- \rightarrow \text{VO}^{2+} + 3\text{H}_2\text{O}$ | 1.00 | $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$ | -0.83 |
| $\text{AlCl}_3 + 3e^- \rightarrow \text{Al} + 4\text{Cl}^-$ | 0.99 | $\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$ | -1.18 |
| $\text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$ | 0.96 | $\text{AP}^{3+} + 3e^- \rightarrow \text{Al}$ | -1.66 |
| $\text{Cl}_2 + e^- \rightarrow 2\text{Cl}^-$ | 0.945 | $\text{H}_2 + 2e^- \rightarrow 2\text{H}$ | -2.23 |
| $2\text{H}^+ + 2e^- \rightarrow 2\text{H}$ | 0.91 | $\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$ | -2.37 |
| $\text{Ag}^+$ + $e^- \rightarrow \text{Ag}$ | 0.80 | $\text{La}^{3+} + 3e^- \rightarrow \text{La}$ | -2.37 |
| $\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}$ | 0.80 | $\text{Na}^{+} + e^- \rightarrow \text{Na}$ | -2.71 |
| $\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$ | 0.77 | $\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$ | -2.76 |
| $\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O}_2$ | 0.68 | $\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$ | -2.90 |
| $\text{MnO}_4^- + e^- \rightarrow \text{MnO}_2$ | 0.56 | $\text{K}^+ + e^- \rightarrow \text{K}$ | -2.92 |
| $\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$ | 0.54 | $\text{Li}^+ + e^- \rightarrow \text{Li}$ | -3.05 |

Spoon Feeding

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

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

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

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

\[
E_{\text{cell}}^\circ = E_{\text{cell}} = E_{\text{anode}} - E_{\text{cathode}} = 0.059 \frac{n}{M} \log \left( \frac{M^{n+}}{M^{n-2}} \right)
\]

\[
E_{\text{cell}}^\circ = -0.059 \frac{n}{M} \log \left( \frac{M^{n+}}{M^{n-2}} \right)
\]

\[
E_{\text{cell}} = \frac{RT}{nF} \ln \left( \frac{[\text{Products}]}{[\text{Reactants}]} \right) + \frac{RT}{nF} \ln \left( \frac{Q}{Q_0} \right)
\]

Temperature (in Kelvin) \quad \text{External Ion Concentration} \quad \text{RT} \quad \log \quad \frac{\text{[ion]}}{\text{[ion]₀}} \quad E_{\text{ion}} = 2.303 \quad \text{Equilibrium Potential} \quad \text{Temperature} \quad \text{Internal Ion Charge Constant} \quad \text{Z}\text{F} \quad \log \quad \frac{\text{[ion]}}{\text{[ion]₀}}
Consider the following set of half-reactions

**Reduction**
\[ \text{Fe}^{2+} + 2e^- \leftrightarrow \text{Fe} \quad E_{\text{red}}^{\circ} = -0.44 \text{ V} \]

**Oxidation**
\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \quad E_{\text{ox}}^{\circ} = +0.76 \text{ V} \]

**Overall**
\[ \text{Zn} + \text{Fe}^{2+} \leftrightarrow \text{Zn}^{2+} + \text{Fe} \quad E_{\text{cell}}^{\circ} = 0.32 \text{ V} \]

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

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

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

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

Recall the relation: \(\Delta G = \Delta G^{\circ} + RT \ln Q\) (for non-standard conditions)

Substitute the new definition of \(\Delta G\) and we get

\[-nFE = -nFE^{\circ} + RT \ln Q\]

\[ E = E^{\circ} - \frac{RT}{nF} \ln Q \] (This is called the Nernst Equation).

Thus, we can calculate the cell potential of any cell, given only the initial conditions (to calculate Q) and the reduction potentials (to calculate \(E^{\circ}\))

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 (\(n = 2\)).
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.
A voltaic cell is made of aqueous Bromine and Zinc. Given -

$$\text{Br}_2(aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2\text{Br}^-(aq) \quad E_{\text{cell}} = 1.83 \text{ V}.$$  

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

Solution :

$$\text{Br}_2(aq) + 2e^- \rightarrow 2\text{Br}^- \quad \text{[reduction; cathode]}$$  

$$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \quad \text{[oxidation; anode]} \quad E_{\text{zinc}}^\circ = -0.76 \text{ V}$$

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

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

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

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?

- Cathode: $\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^- \quad E_{\text{red}}^\circ = 1.09 \text{ V}$

- Anode: $\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \quad E_{\text{ox}}^\circ = -E_{\text{red}}^\circ = -0.34 \text{ V}$

- Cell: $\text{Cu} + \text{Br}_2 \rightarrow \text{Cu}^{2+} + 2\text{Br}^- \quad E_{\text{cell}}^\circ = 0.75$

$$\ln K = \frac{nFE_{\text{cell}}^\circ}{RT} = \frac{2 \times 96458 \text{ C/mol} \times 0.75 \text{ V}}{8.31451 \text{ J/K mol} \times 298.15 \text{ K}} = 58.38 \times 10^{20}$$

$$K = e^{58.38 \times 10^{20}} = 2.2 \times 10^{25}$$

Using half reactions write the spontaneous Redox reactions

$$\text{Sn}^{2+}(aq) + 2e^- \rightarrow \text{Sn}(s) \quad E_{\text{Sn}}^\circ = -0.14 \text{ V}$$  

$$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s) \quad E_{\text{silver}}^\circ = 0.80 \text{ V}$$

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

**Note:** This does not change the voltage obtained

$$2\text{Ag}^+(aq) + 2e^- \rightarrow 2\text{Ag}(s) \quad E_{\text{silver}}^\circ = 0.80 \text{ V}$$
Now we need to add the half reactions to eliminate the electrons, but subtract to get the Voltage correctly. Recall $E^\circ_{\text{cell}} = E^\circ_{\text{Right}} - E^\circ_{\text{Left}} = E_{\text{Cathode}} - E_{\text{Anode}} = (E_{\text{Reduction (Right)}} - E_{\text{Reduction (Left)}})$

\[
\begin{align*}
\text{Sn(s)} & \rightarrow \text{Sn}^{2+}(aq) + 2e^- & E^\circ_{\text{Sn}} & = -0.14 \text{ V} \\
2\text{Ag}^+(aq) + 2e^- & \rightarrow 2\text{Ag(s)} & E^\circ_{\text{silver}} & = 0.80 \text{ V} \\
\text{Sn(s)} & + 2\text{Ag}^+(aq) \rightarrow 2\text{Ag(s)} + \text{Sn}^{2+}(aq) & E^\circ_{\text{cell}} & = 0.94 \text{ V}
\end{align*}
\]

\[
E^\circ_{\text{cell}} = E^\circ_{\text{silver}} - E^\circ_{\text{Sn}} = 0.80 - (-0.14) = 0.94 \text{ V}
\]

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.

- 

**Zinc and Magnesium Oxide Battery**

Anode (oxidation): $\text{Zn(s)} + 2\text{OH}^-(aq) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2e^-$

Cathode (reduction): $\text{MnO}_2(s) + 2\text{H}_2\text{O(l)} + 2e^- \rightarrow \text{Mn(OH)}_2(s) + 2\text{OH}^- (aq)$

Overall (cell) reaction:

\[
\text{Zn(s)} + \text{MnO}_2(s) + 2\text{H}_2\text{O(l)} \rightarrow \text{ZnO(s)} + \text{Mn(OH)}_2(s) \quad E_{\text{cell}} = 1.5 \text{ V}
\]

- 

**Zinc and Magnesium Oxide Battery**

Anode (oxidation): $\text{Zn(s)} + 2\text{OH}^-(aq) \rightarrow \text{ZnO(s)} + \text{H}_2\text{O(l)} + 2e^-$

Cathode (reduction): $\text{Ag}_2\text{O}(s) + \text{H}_2\text{O(l)} + 2e^- \rightarrow 2\text{Ag(s)} + 2\text{OH}^- (aq)$

Overall (cell) reaction:

\[
\text{Zn(s)} + \text{Ag}_2\text{O}(s) \rightarrow \text{ZnO(s)} + 2\text{Ag(s)} \quad E_{\text{cell}} = 1.6 \text{ V}
\]

The mercury battery uses HgO as the oxidizing agent instead of Ag$_2$O and has cell potential of 1.3 V.

- 

**The Lithium Batteries use Silver Vanadium Pentoxide as cathode**

Anode (oxidation):

\[
3.5\text{Li(s)} \rightarrow 3.5\text{Li}^+ + 3.5e^-
\]

Cathode (reduction):

\[
\text{AgV}_2\text{O}_5(s) + 3.5\text{Li}^+ + 3.5e^- \rightarrow \text{Li}_3\text{V}_2\text{O}_5(s)
\]

Overall (cell) reaction:

\[
\text{AgV}_2\text{O}_5(s) + 3.5\text{Li}(s) \rightarrow \text{Li}_3\text{V}_2\text{O}_5(s)
\]
The most commonly used Battery is Lead-Acid Battery

Anode (oxidation): \[ \text{Pb(s) + HSO}_4^-(aq) \to \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \]

Cathode (reduction):
\[ \text{PbO}_2(s) + 2\text{H}^+(aq) + \text{HSO}_4^-(aq) + 2e^- \to \text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \]

Overall (cell) reaction (discharge):
\[ \text{PbO}_2(s) + \text{Pb(s) + H}_2\text{SO}_4(aq) \to 2\text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \quad E_{cell} = 2.1 \text{ V} \]

Overall (cell) reaction (recharge):
\[ 2\text{PbSO}_4(s) + 2\text{H}_2\text{O(l)} \to \text{PbO}_2(s) + \text{Pb(s) + H}_2\text{SO}_4(aq) \]

Nickel Metal Hydride Battery

Anode (oxidation): \[ \text{MH(s) + OH}^-(aq) \to \text{M(s) + H}_2\text{O(l) + e}^- \]

Cathode (reduction): \[ \text{NiO(OH)(s) + H}_2\text{O(l) + e}^- \to \text{Ni(OH)}_2(s) + \text{OH}^-(aq) \]

Overall (cell) reaction:
\[ \text{MH(s) + NiO(OH)(s) \to M(s) + Ni(OH)}_2(s) \quad E_{cell} = 1.4 \text{ V} \]

Laptops, Cell-phones most commonly use Lithium ion Batteries

Anode (oxidation):
\[ \text{Li}_x\text{C}_6(s) \to x\text{Li}^+ + xe^- + \text{C}_6(s) \]

Cathode (reduction):
\[ \text{Li}_y\text{Mn}_2\text{O}_4(s) + x\text{Li}^+ + xe^- \to \text{LiMn}_2\text{O}_4(s) \]

Overall (cell) reaction:
\[ \text{Li}_y\text{O}_2(s) + \text{Li}_x\text{Mn}_2\text{O}_4(s) \to \text{LiMn}_2\text{O}_4(s) \quad E_{cell} = 3.7 \text{ V} \]

Hydrogen Fuel Cell

Anode (oxidation):
\[ 2\text{H}_2(g) \to 4\text{H}^+(aq) + 4e^- \]

Cathode (reduction):
\[ \text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \to 2\text{H}_2\text{O(g)} \]

Overall (cell) reaction:
\[ 2\text{H}_2(g) + \text{O}_2(g) \to 2\text{H}_2\text{O(g)} \quad E_{cell} = 1.2 \text{ V} \]

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

\[
\begin{array}{c|c|c}
\text{Anode} & \text{Ag(s)} & \rightarrow \text{Ag}^+ + e^- \\
\text{Cathode} & \text{AgCl} + e^- & \rightarrow \text{Ag(s)} + \text{Cl}^- \\
\hline
\text{Overall} & \text{AgCl} & \rightarrow \text{Ag}^+ + \text{Cl}^- \\
\end{array}
\]

\[E^{\circ}_{\text{cell}} = -0.58 \text{~V (not very spontaneous)}\]

\[K = 6.3 \times 10^{-9}\]

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

\[E = E^{\circ} - \frac{0.05917 \text{~V}}{2 \ln [\text{H}^+]}\]

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

\[E = E^{\circ} - 0.0257 \text{~V} \ln [\text{H}^+] \quad \text{(Note: } \ln Y = 2.303 \times \log Y \text{ and } -0.257 \times 2.303 = 0.5917)\]

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

\[
E = E^* + 0.05917 \times \text{pH}.
\]

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.

1. The solubility product \((K_{sp})\) of MX\(_2\) at 298 K based on the information available for the given concentration cell (take 2.303 \(RT/F = 0.059\) V at 298 K) is:
   - \((a)\) \(\times 10^{-15}\) mol\(^3\) dm\(^{-6}\)
   - \((b)\) \(\times 10^{-17}\) mol\(^3\) dm\(^{-6}\)
   - \((c)\) \(\times 10^{-10}\) mol\(^3\) dm\(^{-6}\)
   - \((d)\) \(\times 10^{-12}\) mol\(^3\) dm\(^{-6}\)

2. The value of Δ\(G\) for the given cell reaction (take 1F = 96500 C mol\(^{-1}\)) is:
   - \((a)\)\( -5.7\) kJ mol\(^{-1}\)
   - \((b)\)\( 5.7\) kJ mol\(^{-1}\)
   - \((c)\)\( 11.4\) kJ mol\(^{-1}\)
   - \((d)\)\( -11.4\) kJ mol\(^{-1}\)

**Solutions**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Students</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHC: Oxidation</td>
<td>MX(_2) (\rightarrow) M(^{2+}) (_2) (_2) + 2e(^-)</td>
</tr>
<tr>
<td>RHC: Reduction</td>
<td>(M(^{2+}))(_2) (_2) + 2e(^-) (\rightarrow) M(s)</td>
</tr>
</tbody>
</table>

**Overall reaction**

\( (M^{2+})_2 \rightarrow (M^{2+})_2 \)

**The cell potential is**

\[
E = - \frac{RT}{2F} \ln \left( \frac{[M^{2+}]_2}{[M^{2+}]_2} \right) \quad \text{i.e.,} \quad 0.059 = - \frac{0.059}{2} \log \left( \frac{[M^{2+}]_2}{0.001} \right)
\]

This gives \( \log \left( \frac{[M^{2+}]_2}{mol \ dm^{-3}} \right) = 2 + \log (0.001) = -2 + 3 = 1 \quad \text{i.e.,} \quad [M^{2+}]_2 = 1.0 \times 10^{-5} \text{ mol dm}^{-3} \)

From the reaction

\[
MX_2(s) \rightleftharpoons M^{2+}(aq) + 2X^-(aq); \quad (s \text{ is solubility of the salt})
\]

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

The Δ\(G\) 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 second question
Oxidation Methods in Organic Chemistry

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 agent.

Adding of Oxygen, or Halogens (F, Cl, Br, I) or other p-Block elements which accept electrons, is oxidation. So if Potassium (K) gets Oxygen (attaches to O) to form $K_2O$ or $KO_2$ (Superoxide), K is getting oxidized. If Cs attaches with F then Cs is getting oxidized, while F is being reduced. Cs is a reducing agent as it is 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 Organic chemistry. There are many kinds of details of oxidizing agent or Reducing agent that vary from reactions / situations.

I reasonably searched and realized that details of Oxidation or Reduction is scattered. There is no single e-Book that gives all of these as a collection.

So this e-Book is free for you. All information at a single place.

Potassium dichromate, Chromium Trioxide, Sodium dichromate, Potassium Chromate, Sodium Chromate, in acidic medium gives Chromic acid. This becomes the source of Nascent Oxygen atoms. These oxygen atoms oxidizes the molecules in reaction before combining themselves to Oxygen molecule. ($O_2$)
Sarett’s reagent is a “mild oxidizing agent”. So alcohol gets oxidized (Oxygen added) to Aldehyde. While a stronger oxidizing agent would have oxidized up to acid.

Adding Oxygen can happen in different ways. Just by knowing that a molecule is being Oxidized may not help guessing the outcome. R-I being oxidized by different reagents, gives different outcomes.

Making a Cyanide is a common way to add a carbon atom. Cyanides are often converted to acids.
Note: Isocyanides gives Amines.

Amides can be converted to Acids. Amines can be converted to Alcohols.

\[
\text{Aliphatic amides can be converted to carboxylic acids by reaction with } \text{HNO}_3. \\
R\text{--C--NH}_2 + \text{HNO}_3 \xrightarrow{\text{primary amines in similar conditions}} R\text{--C--OH} + N_2 + H_2O
\]

Lactic acid has 3 carbon atoms. So cyanide is added to increase a carbon atom. Subsequently acid is made.

\[
\text{Ethanal is converted into lactic acid by following reaction:} \\
\text{CH}_3\text{CHO} + \text{HCN} \xrightarrow{\text{Cya with } O \text{ in mono-cond.}} \text{CH}_3\text{--CH} + \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CH}_3\text{--CH} + \text{COOH}
\]

Vic-diols are often prepared by an epoxy banana bond. Here Silver with Oxygen is doing the Oxidizing.
Steps showing Alcohol to Acid conversion by strong oxidizing agent.

**Oxidation of primary alcohols to aldehydes**

The alcohol coordinates to the chromium(VI) atom, displacing chlorine, which then acts as a base, resulting in oxidation of the alcohol and reduction of Cr(VI) to Cr(IV).

\[
\text{Alcohol} \rightarrow \text{Aldehyde} + \text{Pyridinium chloride}
\]

PCC is an oxidizing agent (Pyridinium Chlorochromate)

**PCC (Pyridinium Chlorochromate)**

Pyridine is used in mild oxidation. Such as Sarett oxidation.

**CrO_3-Pyridine (Sarett oxidation):**

The image shows a chemical reaction where an alcohol is oxidized to an aldehyde using a strong oxidizing agent, Pyridinium Chlorochromate. The reaction mechanism involves the coordination of the alcohol to the chromium(VI) atom, followed by the displacement of chlorine, which acts as a base to promote the oxidation process. The reaction results in the formation of an aldehyde and Pyridinium chloride. This method is particularly useful for mild oxidations, such as in the Sarett oxidation.
Mechanism for chromic acid oxidation

Addition of a molecule of water to the aldehyde followed by a second oxidation leads to the carboxylic acid.

Oxidation of primary alcohols to aldehydes

Oxidation of secondary alcohols to ketones
Jones Reagent:

CrO₃ in acetone with H₂SO₄ (Jones reagent):

![Chemical structure](image)
Collin’s Reagent:

Corey’s Reagent:

1° Alcohols to 2° Aldehydes:

DMSO, Collins, corey's PDC, Pr₅N, RuO₄, CAN, N₂O₅, Cr₂O₃, in H₂O, Hg₂CO₃, Celite, Hot HNO₃,
CrPyridine-CuCl, LTA-pyridine, Benzoyl peroxide-NiBr₂, in aq H₂O

DMSO (DI methyl sulfoxide):
Moffats Reagent

Ley Oxidation:

MPV (Meerwein Pondarf Vierly) is a Reduction Technique. (Adding Hydrogen)

While MnO₂ is oxidizing (Mild Oxidizing)
Fetizon's reagent

Fetizon's reagent (Ag₂CO₃ on Celite):
2° Alcohols more reactive than 1° alcohols.

AgO or Ag₂O as oxidizing agent
Recall removal of Hydrogen is oxidation

**With di imides:**

\[
\begin{align*}
R - R & \xrightarrow{\text{EtO}_2\text{C}: \text{N}=\text{N}} \xrightarrow{\text{CO}_2\text{Et}} R - R \\
\end{align*}
\]

**Fremy's salt (potassium nitroso di sulphonate)** \(\left([\text{KO}_2\text{S}],\text{NO}^{-}\right)\):

Oxidation of phenolic derivatives to quinoids.

\[
\begin{align*}
\text{OH} & \xrightarrow{\text{MnO}_2, \text{DDQ}, \text{CAN}} \text{O} \\
\text{OH} & \xrightarrow{\text{3 Eq CAN}} \text{OH} \\
\end{align*}
\]

**Uden friends reagent** (\(\text{O}_2\text{Fe}^{2+}:\text{ascorbic acid in presence of EDTA}\)):

Gave good yields of ortho and para phenolic derivatives from phenol acetamide

**Fenton's reagent** (\(\text{H}_2\text{O}_2+:\text{Fe}^{2+}\)):

Converts aromatic derivatives into phenols.
Eib's persulphate oxidation (K₂S₂O₈/KOH)

\[ \text{OH} \rightarrow \text{OH} \]

Following reagents can convert the alkenes into their respective epoxides:

- NBS, H₂O, NaH, TsCl/Pyridine/K₂CO₃/MeOH

Ranking of peroxides:

\[ t-	ext{BuOOH} < HO-\text{OH} < 	ext{CH₃CO₂H} < 	ext{PH₃CO₂H} < 	ext{m-CPBA} < 	ext{H₂O₃H} < \text{H₃C₆H₄\text{CO₂H}} < \text{SF₆CO₂H} \]

Repeating Sarett Oxidation

CrO₃-Pyridine (Sarett Oxidation):

Hydrogen Peroxide Oxidation

Hydrogen peroxide (H₂O₂):

\[ \text{NH}_₂ \rightarrow \text{NO}_₂ \]

Asymmetric epoxidation:

\[ (+)\text{DIPT}, t-	ext{BuO₂H}, \text{Ti(O-}i\text{Pr)}₄, \text{DCM} \rightarrow \text{O} \]

Below the plane

\[ (-)\text{DIPT}, \text{TBHP}, \text{Ti(O-}i\text{Pr)}₄, \text{DCM} \rightarrow \text{O} \]

Below the plane
OsO$_2$-NMO (N-methyl morpholine N-oxide)

Baeyer villiger epoxidation (CF$_3$CO$_2$H):

LTA (Lead tetra acetate):

Sodium per iodate (NaIO$_4$):

Selenium dioxide (SeO$_2$):

Alylic methyl to corresponding alcohols
It had been known since 1894 that ethylene is oxidized to acetaldehyde by Palladium chloride.

The Wacker process or the Hoechst-Wacker process (named after the chemical companies of the same name) originally referred to the oxidation of ethylene to acetaldehyde by oxygen in water in the presence of a tetrachloropalladate(II) catalyst.

The development of the chemical process now known as the Wacker process began in 1956 at Wacker Chemie.

The same basic reaction is currently used to produce aldehydes and ketones from a number of alkenes with the Monsanto process for producing acetic acid.

This chemical reaction, a German invention, was the first organometallic and organopalladium reaction applied on an industrial scale. The Wacker process is similar to hydroformylation, which is also an industrial process and also leads to aldehyde compounds. The differences are that hydroformylation promotes chain extension, and uses a rhodium-based catalyst system. The Wacker process is an example of homogeneous catalysis. The palladium complex with ethylene is reminiscent of Zeise's salt, K[PtCl₃(C₂H₄)] which is a heterogeneous catalyst.

At the time, many simple aliphatic compounds were produced from acetylene (as calcium carbide) but the construction of a new oil refinery in Cologne by Esso close to a Wacker site, combined with the realization that ethylene would be a cheaper raw-material prompted Wacker to investigate its potential uses.

As part of the ensuing research effort, a reaction of ethylene and oxygen over palladium on carbon in a quest for ethylene oxide unexpectedly gave evidence for the formation of acetaldehyde (simply based on smell). More research into this ethylene to acetaldehyde conversion resulted in 1957 in a gas-phase patent using a heterogeneous catalyst. In the meanwhile Hoechst AG joined the race and after a patent filing forced Wacker into a partnership called Aldehyd GmbH. The heterogeneous process ultimately failed due to catalyst inactivation and was replaced by the water-based homogeneous
A peroxy acid (often spelled as one word, peroxyacid, and sometimes called peracid) is an acid which contains an acidic -OOH group. The two main classes are those derived from conventional mineral acids, especially sulfuric acid, and the organic derivatives of carboxylic acids. They are generally strong oxidizers.

Peroxymonosulfuric acid (Caro's acid) is probably the most important inorganic peracid, at least in terms of the scale. It is used for the bleaching of pulp and for the detoxification of cyanide in the mining industry. It is produced by treating sulfuric acid with hydrogen peroxide. Peroxyphosphoric acid (H₃PO₅) is prepared similarly.
The pyridinium chlorochromate (PCC) and Swern oxidation reactions are useful for oxidizing primary alcohols to aldehydes. Further oxidation of the aldehyde to the carboxylic acid stage does not occur with these reagents, because the reactions are carried out in anhydrous (water-free) organic solvents such as dichloromethane, and therefore the hydrate form of the aldehyde is not able to form.

Ozone is used to cut.

Osmium Oxide for oxidation

Alkenes are oxidized to cis,1,2-diol by osmium tetroxide ($\text{OsO}_4$). The stereospecificity is due to the formation of a cyclic osmate ester intermediate. Osmium tetroxide is used in catalytic amounts, and is regenerated by N-methylmorpholine-N-oxide.
1,2-diol compounds can be oxidized to diketones (or diketones, depending on the substitution of the starting diol) using periodic acid.

\[ \text{CF}_3\text{COOH} \rightarrow \text{O} \rightarrow \text{O} \rightarrow 78\% \]

\[ \text{CH}_2\text{COOH} \rightarrow \text{CH}_2\text{COOEt} \rightarrow \text{O} \rightarrow 90\% \]

**Prilezhaev Reaction**

Several oxidizing reagents react with alkenes under mild conditions to give, as the overall result, addition of hydrogen peroxide as \( \text{HO}--\text{OH} \). Of particular importance are alkaline permanganate, \( \text{MnO}_4^- \), and osmium tetroxide \( (\text{OsO}_4) \), both of which react in an initial step by a suprafacial cycloaddition mechanism like that postulated for ozonolysis.

\[ \text{MnO}_4^- \rightarrow \text{[unstable]} \rightarrow \text{H}_2\text{O} \rightarrow \text{CO}_2 \rightarrow \text{OH}^{-} + \text{MnO}_2 \]
Each of these reagents produces cis-1,2-dihydroxy compounds (diols) with cycloalkenes:

1. OsO₄, 25°
2. Na₂SO₃ (or KMnO₄, OH⁻, H₂O)

Alkenes can be oxidized with peroxycarboxylic acids, P₂CO₄H, to give oxacycloprenes (oxiranes, epoxides), which are three-membered cyclic ethers:

The reaction, known as epoxidation, is valuable because the oxacycloprene ring is cleaved easily, thereby providing a route to the introduction of many kinds of functional groups. In fact, oxidation of alkenes with peroxymethanoic acid (peroxymethylene acid), prepared by mixing methanoic acid and hydrogen peroxide, usually does not stop at the oxacycloprene stage, but leads to ring-opening and the subsequent formation of a diol:

not stable under the reaction conditions
This is an alternative scheme for the hydroxylation of alkenes. However, the overall stereochemistry is opposite to that in permanganate hydroxylation. For instance, cyclopentene gives trans-1,2-cyclopentanediol. First the epoxime forms by suprafacial addition and then undergoes ring opening to give the trans-product:

\[
\text{trans-1,2-cyclopentanediol}
\]

The ring opening is a type of $\text{S}_{\text{n}}2$ reaction. Methanoic acid is sufficiently acidic to protonate the ring oxygen, which makes it a better leaving group, thus facilitating nucleophilic attack by water. The nucleophile always attacks from the side remote from the leaving group:
The peroxycarboxylic acids that are used in the formation of oxacyclopropanes include peroxynitric acid (H2NClO3), peroxycetic acid (CH3COClO3), and trifluoroperoxycetic acid (CF3COClO3) acids. A particularly useful peroxycarboxylic acid is 3-chloroperoxybenzoic acid, because it is relatively stable and is handled easily as the crystalline solid. The most reactive reagent is trifluoroperoxycetic acid, which suggests that the peroxycarboxylic acid behaves as an electrophile (the electron-withdrawing ability of the Cl group strongly electron-attracting). The overall reaction can be viewed as a cycloaddition, in which the proton on oxygen is transferred to the neighboring carbon; oxygen more or less simultaneously with formation of the three-member ring:

\[
\begin{align*}
\text{CHO} & \quad \text{TBHP, catalyst, reflux} \quad \text{COOH} \\
\end{align*}
\]

A reaction of immense industrial importance is the formation of oxacyclopropane itself (most often called ethylene oxide) by oxidation of ethene with oxygen over a silver oxide catalyst at 300°C:

\[
\text{CH}_2=\text{CH}_2 + \frac{1}{2} \text{O}_2 \underset{300^\circ}{\text{Ag}_2\text{O}} \rightarrow \text{H}_2\text{C} = \text{CH}_2 \\
\text{oxypropane}
\]

Oxacyclopropane is used for many purposes, but probably the most important reaction is the reaction opening with water to give 1,2-ethanediol (ethylene glycol, bp 197°C). This diol, mixed with water, is employed widely in automotive cooling systems to provide both a higher boiling and lower freezing coolant than water alone:

\[
\text{CH}_2=\text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{HOCH}_2\text{CH}_2\text{OH} \\
1,2\text{-ethanediol (ethylene glycol)}
\]

Propene and higher alkenes are not efficiently epoxidized by oxygen and Ag2O in the same way as ethene is because of competing attack at other than the double-bond carbons. Hydroxylation and oxidation of alkenes are reactions that produce alcohol.
tert-Butyl hydroperoxide (tBuOOH) is an organic peroxide widely used in a variety of oxidation processes, for example Sharpless epoxidation. It is normally supplied as a 69-70% aqueous solution. Industrially, tert-butyl hydroperoxide is used as a starter of radical polymerization.
Magnesium monoperoxyphthalate (MMPP) is a water-soluble peroxy acid used as an oxidant in organic synthesis. Its main areas of use are the conversion of ketones to esters (Baeyer-Villiger oxidation), epoxidation of alkenes (Prilezhaev reaction), oxidation of sulfides to sulfoxides and sulfones, oxidation of amines to produce amine oxides, and in the oxidative cleavage of hydrazones. Due to its insolubility in nonpolar solvents MMPP has seen less use than the more widely used meta-chloroperoxybenzoic acid (mCPBA). Although work up procedures are more simply handled in polar solvents, usage of MMPP to oxidize nonpolar substrates in biphasic media combined with a phase transfer catalyst have been inefficient. Despite this MMPP has certain advantages over mCPBA including a lower cost of production and increased stability.

MMPP is also used as the active ingredient in certain surface disinfectants such as Dismozon Pur. As a surface disinfectant MMPP exhibits a broad spectrum biocidal effect including inactivation of endospores. Its wide surface compatibility enables its use on sensitive materials, such as plastic and rubber equipment used in hospitals. Additionally MMPP has been investigated as a potential antibacterial agent for mouthwashes and toothpaste.
Mn(OAc)₂ oxidation

Metal-promoted radical reactions have found widespread use in organic synthesis, in which one of the well-known examples of this application is the manganese(III) acetate mediated reactions. The exciting development in this area is beginning to show its true potential, as evidenced from the application of this methodology in strategy-level bond formation during the synthesis of complex molecules. Manganese(III) acetate dihydrate [abbreviated herein as Mn(OAc)₃] mediated free radical reactions have emerged as important synthetic methods for a new bond formation and bond breaking. In view of its importance in organic synthesis, this present review highlights the application of Mn(OAc)₃ promoted freeradical reactions in carbon-carbon, carbonheteroatom bond formation, and covers the literature since 1993.
Topic wise grouping of information kind of Dictionary of General Chemistry

Graphite and Diamond comparison

With respect to graphite and diamond, which of the following statement(s) given below is(are) correct?
(a) Graphite is harder than diamond.
(b) Graphite has higher electrical conductivity than diamond.
(c) Graphite has higher thermal conductivity than diamond.
(d) Graphite has higher C—C bond order than diamond.

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

Stability of lyophobic colloidal particles

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

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

Physiorption and Chemisorption comparison

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

![Graph I](image1)

![Graph II](image2)
(a) 1 is physisorption and II is chemisorption  
(c) IV is chemisorption and II is chemisorption
(b) 1 is physisorption and III 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 \(M_nX_{14}\) 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_3X_{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\textsubscript{3} to give a precipitate that dissolves in Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}

Which of the following halides react with AgNO\textsubscript{3}(aq) to give a precipitate that dissolves in Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}(aq)?

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

**Solution:**

The precipitates of AgCl, AgBr and AgI are soluble in Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}(aq) forming the complex Na\textsubscript{2}[Ag(S\textsubscript{2}O\textsubscript{3})\textsubscript{2}]. For example,

\[ Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 + 2NaBr \]

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.

\(T_2 < T_1\) 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

$$a_0 = \frac{\hbar^2}{m_e k c^2}$$

Boiling Point Elevation

$$\Delta T_b = i K_b \times molality$$

Buffer Design Equation

$$pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$$

Cell Voltage

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q$$

Charles' Law

$$\frac{V}{t} = k$$

Atomic Structure

**DESCRIPTION**

**EQUATION**

Bohr Radius

$$a_0 = \frac{\hbar^2}{m_e k c^2}$$

De Broglie Wavelength

$$\lambda = \frac{\hbar}{mv}$$

Linear Momentum

$$p = mv$$

Planck's Quantized (Quantum) Energy Equation

$$\Delta E = h\nu$$

Radii of stable orbits in the Bohr model

$$r = n^2 \frac{\hbar^2}{m_e k Z^2 c^2} = n^2 a_0 Z$$

Relationship between Energy and Principal Quantum Number

$$E_n = -R_H \left( \frac{1}{n^2} \right) = -2.178 \times 10^{-18} \frac{1}{n^2} \text{joule}$$
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

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>EQUATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell Voltage</td>
<td>[ E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q ]</td>
</tr>
<tr>
<td>Electric Current</td>
<td>[ I = \frac{q}{l} ]</td>
</tr>
</tbody>
</table>
| 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

<table>
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</tr>
<tr>
<td>Base Ionization Constant</td>
<td>[ K_b = \frac{[OH^-] [HB^+]}{[B]} ]</td>
</tr>
<tr>
<td>Buffer Design Equation</td>
<td>[ pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0} ]</td>
</tr>
<tr>
<td>Gas Pressure and Concentration Relationship</td>
<td>[ K_p = K_c \left( \frac{RT}{V} \right)^{\Delta n} ]</td>
</tr>
</tbody>
</table>
| Ion Product Constant for Water | \[ K_w = [OH^-] [H^+] = K_a \times K_b \]  
  \[ = 1.0 \times 10^{-14} \text{ at } 25^\circ C \] |
| pH and pOH Relationship | \[ 14 = pH + pOH \] |
| pH Defined | \[ pH = - \log [H^+] \] |
| pK_a Definition | \[ pK_a = - \log K_a \] |
**Gases, Liquids, and Solutions**

<table>
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<td>Adiabatic change</td>
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<td>$\Delta T_b = iK_b \times \text{molality}$</td>
</tr>
<tr>
<td>Charles’ Law</td>
<td>$\frac{V}{t} = k$</td>
</tr>
<tr>
<td>Combined Gas Law</td>
<td>$\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$</td>
</tr>
<tr>
<td>Density of a Material</td>
<td>$D = \frac{m}{V}$</td>
</tr>
<tr>
<td>Freezing Point Depression</td>
<td>$\Delta T_f = iK_f \times \text{molality}$</td>
</tr>
<tr>
<td>Graham’s Law of Effusion</td>
<td>$r_1 = \sqrt{\frac{M_2}{M_1}}$</td>
</tr>
<tr>
<td>Ideal gas equation</td>
<td>$PV = nRT$</td>
</tr>
<tr>
<td>Kinetic Energy per Mole</td>
<td>$\frac{KE}{\text{mole}} = \frac{3}{2}RTn$</td>
</tr>
<tr>
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<td>$\frac{KE}{\text{mole}} = \frac{3}{2}RTn$</td>
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**Thermochemistry**

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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
\[ E_{cell} = E_{cell}^0 - \frac{RT}{n F} \ln Q = E_{cell}^0 - \frac{0.0592}{n} \log Q \]

Charles’ Law
\[ \frac{V}{T} = k \]

Vander waal’s force

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

The value of the van der Waals constant \( a \) is
(a) 1.0 L^2 atm mol^{-2}  (b) 4.5 L^2 atm mol^{-2}  (c) 1.5 L^2 atm mol^{-2}  (d) 3.0 L^2 atm mol^{-2}

**Solution:**

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

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

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

Equating this to \(-a\), we get
\[ a = 1.5 \text{ L}^2 \text{ atm mol}^{-2} \]

Hence, 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 \( \Delta T_p = K_b m \), we find that the molality of solute \((m)\) in the solution is
\[
m = \frac{\Delta T_p}{K_b} = \frac{2 \text{ K}}{0.76 \text{ K kg mol}^{-1}} = \frac{2}{0.76} \text{ mol kg}^{-1}
\]

Since \( m = \frac{n_2}{m_1} \) (where \( n_2 \) is the amount of solute and \( m_1 \) is the mass of solvent expressed in kg), we get
\[
n_2 = m m_1 = \left( \frac{2}{0.76} \text{ mol kg}^{-1} \right) (0.1 \text{ kg}) = \frac{2}{7.6} \text{ mol}
\]

From the expression \( -\Delta p = x_2 p_1^0 \) of the relative lowering of vapour pressure of solvent (whose vapour pressure is 1 atm as the solute is non-volatile), we find that
\[
x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1/n_1} = \frac{(2/7.6) \text{ mol}}{(100 \text{ g}/18 \text{ g mol}^{-1})} = \frac{36}{760} \text{ (760 mmHg)} = 36 \text{ mmHg}
\]

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

\[
p = p_1^0 + \Delta p = 760 \text{ mmHg} - 36 \text{ mmHg} = 724 \text{ mmHg}
\]

Therefore, the choice (a) is correct.

**shape of XeO₂F₂ molecule is seesaw**

The shape of XeO₂F₂ molecule is
(a) trigonal bipyramidal  (b) square planar  (c) tetrahedral  (d) see-saw

**Solution:**
The number of valence electrons in XeO₂F₂ 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 dsp³ hybridization leading to the trigonal bipyramidal arrangement of five pairs of electrons. The structure of XeO₂F₂ is

The shape of XeO₂F₂ is sea-saw.
Therefore, the choice (d) is correct.
Various increasing and decreasing properties

Decreasing order of reactivity towards $S_n^2$ displacement:
- $n$-Butyl bromide, isobutyl bromide, sec-butyl bromide, tert-butyl bromide

Decreasing order of reactivity towards $S_{n1}$ displacement:
- 1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

Increasing reactivity sequence of $S_{n1}$ displacement of halogen:
- $CH_3X$, $1^o X$, $2^o X$, $3^o X$

Increasing reactivity sequence of $S_{n2}$ displacement of halogen:
- $CH_2X$, $1^o X$, $2^o X$, $3^o X$

Increasing reactivity of alcohols towards gaseous HBr:
- 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol

Increasing order or reactivity towards E2 dehydrohalogenation of the bromides:
- Ethyl bromide, $n$-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 $C_2H_2$.

$\Delta H_1 = 225 \text{ kJ mol}^{-1}$

$\Delta H_2 = 1410 \text{ kJ mol}^{-1}$

$\Delta H_3 = 330 \text{ kJ mol}^{-1}$

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

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

**Solution:**

Consider the following transformations.

According to Hess’s law:

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

This gives:

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

Therefore, the choice (d) is correct.

Some facts student must know
Largest Anion - $\text{At}^-$

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, Ek)

Liquid radioactive element - Francium

N. metal with highest m.pt - Carbon

Metal with highest valency = Plutonium

Highest tensile strength - Boron

Most ionic compound = CsF

Strongest base = Cs(OH)

Strongest basic oxide = Cs$_2$O

Most conducting metal = Ag

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

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

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

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

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

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

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; CH3CHO) reacts with ethanol (C2H5OH) as follows: CH3CHO + C2H5OH ⇌ CH(OH)(CH3)(C2H5O) The hemiacetal has a central carbon atom (from the aldehyde) attached to a hydrogen, a hydroxyl group, a hydrocarbon group (methyl - CH3), and an alkoxy group (C2H5O). If a ketone is used rather than an aldehyde, the resulting hemiacetal contains two hydrocarbon groups. For example, reaction of the ketone R1COR2 with the alcohol R3OH is:
R1COR2 + R3OH ⇌ CR1R2(OH)(OR3)

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

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

Further reaction of hemiacetals with another molecule of alcohol leads to a full acetal. For example: CH(OH)(CH3)(OC2H5)_2 + C2H5OH ⇌ CH(OH)(CH3)(OC2H5)_2

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

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

May be a hydrogen atom. The mechanism of formation of an acetal from a hemiacetal is acid catalyzed. It involves protonation of the -OH group of the hemiacetal followed by loss of water to form an oxonium ion, which is attacked by the alcohol molecule.
Formerly it was conventional to use the terms ‘hemiacetal’ and ‘acetal’ for compounds formed by reaction between aldehydes and alcohols. Similar reactions between ketones and alcohols gave rise to compounds called hemiketals and ketals. Current nomenclature uses ‘hemiacetal’ and ‘acetal’ for compounds derived from either an aldehyde or a ketone, but reserves ‘hemiketal’ and ‘ketal’ for those derived from ketones. In other words, the ketals are a subclass of the acetals and the hemiketals are a subclass of the hemiacetals.

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

Bond fission

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

Homolytic fission

Homolysis

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

Heterolysis

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

Free radicals

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

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

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

If the centre carbon atom of the radical is sp\(^3\) hybridized (remember the one which was made of one s and three orbitals as in CH\(_4\)), the geometry will be tetrahedral. But in the case of a radical there are only three groups attached to the sp\(^3\) hybridized carbon atom so they we will have a shape of what resembles a pyramid—it’s a tetrahedron with its head cut off. So sp\(^3\) hybridized radicals are pyramidal in shape. The single electron of the radical would then be housed in a sp\(^3\) orbital. The other option is sp\(^2\) hybridization. In that case the C atom is sp\(^2\) hybridized, so as discussed previously the shape would be planar with the single electron in the unhybridized p-orbital with the three substituents having sp\(^2\) hybridized bonds.

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 carboxcation 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. ]

$RX + NaI \rightarrow RI + NaX$ where $X = Cl, Br,$ and $R$ is an Alkyl group

Sodium chloride and sodium bromide being less soluble in acetone get precipitated from the solution and can be removed by filtration. This also prevents the backward reaction to occur according to Le Chatelier's principle. The reaction gives the best results with primary halides.
With iodide, the solvate $\text{NaI} \cdot 3(\text{CH}_3)_2\text{CO}$ 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 sp$^2$ hybridized, which means it’s planar as we know by now. The three substituents of the carbocation lie in a plane leaving the unhybridized empty p orbital perpendicular to them.

These intermediates react with species which are electron rich (quite obvious) and being charged are stabilized in polar solvents. (Just as Na$^+$ is soluble and stable in polar water). Carbocations are important intermediates in most mechanisms along with carbanions as we shall see later.

To summarize carbocations:

- Formed due to heterolysis of a C-X bond (where X is more electronegative) and thus has a positive charge.
- Planar in shape (sp$^2$ hybridized carbon), with empty p orbital perpendicular to the plane of the molecule.
- Reactive towards electron rich species.

Carbanions

These are intermediates also formed as a result of heterolysis, but here the electron pair from the bond is kept by the carbon atom. From what we saw earlier the more electronegative atom keeps the electrons, so in this case carbon must the more electronegative of the two atoms making up the bond. Now there are only a few atoms (non-metals; metals are not usually part of organic chemistry) which are less electronegative, so the most common bond cleavage which yields carbanions is the C-H bond. The ease of breaking this bond and creating a carbanion is also a measure of the compound’s acidity, because a H$^+$ is also generated with the carbanion, which makes the molecule an acid in the Bronsted sense.

Carbanions have three groups attached to each other and a lone pair of electrons which gives it its negative charge (similar to the ammonia molecule where the central N has 3 Hs and a lone pair of electrons). So its geometry is pyramidal (tetrahedral but since there is no fourth group again it’s like a tetrahedral with head cut off) and the carbon atom is sp$^3$ hybridized.

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

To summarize carbanions:

- Formed due to heterolysis of a C-X bond (where X is less electronegative) and thus has a negative charge.
- Pyramidal is shape (sp$^3$ hybridized) with the excess electrons placed in one sp$^3$ hybrid orbital.
- Reactive towards positively charged (electron deficient species).
Stability of intermediates

Most organic reactions take place via formation of intermediates. So the study of different intermediates would help us predict the course of the reaction and the main aspect to look at would be their stability. No organic mechanism has been conclusively ‘PROVEN’, all the mechanism we see are the most plausible ones derived from many experiments, a major component of which is isolating and studying the intermediates. It is difficult to say that a certain mechanism is absolutely correct, but it is quite simple to point out an incorrect mechanism. One of the ways a chemist would confirm an incorrect mechanism is if it involves a very unstable intermediate. The good thing about this is that with a few empirical rules and principles in mind, it is quite simple to assign relative stability of intermediates like radicals, carbocations and carbanions. And what is even better is that we have already discussed these principles.

For carbocations and free radicals (both electron poor species), any group which donates electron density to the carbon centre would stabilize it and inversely electron withdrawing groups would increase electron deficiency on the carbon centre leading to destabilization. (Remember charge is not desirable, the most stable species are usually neutral). So following the same logic the effect should just be opposite in the case of carbanions as they are electron rich (negatively charged) instead of being electron deficient like the above two. So groups which pull away electrons from the charged carbon atom would have a stabilizing effect whereas electron donation would destabilize the intermediate as it loads more negative charge on an already negatively charged atom.

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

2,3,5-Trimethyl-4-propylheptane (not 3,5,6-Trimethyl-4-propylheptane)
Alphabetical order of numbering

Cyclopentane 1-Methyl-3-propylcyclohexane

More branched carbon gets lower number

3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane)

CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds

Acyclic or Open chain compounds (I)

Cyclic or Closed chain or Ring compounds (II)

Homocyclic or Carbocyclic compounds

Heterocyclic compounds

Alicyclic compounds

Aromatic compounds

Benzenoid compounds

Non-benzenoid compounds
**Alicyclic or closed chain or ring compounds**

Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocyclic).

Some examples are

- Cyclopropane
- Cyclohexane
- Cyclohexene
- Tetrahydrofuran

**Nomenclature of Substituted Benzene Compounds**

For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene as shown in the following examples.

- Methylbenzene (Toluene)
- Chlorobenzene (Aniseole)
- Amino-benzene (Aniline)
- Nitrobenzene
- Bromobenzene

**How Isomers are made?**

(a) **Normal to branched chain in alkane**

\[ \text{n-Alkane} \xrightarrow{\text{AlCl}_3, 570 \, \text{K}} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \]

(b) **Shift of double bond**

In the presence of catalyst like AlCl_3(SO_3)_2, alkene undergo isomerization at high temperature (770 – 970 K).

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}==\text{CH}_2 \xrightarrow{\text{AlCl}_3, 570 \, \text{K}} \text{CH}_3\text{CH}_2\text{CH}==\text{CHCH}_3 \]

(c) **Shift of triple bond**

\[ \text{CH}_3\text{CH}_2\text{C}==\text{CH} \xrightarrow{\text{KOH, ethanol}} \text{[CH}_3\text{CH}==\text{CH}_2] \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{C}==\text{C}==\text{CH}_3 \]

\[ \xrightarrow{\text{NaOH in inert solvent}} \text{CH}_3\text{CH}_2\text{C}==\text{C}==\text{CH}_3 \]
Heating with ethanolic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodamide in an inert solvent shifts the bond towards the end of chain.

The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is: -COOH, -SO3H, -COOR (R=alkyl group), COCl, -CONH2, -CN, -HC=O, >C=O, -OH, -NH2, >C=C<, -C≡C-. 

Epimers

Anomers

Epimer Anomer comparison
Epimers are monosaccharides that differ in chirality at only one carbon. In the straight-chain format, epimers will have H and OH-substituents switched at one backbone carbon, but not at any others.

Anomers are special epimers; in cyclic forms of one single monosaccharide, anomers differ in chirality at the anomeric (hemiacetal) carbon only. In the straight-chain format, anomers will have the same configuration.
Various Methods of Reduction used in Organic Chemistry

(a) \( \text{CH}_3\text{CH} = \text{CHCHO} \xrightarrow{\text{H}_2, \text{Ni}} \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH} \)

(b) \( \text{CH}_3\text{CH} = \text{CHCHO} \xrightarrow{\text{9-BBN}, \text{Zn}} \text{HOCH}_2\text{CH}_2\text{NH}_2 \xrightarrow{\text{conc. HCl}} \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH} \), 9-BBN is 9-Borabicyclo[3.3.1]nonane

(c) \( \text{CH}_2\text{CH}_2\text{CHO} \xrightarrow{\text{NaOH}, \text{H}_2\text{O}, \text{KOH}} \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \), Weisz-Kosher reduction

(d) \( \text{CH}_3\text{COCH}_3 \xrightarrow{\text{LiAIH}_4} \text{CH}_3\text{CHCH}_3 \)x_2 \)

(e) \( \text{RCOOH} \xrightarrow{1\text{LiAIH}_4, 2\text{H}_2\text{O}} \text{RCH}_2\text{OH} \)

(f) \( \text{NO}_2 \xrightarrow{\text{H}_2, \text{Pt} \text{ or SO}_2, \text{HCl} \text{ or Fe, HCl}} \text{NH}_2 \)

(g) \( \text{CH}_2\text{CN} \xrightarrow{\text{H}_2, \text{Ni} \text{140°C}} \text{CH}_2\text{CH}_2\text{NH}_2 \)

(h) \( \text{C}_6\text{H}_5\text{NO}_2 \xrightarrow{(\text{NH}_3)_2\text{S}} \text{C}_6\text{H}_5\text{NH}_2 \), Only one nitro group is reduced.

(i) \( \text{RC} = \text{MgCl} \xrightarrow{\text{H}_2\text{O}} \text{RH} + \text{MgCl} \xrightarrow{\text{LiAIH}_4} \text{RH} \)

(j) Rosenmund's reduction

Various methods of Oxidation

**Oxidation**

(a) \( \text{RCH}_2\text{OH} \xrightarrow{\text{Pyridinium chlorochromate}} \text{RCOCl} \xrightarrow{\text{H}_2} \text{RCHO} \)

(b) \( \text{R} = \text{CHOH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{RC} = \text{O} \)

(c) \( \text{RCH}_2\text{OH} \xrightarrow{\text{KMnO}_4} \text{RCOOH} \)

(d) \( \text{CH}_3\text{CH} = \text{COOH} \xrightarrow{\text{Tollens reagent}} \text{CH}_3\text{CH} = \text{CHCOOH} \)

(e) \( \text{CH}_3\text{CN} \xrightarrow{\text{KMnO}_4} \text{COOH} \)

(f) \( \text{CH}_2\text{CN} \xrightarrow{\text{CrO}_3} \text{H}_2\text{O} \xrightarrow{\text{H}^+} \text{CHO} \)

(g) \( \text{CH}_2\text{CN} \xrightarrow{\text{KMnO}_4} \text{COOH} \)

(h) \( \text{RCH} = \text{CHCHO} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{RCH} = \text{CHCOOH} \)

(i) \( \text{RCH}_2\text{OH} \xrightarrow{\text{KMnO}_4} \text{RCOOH} \)

(j) Rosenmund's reduction
Synthesis of p-bromonitrobenzene in 2 steps

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

\[ \text{Br}_2 + \text{Fe} \rightarrow \text{Br} \]
\[ \text{HNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Br} \quad \text{NO}_2 \]
\[ \text{Br} \quad \text{ortho} \quad 38\% \]
\[ \text{Br} \quad \text{para} \quad 62\% \]

Fractional crystallization para-isomer crystallizes out first.
```

Secondary alcohol to tertiary alcohol

```
CH_3CHCH_3 \rightarrow CH_3CCH_3
\[ \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{CH}_3\text{MgBr} \]
\[ 1. \text{CH}_3\text{MgBr} \quad 2. \text{H}^+ \rightarrow \text{CH}_3\text{C}\text{OH} \]
```

Prepare m-bromodobenzene from benzene.

```
prepare m-bromodobenzene from benzene (in not more than 5-7 steps)?
```

Alternatively, we may proceed as follows:

```
\[ \text{HNO}_3 + \text{H}_2\text{SO}_4 \quad 80\degree \text{C} \rightarrow \] 
\[ \text{(NH}_4)_2\text{S} \rightarrow \] 
\[ \text{NO}_2 \quad \text{NH}_2 \]
\[ \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Br} \]
\[ \text{NaNO}_2 + \text{HCl} \quad 0\degree \text{C} \rightarrow \] 
\[ \text{KI} \rightarrow \]
```

CBSE Standard 12 Chemistry Survival Guide - Oxidation Methods by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams
Secondary alcohol to Primary alcohol

\[ \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{Br}_2, \text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \]

To convert Ethylebenzene to Benzene and Ethylebenzene to phenylpropionic acid

Show the steps to carry out the following transformations.

(i) Ethylebenzene → benzene

(ii) Ethylebenzene → 2-phenylpropionic acid.

Alcohol to alcohol with one carbon more

\[ \text{CH}_3\text{OH} \xrightarrow{\text{PBr}_3} \text{CH}_3\text{Br} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{[\text{H}]^{-}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_3} \text{CH}_3\text{CH}_2\text{OH} \]

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

Alcohol to alcohol with one carbon less

\[ \text{CH}_3\text{OH} \xrightarrow{[\text{O}]} \text{CH}_3\text{COOH} \xrightarrow{\text{soda lime}} \text{CH}_4 \xrightarrow{\text{Cl}_2, \text{hv}} \text{CH}_3\text{Cl} \xrightarrow{\text{aq. KOH}} \text{CH}_3\text{OH} \]
Conversion of Aniline to Benzylamine

How would you bring about the following conversion (in 3 steps)?
Aniline $\rightarrow$ Benzylamine

(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

\[
\text{RCH}_2\text{NH}_2 + \text{HNO}_2 \rightarrow \text{RCH}_2\text{OH} + \text{NO}_2\text{H}
\]

\[
\text{RCH}_2\text{OH} + \text{PBr}_3 \rightarrow \text{RCH}_2\text{Br}
\]

\[
\text{RCH}_2\text{Br} + \text{NaCN} \rightarrow \text{RCH}_2\text{CN}
\]

\[
\text{RCH}_2\text{CN} + \text{H}_2/\text{Ni} \rightarrow \text{RCH}_2\text{CH}_2\text{NH}_2
\]

Synthesis of 4-methoxyphenol from bromobenzene

How would you synthesise 4-methoxyphenol from bromobenzene is NOT more than five steps? State clearly the reagents used in each step and show the structure of the intermediate compounds in your synthetic scheme.

The introduction of \(-\text{NO}_2\) 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

**Solution.** Formic acid \(\text{H-C-OH}\) contains both an aldehyde \(\text{H-C}=\text{O}\) as well as carboxyl
Convert Benzoic acid to meta fluorobenzoic acid (2-fluorobenzoic acid)

Convert

\[
\begin{align*}
\text{metafluoro benzoic acid} \\
\end{align*}
\]
Convert Nitrobenzene to meta hydroxynitrobenzene (or 4-nitrophenol)

Nitrobenzene resonance structure

4 nitrophenol or meta hydroxynitrobenzene
Many conversions or preparations

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

(i) Ethylbenzene from benzene \([\text{C}_6\text{H}_5\text{CH}_3, \text{PCl}_3, \text{anhydrous AlCl}_3]\)
(ii) Propanoic anhydride from propanol \([\text{AgNO}_3/\text{NH}_4\text{OH}, \text{PCl}_3]\)
(iii) Acetoxime from acetaldehyde \([\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+, \text{Ca(OH)}_2 \text{and } \text{NH}_2\text{OH.HCl}]\)

(i) \(\text{C}_6\text{H}_5\text{CH}_3 + \text{PCl}_3 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{Cl} + \text{POCl}_3 + \text{HCl}\)

\(\text{C}_6\text{H}_5\text{CH}_2\text{Cl} \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_4\text{CH}_2\text{H}_3 + \text{HCl}\)

(ii) \(\text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{AgNO}_3/\text{NH}_4\text{OH}} \text{C}_6\text{H}_5\text{COOH}\), \(2\text{C}_2\text{H}_5\text{COOH} \xrightarrow{\text{P}_{2}\text{O}_5} \left(\text{C}_2\text{H}_5\text{COO}\right)_2\text{O}\)

(iii) \(\text{CH}_2\text{CHO} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7/\text{H}^+} \text{CH}_3\text{COOH}\), \(\text{CH}_3\text{COOH} \xrightarrow{\text{Ca(OH)}_2} \left(\text{CH}_3\text{COO}\right)_2\text{Ca}\)

\((\text{CH}_3\text{COO})_2\text{Ca} \xrightarrow{\text{heat}} \text{CH}_3\text{COCH}_3 + \text{CaCO}_3\), \(\text{CH}_3\text{COCH} \xrightarrow{\text{NH}_2\text{OH}} \text{C}=\text{N}–\text{OH}\)

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

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{AlCl}_3} \text{CH}_3 \xrightarrow{\text{KMnO}_4} \text{COOH}
\end{align*}
\]

Acetic acid to Malonic acid

\[
\text{Acetic acid to malonic acid}
\begin{align*}
\text{CH}_3\text{COOH} & \xrightarrow{\text{Br}_2, \text{P}} \text{BrCH}_2\text{COOH} \xrightarrow{\text{KCN}} \text{CNCH}_2\text{COOH} \xrightarrow{\text{H}_2\text{O}} \text{HOOCCH}_2\text{COOH}
\end{align*}
\]

Ethynyl to propanoic acid

\[
\text{Ethynyl to propanoic acid}
\begin{align*}
\text{HC≡CH} & \xrightarrow{\text{Lindlar catalyst}} \text{H}_2\text{C≡CH} \xrightarrow{\text{HCl}} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{C}_3\text{H}_5\text{CN} \xrightarrow{\text{H}_2\text{O}} \text{C}_2\text{H}_4\text{COOH}
\end{align*}
\]

Isopropyl alcohol to β-hydroxybutyric acid

\[
\text{Isopropyl alcohol to β-hydroxybutyric acid}
\begin{align*}
\text{CH}_3\text{CHCH}_3 & \xrightarrow{\text{AlCl}_3, 250^\circ\text{C}} \text{CH}_3\text{CH}≡\text{CH}_2 \xrightarrow{\text{HOCl}} \text{CH}_3\text{CHCH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CHCHCN} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHCHCOOH}
\end{align*}
\]

Acetic acid to Propanoic acid

\[
\text{Acetic acid to propanoic acid}
\begin{align*}
\text{CH}_3\text{COOH} & \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_3} \text{CH}_3\text{CH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CHCN} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{COOH}
\end{align*}
\]

Ethanoic acid to a mixture of methanoic acid and diphenyl ketone
Propanoic acid to acetic acid

\[
\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow{\text{NH}_3, \text{heat}} \text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_3} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Cu}_2\text{O}^+/\text{H}^+} \text{CH}_3\text{COOH}
\]
Ethanal to 2-hydroxy-3-butoenoic acid

Ethanal to 2-hydroxy-3-butoenoic acid
\[ \text{CH}_3\text{CHO} + \text{HCHO} \xrightarrow{\text{H}^+ \text{ or } \text{OH}^-} \text{CH}_3\text{CHCH}_2\text{CHO} \xrightarrow{\text{dil. HCl}} \text{CH}_2=\text{CHCH}_2\text{CHO} \]

Ethanal to 2-hydroxy-3-butoenoic acid
\[ \xrightarrow{\text{HCN}} \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CN} \xrightarrow{\text{H}^+} \text{CH}_2=\text{CHCH}_2\text{COOH} \]

Benzene to m-bromophenol

Benzene to m-bromophenol
\[ \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NO}_2 \xrightarrow{\text{Br}_2, \text{Fe}} \text{NO}_2 \xrightarrow{\text{Sn}, \text{HCl}} \text{NO}_2 \xrightarrow{\text{NaNO}_2, \text{HCl}} \text{OH} \]

Ethyl alcohol to Vinyl alcohol

Ethyl alcohol to vinyl acetate
\[ \text{CH}_3\text{CHOH} \xrightarrow{\text{Al}_{2}\text{O}_{3}} \text{CH}_2\text{C} \xrightarrow{\text{Br}_2} \text{CH}_2\text{Br} \xrightarrow{1. \text{alc. KOH}} \text{CH}_2=\text{CH} \xrightarrow{2. \text{NaNH}_2} \text{CH}_2\text{COOH} \]

Methylamine to ethylamine

Methylamine to ethylamine
\[ \text{CH}_3\text{NH}_2 \xrightarrow{\text{HNO}_3} \text{CH}_3\text{OH} \xrightarrow{\text{P}_{4}\text{C}_6} \text{CH}_3\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{Sn}, \text{HCl}} \text{CH}_3\text{CH}_2\text{NH}_2 \]
Benzene to m-bromotoluene

Benzaldehyde to cyanobenzene

Aniline to Chlorobenzene

Ethylamine to Methylamine
Benzene to m-dibromobenzene

Aniline to p-nitroaniline

Toluene to m-nitrotoluene
Convert Benzene + Alcohol to α-methylphenylacetic acid

Benzene + alcohol to α-methylphenylacetic acid

$$\text{C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_5\text{NH}^+\text{CrO}_3\text{Cl}^- \rightarrow \text{CH}_3\text{CHO}$$

Toluene to 3,5 dibromotoluene

Benzene to p-chloronitrobenzene
Toluene to 2,6-dibromotoluene

Benzene to 3,4-dibromonitrobenzene

Benzene to m-chloronitrobenzene
Nitrobenzene to benzamide

\[
\begin{align*}
\text{Nitrobenzene} & \xrightarrow{\text{SnHCl [H]}} \text{Aniline} & \xrightarrow{\text{NaNO}_2+4\text{HCl}} \text{Nitroaniline} & \xrightarrow{\text{KCN}} \text{Hydrazine} & \xrightarrow{\text{NH}_3, \text{heat}} \text{Primary Amine} & \xrightarrow{\text{H}^+} \text{Benzamide}
\end{align*}
\]

Benzene to 4-nitrobenzaldehyde

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{CH}_3\text{Cl, AlCl}_3} \text{Toluene} & \xrightarrow{\text{HNO}_2, \text{H}_2\text{SO}_4} \text{Nitrotoluene} & \xrightarrow{\text{CrO}_3, (\text{CH}_3\text{CO})_2\text{O}} \text{Nitranilide} & \xrightarrow{\text{H}_2\text{O, H}_2\text{SO}_4} \text{Benzaldehyde}
\end{align*}
\]

Benzene to 4-amino-2-bromotoluene

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{CH}_3\text{Cl, AlCl}_3} \text{Toluene} & \xrightarrow{\text{HNO}_2, \text{H}_2\text{SO}_4} \text{Nitrotoluene} & \xrightarrow{\text{Br}_2, \text{Fe}} \text{Bromotoluene} & \xrightarrow{\text{Fe, H}^+} \text{Amino-toluene}
\end{align*}
\]
Convert a mixture of cis-2-pentene and trans-2-pentene into cis-2-pentene or trans-2-pentene

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

Benzene to p-chlorobenzylalcohol

Benzene to p-chlorobenzylalcohol
Convert Propanol to α-hydroxypropanoic acid

\[
\text{Propanol} \xrightarrow{\text{KMN}_4} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{Br}_2/P} \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CH}_2\text{COOH}
\]

4-chloropentane-2-one

\[
\text{CH}_3\text{C} \xrightarrow{\text{Cl}} \text{CH}_2\text{CH}_3
\]

3-Bromo-4-methylpentanoic acid

\[
\text{CH}_3\text{C} \xrightarrow{\text{Br}} \text{CH}_2\text{CH}_3
\]

\[
\text{CH}_2\text{OH}
\]

\[
\text{CH}_3\text{C} \xrightarrow{\text{CHO}} \text{CH}_2\text{CH}_3
\]

\[
\text{CHO}
\]

\[
\text{CH}_2\text{OH}
\]

\[
\text{CH}_3\text{C} \xrightarrow{\text{C} = \text{CHO}} \text{CH}_2\text{CH}_3
\]

\[
\text{CHO}
\]

\[
\text{CH} = \text{CHO}
\]

\[
\text{Vanillin}
\]

\[
\text{Salicylaldehyde}
\]

\[
\text{Cinnamaldehyde}
\]

\[
p,p'\text{-dihydroxybenzophenone}
\]

\[
\text{CH}_3\text{C} \xrightarrow{\text{C} = \text{CHO}} \text{CH}_2\text{CH}_3
\]

Hex-2-ene-4-ynoic acid

\[
\text{CH}_3\text{C} \xrightarrow{\text{O}} \text{CH}_2\text{CH}_3
\]

Heptan-2-one

\[
\text{CH}_3\text{C} \xrightarrow{\text{O}} \text{CH}_2\text{CH}_3
\]
Benzene to Mandelic Acid

4-Bromo-2-methylhexane

Heptanal

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

\[
RCHO(\text{aq}) + 2\text{Ag}(\text{NH}_3)_2^+(\text{aq}) + 3\text{OH}^- (\text{aq}) \rightarrow \text{R}COO^-(\text{aq}) + 2\text{Ag(s)} + 4\text{NH}_3(\text{aq}) + 2\text{H}_2\text{O}
\]

An aldehyde

\[
\text{RCOO}^-(\text{aq}) + 2\text{Ag(s)} + 4\text{NH}_3(\text{aq}) + 2\text{H}_2\text{O}
\]

Free silver

An aldose

Tollen’s reagent (clear solution)

Carboxylate anion

Silver

An aldose

Benedict’s reagent (blue solution)

Carboxylate anion

Brick-red precipitate

Benzene to 2,4-dinitrobenzaldehyde

Acetaldehyde to Acetylene

\[
\text{CH}_3\text{CHO} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{alc KOH}} \text{CH}_2=\text{CH}_2 \xrightarrow{\text{Br}_2} \text{CH}_2=\text{CH}_2 \xrightarrow{\text{alc KOH}} \text{NaNH}_2 \rightarrow \text{CH}≡\text{CH}
\]
Identify the compounds

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

A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff’s reagent. On refluxing with an excess of hydroiodic acid, X yields only one organic product Y. On hydrolysis Y yields a new compound Z which can be converted to Y by reaction with red phosphorus and iodine. The compound Z on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds X, Y and Z? Write chemical equations leading to the conversion of X to Y. (1981)

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

```
\[
\begin{align*}
ROR & \xrightarrow{HI} 2R(I) \\
(X) & \xrightarrow{H_2O} 2ROH & \xrightarrow{10I} 2R'COOH \\
(Y) & \xrightarrow{I_2/P} (Z)
\end{align*}
\]
```

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

- X : CH₃CH₂OCH₂CH₃
- Y : CH₃CH₂I
- Z : CH₃CH₂OH

**Steric Effects and the Relative Reactivity of Carboxylic Acid Derivatives**

[Diagram showing steric effects and relative reactivity of carboxylic acid derivatives]
Identify the compound
A hydrocarbon reacts with Bromine to give dibromo compound

Identify the compound
An alkene A on ozonolysis yields acetone and an aldehyde
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:

\[2\text{NH}_4 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_3)_2\text{SO}_4\]
\[\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}\]

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

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

Amount of sulphuric acid taken to start with = (50 mL) \(\frac{0.05 \text{ mol}}{1000 \text{ mL}}\) = \(\frac{1}{400}\) mol
Identify the compound

An Organic compound CxH2yOy was burnt with twice the amount of Oxygen

An organic compound C\textsubscript{x}H\textsubscript{y}O\textsubscript{z} was burnt with twice the amount of oxygen needed for complete combustion to CO\textsubscript{2} and H\textsubscript{2}O. 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 vapor 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 \textit{C}_x\textit{H}_y\textit{O}_z + \textit{x} \textit{O}_2 \rightarrow \textit{x} \text{CO}_2 + \textit{y} \text{H}_2\text{O}

To start with, the amount of O\textsubscript{2} taken is 2x; Hence, after the combustion reaction, we will be left with the following amounts.

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

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,

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

Now,

\[
\text{Mass of water collected} = 0.9 \text{ g}; \quad \text{Amount of water collected} = \frac{0.9 \text{ g}}{18 \text{ g mol}^{-1}} = 0.05 \text{ mol}
\]

Thus, the empirical formula of the compound is C\textsubscript{0.05}H\textsubscript{0.80}O\textsubscript{0.05} i.e., CH\textsubscript{2}O. Now, according to Raoult’s law

\[
\frac{\Delta p}{p} = x_2 \text{ i.e., } \frac{0.104 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{(50 \text{ g/M})}{(1000 \text{ g/18 g mol}^{-1})}
\]
Solving for $M$, we get $M = 150.5 \text{ g mol}^{-1}$

Number of repeating units of $\text{CH}_2\text{O}$ in the molecular formula $= \frac{150.5}{12 + 2 + 16} = 5$

Hence, the molecular formula of the compound is $\text{C}_3\text{H}_{16}\text{O}_5$.

Identify the Compound

Alcohol when heated with concentrated $\text{H}_2\text{SO}_4$

An alcohol $A$, when heated with concentrated $\text{H}_2\text{SO}_4$ gives an alkene $B$. When $B$ is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodium, a new compound $C$ is obtained. The compound $C$ gives $D$ when treated with warm dilute $\text{H}_2\text{SO}_4$ in presence of $\text{HgSO}_4$. $D$ can also be obtained either by oxidizing $A$ with $\text{KMnO}_4$ or from acetic acid through its calcium salt. Identify $A$, $B$, $C$ and $D$.

**Solution** The given reactions are as follows.

$A_{\text{alcohol}} \xrightarrow{\text{conc. H}_2\text{SO}_4} B_{\text{alkene}} \xrightarrow{1\text{ Br}_2, 2\text{-HBr}} C_{\text{HgSO}_4/\text{H}_2\text{SO}_4} \rightarrow D$

The reaction of obtaining $D$ from calcium acetate is

$(\text{CH}_3\text{COO})_2\text{Ca} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CaCO}_3$

Hence, $D$ is acetone. Since the latter is also obtained from the oxidation of alcohol $A$, compound $A$ will be $\text{CH}_3\text{CHCH}_3$.

Hence, the reactions depicted above are as follows.

$\text{CH}_3\text{CHCH}_3_{\text{2-propanol}} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CH}_3\text{CH} \equiv \text{CH}_2_{\text{propene}} \xrightarrow{\text{Br}_2} \text{CH}_3\text{CH} \\text{Br} \equiv \text{CH}_2_{\text{propyne}}$

$\text{CH}_3\text{C} \equiv \text{CH}_{\text{acetylene}}$
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 K₂MnO₄, gave compound C (molecular formula C₆H₁₀O₂) 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 $\text{CH}_2$.

Since the compound A consumes 1 mol of hydrogen, the molecule of A contains only one carbon-carbon double bond. From the data on the absorption of bromine, we can calculate the molar mass of A as shown in the following.

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

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

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 $\text{C}_6\text{H}_{12}$.

Now, it is given that

\[
\text{C}_6\text{H}_{12}(\text{con. K}_2\text{MnO}_4) \rightarrow \text{C}_4\text{H}_8\text{O} + \text{CH}_3\text{COOH}
\]

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

\[
\text{CH}_3\text{C} \equiv \text{CH}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C} \equiv \text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4/\text{H}_2\text{SO}_4} \text{CH}_3\text{C} \equiv \text{CH}_3 \xrightarrow{\text{OH}} \text{CH}_3\text{C} \equiv \text{CH}_3 \xrightarrow{\text{O}} \text{CH}_3\text{C} \equiv \text{CH}_3
\]

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

\[
\text{R'OH} \xrightarrow{[\text{O}]} \text{RCOOH} \quad \text{or} \quad \text{RCH}_2\text{OH} \xrightarrow{[\text{O}]} \text{RCOOH}
\]

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

\[
2\text{RCOOCH}_2\text{H} = \text{C}_4\text{H}_8\text{O} = \text{C}_2\text{H}_4\text{O} \quad \text{or} \quad \text{R} = \text{C}_2\text{H}_4
\]

\[
\text{X} : \text{CH}_3\text{CH}_2\text{COOCH}\text{CH}_2\text{CH}_3 \quad \text{Propylpropanoate} \quad \text{Y} : \text{CH}_3\text{CH}_2\text{COOH} \quad \text{Propanoic acid}
\]

\[
\text{Z} : \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \quad \text{Propanol}
\]
Identify the compound

An unknown compound of carbon, hydrogen, and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molar mass of 86 g mol⁻¹. It does not reduce Fehling’s solution, but forms a bisulphite addition compound and gives a positive iodine starch 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 CH₂CO group as it shows positive iodine starch test.

The ratios of atoms in the compound are

$$\text{C : O : H} = \frac{69.77}{12} : \frac{11.63}{16} : \frac{5.18}{1} = 5.81 : 1 : 11.63 : 5 : 1 : 10$$

Hence, **empirical formula** is C₇H₁₀O₅. Thus, **molecular formula** is C₁₅H₂₆O₉.

The structure of the compound will be

\[
\begin{align*}
\text{CH}_3 \text{C} & \text{CH}_3 \\
\text{CH}_2 & \text{CH}_2 \text{CH}_3
\end{align*}
\]

or

\[
\begin{align*}
\text{CH}_3 \text{C} & \text{CH}_3 \\
\text{O} & \text{O}
\end{align*}
\]

Identify the compound

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

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

$$\text{A} + \text{CH}_3\text{COOH} \xrightarrow{\text{H}_2\text{SO}_4} \text{ester} \xrightarrow{\text{B}} \text{mild oxidation} \xrightarrow{\text{C}, 50\% \text{ KOH}} \text{A} + \text{D}$$

$$\text{D} \xrightarrow{\text{chlorination}} \text{C} \xrightarrow{\text{50\% KOH}} \text{A} + \text{D}$$

The reaction C - 50% KOH → A + D is a Cannizzaro reaction and thus the compound C is an aldehyde with no α-hydrogen. C must be HCHO. From this it follows that A must be CH₃OH as its mild oxidation gives HCHO.

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

$$\text{CH}_3\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_3 \xrightarrow{\text{methyl acetate}} \text{CH}_3\text{CHO} \xrightarrow{\text{I}_2} \text{HCHO} \xrightarrow{\text{50\% KOH}} \text{CH}_3\text{OH} + \text{HCOOH}$$

Hence

$$\text{HCOOH} \xrightarrow{\text{PCl}_5} \text{HCOCl} \xrightarrow{\text{NH}_3} \text{HCONH}_2 \xrightarrow{-\text{H}_2\text{O}} \text{HCN}$$

A : CH₃OH methanol  B : CH₃COOCH₃ methylethonate
C : HCHO methanal  D : HCOOH methanoic acid
E : HCONH₂ methanamide
Iodoform Test

\[
\text{R} - \text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{R} - \text{CO}^-\text{Na}^+ + 3\text{NaI} + 3\text{H}_2\text{O} + \text{CH}_3\text{I} (s)
\]

\[
\begin{align*}
\text{HO:} & \quad \text{I} \quad \text{I} \\
\text{R} - \text{C} - \text{H}_3 & \rightarrow \text{R} - \text{C} - \text{O}^-\text{Na}^+ + \text{CH}_3 \\
\text{R} - \text{CH}_3 - \text{OH} & \rightarrow \text{R} - \text{C} - \text{O}^-\text{Na}^+ + \text{CH}_3
\end{align*}
\]
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 dihydroxyl 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

\[
\frac{m_{AgCl}}{M_{AgCl}} \times \frac{m_{compound}}{100} = \frac{35.5}{143.5} \times \frac{2.90}{1.0} \times 100 = 71.21
\]

The ratios of atoms in the molecule of X are

\[
\frac{C}{\text{H}} : \frac{Cl}{\text{Cl}} : \frac{2.44}{4.04} : \frac{1}{71.72} : \frac{1}{35.5} :: 2 : 4 : 2 :: 1 : 2 : 1
\]

Empirical formula of X is CH₂Cl₂

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 C₃H₆Cl₂.

Its two isomers are \( \text{CH}_3\text{CHCl}_2 \) and \( \text{ClCH}_2\text{CHCl} \).

The reaction are

\[
\begin{align*}
\text{CH}_3\text{CHCl}_2 & \xrightarrow{\text{aq. KOH}} [\text{CH}_3\text{CH}(\text{OH})_2] \rightarrow \text{CH}_3\text{CHO} \\
\text{ClCH}_2\text{CH}_2\text{Cl} & \xrightarrow{\text{aq. KOH}} \text{HOCH}_2\text{CH}_2\text{OH}
\end{align*}
\]

ethanal

ethyleneglycol

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)
Match the entries given on the left with those given on the right.
(a) Pyrolysis of alkanes
(b) Benzene + Chloroethane
(c) CH$_2$COOC$_2$H$_5$ + NaOH
(d) Preparation of alkanes
(e) Phenol + CHCl$_3$ (NaOH)
(f) C$_2$H$_5$Br + alcKOH
(p) Elimination reaction
(q) Saponification
(r) Wurtz reaction
(s) Friedel-craft reaction
(t) Reimer-Tiemann reaction
(u) Cracking

Ans:
(a) – (u);
(b) – (s);
(c) – (q);
(d) – (r);
(e) – (t);
(f) – (p)

Identify the compound

A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C (C$_2$H$_5$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 C$_2$H$_4$O$_2$. Identify the compounds A, B, C, D, and E and write their structures.

Solution We have

- **Mixture of A and B**
  - **CHCl$_3$ + KOH**
  - **Organic layer (A)**
    - alc. KOH
    - C$_2$H$_5$N
  - **Aqueous layer (B)**
    - CHCl$_3$
    - H$^+$
    - C$_2$H$_4$O$_2$
    - C$_2$H$_4$O$_2$

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

- N = C
- NH$_3$

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

OH

1. CHCl$_3$
2. H$^+$

- salicylaldehyde (chief product)
- CHO

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

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{Cl}_2 & \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \text{ (Cl\text{\textsuperscript{2}O})} \\
\text{CH}_3\text{CHBrCH}_3 & \rightarrow \text{CH}_3\text{CHBrCH}_2\text{Br} \text{ (Cl\text{\textsuperscript{2}O})} \\
\end{align*}
\]

Chlorination of either isobutyl or tert-butyl bromide gives 1-bromo-2-chloro-2-methylpropane.

\[
\begin{align*}
\text{Cl}^- \quad \text{Br}^- \quad \text{Cl}^-
\end{align*}
\]

Identify the Compound

An organic compound containing C, H and O exists in two isomeric forms A and B. A mass of 0.108 g of one of the isomers gives on combustion 0.308 g of CO\textsubscript{2} and 0.072 g of H\textsubscript{2}O. A is insoluble in NaOH and NaHCO\textsubscript{3} while B is soluble in NaOH. A reacts with concentrated H\textsubscript{2}SO\textsubscript{4} to give compounds C and D. C can be separated from D by the ethanolic AgNO\textsubscript{3} solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula, C\textsubscript{10}H\textsubscript{16}OBr\textsubscript{4}. Identify A, B, C, D and E with justification and give their structures.

Solution
We have

\[
\begin{align*}
\text{Per cent of carbon in the compound} & = \frac{M_C}{M_{\text{CO}_2}} \times \frac{m_{\text{CO}_2}}{m_{\text{compound}}} \times 100 = \left( \frac{12}{44} \right) \left( \frac{0.308}{0.108} \right) (100) = 77.78 \\
\text{Per cent of hydrogen in the compound} & = \frac{2M_H}{M_{\text{H}_2\text{O}}} \times \frac{m_{\text{H}_2\text{O}}}{m_{\text{compound}}} \times 100 = \left( \frac{2}{18} \right) \left( \frac{0.072}{0.108} \right) (100) = 7.41 \\
\text{Per cent of oxygen in the compound} & = 100 - (77.78 + 7.41) = 14.81.
\end{align*}
\]

The ratios of atoms in the compound are

\[
\begin{align*}
\text{C} : \text{H} : \text{O} : & = \frac{77.78}{12} : \frac{7.41}{1} : \frac{14.81}{16} : \frac{6.48}{1} : \frac{7.41}{7} : \frac{0.926}{8} : 1 \\
\text{Hence, Empirical formula of the compound is C}_7\text{H}_8\text{O.}
\end{align*}
\]

Since the isomer B reacting with bromine water gives compound E (C\textsubscript{10}H\textsubscript{16}OBr\textsubscript{4}), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and NaHCO\textsubscript{3} and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are

\[
\begin{align*}
\text{(A) anisol} & \quad \text{(B) m-cresol}
\end{align*}
\]

The bromination of B gives
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 NaNO₂ solution at 0 °C liberated a colourless, odorless 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 CHCl₃ and alcoholic KOH, the compound must be a primary amine.

\[ \text{RNH}_2 + \text{CHCl}_3 + 3\text{KOH} \rightarrow \text{RNC} + 3\text{KCl} + 3\text{H}_2\text{O} \]

(alkyl isocyanide)

(foul smelling gas)

Since the compound on treating with NaNO₂/HCl at 0 °C produces a colourless gas, the compound must be an aliphatic primary amine.

\[ \text{RNH}_2 + \text{HNO}_2 \rightarrow \text{ROH} + \text{N}_2 + \text{H}_2\text{O} \]

Thus, the gas produced is nitrogen.

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 \((59 - 16) = 43 \text{ g mol}^{-1}\), i.e. 43 g mol\(^{-1}\). Hence, \( R \) must be \( \text{C}_3\text{H}_7\).

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 \( \text{CH}_3 - \text{C} \quad \text{OH} \) group. Hence, it is concluded that ROH is \( \text{CH}_3 - \text{CH} - \text{CH}_3 \). Thus, the original compound is \( \text{CH}_3 - \text{CH} - \text{CH}_3 \quad \text{OH} \quad \text{NH}_2 \) isopropylamine.

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

(a) Lucas test  
(b) Neutral FeCl\(_3\)  
(c) Dye test  
(d) Tollens test

(p) Phenol  
(q) Glucose  
(r) Tertiary alcohol  
(s) Aniline

Ans :

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

Identify the compound

An organic compound \( A \), \( \text{C}_6\text{H}_{14} \), 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

\[ \text{C}_6\text{H}_{14} \xrightleftharpoons{} \text{dil. H}_2\text{SO}_4 \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_6 \quad \text{acid chloride} \]

\[ \xrightarrow{\text{I}_2/\text{KOH}} \text{C} + \text{D} \]

The reaction of \( B \) with \( I_2 \) in KOH is iodoform reaction. The compound \( D \) is iodoform, \( \text{CHI}_3 \). 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 \( \text{C}_6\text{H}_5\text{C}_2\text{H}_5 \). Since it gives \( \text{C}_6\text{H}_5\text{COCH}_3 \) on treating with dilute \( \text{H}_2\text{SO}_4 \) and \( \text{HgSO}_4 \), it must contain a triple bond \((-\text{C}==\text{CH})\) 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\((C_9H_{12})\). 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

\[
C_9H_{12} \xrightarrow{4\text{H}} C_5H_8
\]

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

\[
C_5H_8 \xrightarrow{O_3} \text{HCHO} + \text{CH}_3\text{C}==\text{CHO}
\]

Since there is no loss of carbon atoms in an ozonolysis reaction, probably 2 molecules of formaldehyde are formed. In 2-ketopropanal, \(\text{C}==\text{CH}==\text{C}==\text{CHO}\) groups must have resulted due to the cleavage of double bonds. Hence, the net reaction can be explained as follows.

\[
\begin{align*}
\text{H}_2\text{C}==\text{O} + \text{O}==\text{CH}==\text{C}==\text{CH}_3 & \xrightarrow{O_3} \text{CH}_2\text{C}==\text{C}==\text{CH}_3 \\
+ & \text{CH}_2
\end{align*}
\]

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

An Organic compound A has 76.6% C and 6.38% H (Aspirin)

Solution: The ratios of atoms present in one molecule of A are

\[ \frac{C}{H} : \frac{O}{H} = \frac{76.6}{12} : \frac{6.38}{16} = \frac{6.38}{6.38} : \frac{1.064}{6.38} = 6 : 6 : 1 \]

Hence, the empirical formula of A is \( C_6H_6O \). Molar empirical formula mass of A = 94 g mol\(^{-1}\).

This tallies with the given molar mass (\( 2 \times 47 \) g mol\(^{-1}\)). Thus molecular formula of A is \( C_9H_8O_2 \).

Since, the compound A gives characteristic colour with FeCl\(_3\) it must be a phenol. The given reactions are:\n
\[ \text{Aspirin (pain killer)} \]
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, \(\text{C}_6\text{H}_5\text{O}\). Compound B can be oxidized under mild conditions to compound C, \(\text{C}_6\text{H}_4\text{O}\). Compound C forms a phenylhydrazone D with \(\text{PhNHNNH}_2\) 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

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

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

This tallies with the given molar mass. Thus, molecular formula of A is \(\text{C}_{16}\text{H}_{16}\text{Cl}\).

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 alphiphatic portion of the molecule.

Since the compound C gives a positive iodoform test, it must contain —COCH\(_3\) group.

Since the compound C is obtained by mild oxidation of B, the latter must be a secondary alcohol. Hence, the compound A also contains secondary chlorine atom. Consistent with this, the given reactions are as follows.

\[
\begin{align*}
\text{Cl} & \quad \text{H--C--CH}_3 \\
\text{H} & \quad \text{H--C--CH}_3 \\
\text{OH} & \quad \text{H--C--CH}_3 \\
\text{O} & \quad \text{H--C--CH}_3 \\
\text{CH}_3 & \quad \text{C=}\text{NNHPh} \\
\end{align*}
\]
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 Na₂S₂O₃ 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) Cl₂O  
(b) Cl₂O₇  
(c) ClO₂  
(d) Cl₂O₆

**Solutions:**

For Q.11, we may write

\[ \text{Household bleach} + 2 \text{ KI} \rightarrow \text{I}_2 + \text{products} \]

\[ \text{I}_2 + 2\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]

Amount of Na₂S₂O₃ used = \( \nu M = (48 \times 10^{-3} \text{ L}) (0.25 \text{ mol L}^{-1}) = 12 \times 10^{-3} \text{ mol} \)

Amount of I₂ 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 I₂, we will have

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 Ca(OCl)Cl.

The oxoacid of this salt is HOCl. The formation of this acid through its anhydride is

\[ \text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HOCl} \]

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.**

<table>
<thead>
<tr>
<th>Column I</th>
<th>Column II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) C₆H₄CHO</td>
<td>(p) gives precipitate with 2,4-dinitrophenylhydrazine</td>
</tr>
<tr>
<td>(b) CH₃C≡CH</td>
<td>(q) gives precipitate with AgNO₃</td>
</tr>
<tr>
<td>(c) CN⁻</td>
<td>(r) is a nucleophile</td>
</tr>
<tr>
<td>(d) I⁻</td>
<td>(s) is involved in cyanohydrin formation</td>
</tr>
</tbody>
</table>

**Ans:**

(a) – (p), (q), (s);  
(b) – (q);  
(c) – (q), (r), (s);  
(d) – (q)
In decreasing order of Oxidation state of Nitrogen

Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
(a) HNO₃, NO, NH₄Cl, N₂
(b) HNO₃, NO, N₂, NH₄Cl
(c) HNO₃, NH₄Cl, NO, N₂
(d) NO, HNO₃, NH₄Cl, N₂

Solution:
The oxidation states of nitrogen in the given compounds are as follows.
HNO₃: +1 + x + 3 (-2) = 0 \Rightarrow x = +5
NO: x + (-2) = 0 \Rightarrow x = +2
NH₄Cl: x + 4 (+1) + (-1) = 0 \Rightarrow x = -3
N₂: 2(x) = 0 \Rightarrow x = 0
Thus, the decreasing oxidation numbers of nitrogen is HNO₃, NO, N₂ and NH₄Cl.
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 (a₀ is Bohr radius) is
(a) \( \frac{\hbar^2}{4\pi^2ma_0^2} \)  
(b) \( \frac{\hbar^2}{16\pi^2ma_0^2} \)  
(c) \( \frac{3\hbar^2}{2\pi^2ma_0^2} \)  
(d) \( \frac{\hbar^2}{64\pi^2ma_0^2} \)

Solution:
Bohr model of an atom satisfies the following two requirements.
• Equality of centripetal and centrifugal forces, i.e.

\[ \frac{(Ze)(e)}{(4\pi\varepsilon_0)r^2} = \frac{ma^2}{r} \]

Quantization of angular momentum, i.e.

\[ mvr = n \left( \frac{\hbar}{2\pi} \right) \]

Eliminating \( v \) in these two expressions, we get

\[ r = n^2 \left[ \frac{\hbar^2}{4\pi^2m(Ze/4\pi\varepsilon_0)} \right] = \frac{n^2a_0}{Z} \]

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

\[ KE = \frac{1}{2} \frac{mv^2}{r} = \frac{1}{2} m \left( \frac{n}{mv} \right)^2 \frac{h}{2\pi} = \frac{1}{2} m \left( \frac{n}{m(n^2a_0/Z)} \right) \left( \frac{h}{2\pi} \right)^2 = \frac{n^2}{Zn^2} \left( \frac{h^2}{8\pi^2ma_0^2} \right) \]

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

\[ KE = \frac{1}{32} \left( \frac{h^2}{\pi^2ma_0^2} \right) \]

Therefore, the choice (c) is correct.
Question on Aldol reaction

The number of aldol reaction(s) that occurs in the given transformation

\[ \text{CH}_3\text{CHO} + 4\text{HCHO} \xrightarrow{\text{conc. aq. NaOH}} \]

is (a) 1 (b) 2 (c) 3 (d) 4

**Solution:**
The given reaction may be formulated as follows.

- **First aldol condensation**
  \[ \text{HCHO} \xrightarrow{\text{OH}^-} \text{CH}_3\text{CHO} \]

- **Second aldol condensation**
  \[ \text{HCHO} \xrightarrow{\text{OH}^-} \text{HOCH}_2\text{CH}_2\text{CHO} \]

- **Third aldol condensation**
  \[ \text{HCHO} \xrightarrow{\text{OH}^-} \text{HOCH}_2\text{CH}_2\text{CHO} \]

- **Cannizzaro reaction**
  \[ \text{HCHO} \xrightarrow{\text{OH}^-} \text{HCOO}^- + \text{HOCH}_2\text{CH}_2\text{CHO} \]

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 \( \frac{\ln(1/8)}{\ln(1/10)} = \frac{t_{1/8}}{t_{1/10}} \) 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$_3$H$_4$), 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$^3$ and sp$^3$

**Solution:**
The structure of allene is

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

CH$_3$−CH=CH−C−CH=CH−C−CH=CH−CH$_3$
is

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

**Solution:**

CH$_3$−CH=CH−C−CH=CH−C−CH=CH−CH$_3$ → CH$_3$CHO + OCH$_3$ + OCH$_3$ + CH$_3$

None of the products will be optically active.
Therefore, the choice (a) is correct.
Carboxylic functional group is present in aspirin

The carboxylic functional group (—COOH) is present in
(a) picric acid  (b) barbituric acid  (c) ascorbic acid  (d) aspirin

**Solution:**
The structures of the given compounds are as follows.

![Picric acid structure](image1)

![Barbituric acid structure](image2)

![Ascorbic acid structure](image3)

![Aspirin structure](image4)

Therefore, the choice (d) is correct.

**Identify the compound**

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

\[
\begin{align*}
I & \xrightarrow{\text{CH}_2\text{CO}, \text{D}} J \\
\xrightarrow{\text{H}_2\text{Pd/C}} & K
\end{align*}
\]

J(C_6H_6O_2) gives effervescence on treatment with NaHCO_3 and positive Baeyer’s test.

Q - The compound K is

(a) ![Structure A](image5)  (b) ![Structure B](image6)  (c) ![Structure C](image7)  (d) ![Structure D](image8)

Q - The compound I is

(a) ![Structure A](image9)  (b) ![Structure B](image10)  (c) ![Structure C](image11)  (d) ![Structure D](image12)
Perkin Condensation

**Solutions:**

The compound J must contain a $-\text{COOH}$ group as it gives effervescence with $\text{NaHCO}_3$. Also, it is an unsaturated compound as it gives positive Baeyer’s test (decolourization of pink colour of alkaline $\text{KMnO}_4$). Since the compound J is obtained by treating the compound I with $(\text{CH}_3\text{CO})_2\text{O}$ and $\text{CH}_3\text{COONa}$, 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

$$\text{CHO} + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow{\Delta} \text{CH}==\text{CHCOOH}$$

$\alpha, \beta$-unsaturated carboxylic acid

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
Aldohexose exists in D configuration

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

CHO
CH₂
CHOH
CHOH
CH₂OH

*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
Peptides

The substituents $R_1$ and $R_2$ for nine peptides are listed in the table given below. How many these peptides are positively charged at pH = 7.0?

<table>
<thead>
<tr>
<th>Peptide</th>
<th>$R_1$</th>
<th>$R_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>II</td>
<td>H</td>
<td>CH$_3$</td>
</tr>
<tr>
<td>III</td>
<td>CH$_3$COOH</td>
<td>H</td>
</tr>
<tr>
<td>IV</td>
<td>CH$_2$CONH$_2$</td>
<td>(CH$_3$)$_2$NH$_2$</td>
</tr>
<tr>
<td>V</td>
<td>CH$_3$CONH$_2$</td>
<td>CH$_2$CONH$_2$</td>
</tr>
<tr>
<td>VI</td>
<td>(CH$_3$)$_2$NH$_2$</td>
<td>CH$_2$NH$_2$</td>
</tr>
<tr>
<td>VII</td>
<td>CH$_2$COOH</td>
<td>CH$_2$CONH$_2$</td>
</tr>
<tr>
<td>VIII</td>
<td>CH$_3$OH</td>
<td>(CH$_3$)$_2$NH$_2$</td>
</tr>
<tr>
<td>IX</td>
<td>(CH$_3$)$_2$NH$_2$</td>
<td>CH$_3$</td>
</tr>
</tbody>
</table>

Solution

In general, the pH of the solution at which amino acids exist as zwitterion follows the order:

Accidic side chain < neutral chain < basic side chain

(pH = 3)     (pH = 5.5 – 6.0)     (pH = 9–10)

This pH is known as isolectric point.

At pH = 7, the acidic side chain (for which isolectric point < 7) exists as a negatively charged species (e.g., $-\text{COO}^-$) and the basic side chain (for which isolectric 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 $R_2$ 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 < iso-butyl alcohol < sec-butyl alcohol < tert-butyl alcohol. Polarity of O—H bond increases in the same order.

CH₃CH₂COOH < (CH₃)₂CHCOOH < CH₃CH₂COOH < CH₃COOH < HCOOH

The presence of bulky groups near the site of reaction, whether in the alcohol or in the acid, slows down esterification as well as de-esterification (hydrolysis).

(CH₃)₂CCOOCH₃ < (CH₃)₂CHCOOCH₃ < CH₃COOCH₃ < HCOOCH₃
CH₃COOC(CH₃)₂ < CH₃COOCH(CH₃)₂ < CH₃COOC₂H₅ < CH₃COOCH₃

Try to figure out the sequences

COOCH₃ < COOCH₃ < COOCH₃ < COOCH₃

OCH₃ Cl NO₂

adipic acid < succinic acid < malonic acid < oxalic acid
Acidity decreases with increase in the intervening CH₂ 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: CH₃CHO, CH₃COCH₃, HCHO, C₂H₅COCH₃
Increasing basicity: p-toluidine, N, N-dimethyl-p-toluidine, p-nitroaniline, aniline.
Increasing ease of hydrolysis: CH₃COOC₂H₅, CH₃COCl, (CH₃CO)₂O, CH₃CONH₂
Increasing order of acid strength:
ClCH₂COOH, CH₃CH₂COOH, CIC₆H₄CH₂COOH, (CH₃)₂CHCOOH, CH₃COOH

Increasing reactivity in nucleophilic substitution reactions: CH₃F, CH₃I, CH₃Br, CH₃Cl

Major product H in the given reaction sequence

The major product H in the given reaction sequence

\[
\text{C₂H₅CH₃ - CO - CH₃ \xrightarrow{\text{HCN}} G \xrightarrow{95\% \text{ H₂SO₄, Heat}} H}
\]

is

(a) \( \text{CH}_3\text{CH} = \text{C} - \text{COOH} \)

(b) \( \text{CH}_3\text{CH} = \text{C} - \text{CN} \)

(c) \( \text{CH}_3\text{CH} = \text{C} - \text{COOH} \)

(d) \( \text{CH}_3\text{CH} = \text{C} - \text{CO} - \text{NH}_2 \)

**Solution:**
The first reaction is nucleophilic addition reaction across the \(-\text{C=O}\) 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 aciadtity 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:
- Anilines, anilines, cyclohexylamine

Decreasing order of basicity:
- Ethylamine, 2-aminoethanol, 3-amino-1-propanol

Decreasing order of basicity:
- Anilines, p-methoxyanilines, p-nitroanilines

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 phenols:
- p-chlorophenol, 2, 4-dichlorophenol, 2, 4, 6-trichlorophenol

Decreasing order of reactivity towards KCN: benzyl chloride, chlorobenzene, ethyl chloride

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-chloropropane, 3-chloropropane, n-propylchloride

Decreasing acidity:
- H_2O, HC≡CH, NH_3, RH, ROH

Decreasing basicity:
- R^−, HC≡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: $\cdot CH_3$, $1^\circ$, $2^\circ$, $3^\circ$, allyl, vinyl

Increasing stability of carbocation: $CH_3^+$, $1^\circ$, $2^\circ$, $3^\circ$

Increasing enthalpy of reaction:

$$CH_3Br \rightarrow CH_3^+ + Br^- \quad \Delta H_1$$
$$CH_3CH_2Br \rightarrow CH_3CH_2^+ + Br^- \quad \Delta H_2$$
$$CH_3CHCH_3 \rightarrow CH_3CHCH_2 + Br^- \quad \Delta H_3$$
$$\text{Br}$$
$$\text{Br}$$

$$\begin{align*}
CH_3 \quad \text{CH} \quad CH_3 & \rightarrow \quad CH_3 \quad \text{C} \quad CH_3 + Br^- \quad \Delta H_4
\end{align*}$$

Increasing order of reactivity towards $S_N2$ displacement:

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

The compound that undergoes decarboxylation most readily under mild condition is

(a) ![COOH](attachment:co2.png)
(b) ![COOH](attachment:co2.png)
(c) ![COOH](attachment:co2.png)
(d) ![COOH](attachment:co2.png)

**Solution:**

$\beta$-Ketocarboxylic acid is unstable acid. It readily undergoes decarboxylation through a cyclic transition state.

$$\begin{align*}
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{O} \\
\text{O} & \quad \text{C} \\
\text{O} & \quad \text{H}
\end{align*}$$

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

A compound contains 88.89% C and 11.11% H. It gives white precipitate with ammoniacal silver nitrate. The compound is

(a) $C_3H_6C \equiv CH$  (b) $C_4H_8C \equiv CH$  (c) $C_4H_4C \equiv CH$  (d) $C_5H_6C \equiv CH$

**Ans:**
Empirical formula contains \( \frac{C : H}{12} : \frac{11.1}{1} :: 7.4 : 11.1 :: 2 : 3 \)

Only the compound \( C_6H_5CH = CH \) has composition 4 times the composition of empirical formula.

More the number of electron withdrawing group stronger is the acid

\[
\text{Cl}_2\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}
\]

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

Try to figure out what sequence is depicted

\[
\text{FCH}_3\text{COOH} > \text{ClCH}_2\text{COOH} > \text{BrCH}_2\text{COOH} > \text{ICH}_2\text{COOH}
\]

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

\[
\text{CH}_3\text{COOH} < \text{ClCH}_2\text{CH}_2\text{COOH} < \text{ClCH}_2\text{COOH}
\]

\[
\text{HO} - \text{COOH} < \text{H}_2\text{C} - \text{CH}_{2} \text{COOH} < \text{Br} - \text{COOH}
\]

\[\text{H}_2\text{O} < \text{C}_2\text{H}_5\text{OH} < \text{C}_6\text{H}_5\text{COOH} < \text{HCOOH} < \text{HCl}\]

phenol < \text{p-nitrophenol} < \text{H}_2\text{CO}_3 < \text{C}_6\text{H}_5\text{COOH}

\( \text{C}_6\text{H}_5\text{NH}_2 < \text{C}_6\text{H}_4\text{NHCH}_3 < \text{NH}_3 < \text{CH}_3\text{NH}_2 < \text{(CH}_3\text{)}_2\text{NH} \)

\( \text{CH}_3\text{NH}_2 < \text{CH}_2\text{NH}_2 < \text{(CH}_3\text{)}_2\text{NH} \).  \( \text{(CH}_3\text{)}_2\text{N} \) 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 \( \text{CH}_3\text{OH} > 1^\circ > 2^\circ > 3^\circ \).

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

\[
\text{(a)} \text{CH}_3\text{CONH}_2 \quad \text{(b)} \text{C}_2\text{H}_5\text{CONH}_2 \quad \text{(c)} \text{C}_3\text{H}_7\text{CONH}_2 \quad \text{(d)} \text{C}_4\text{H}_9\text{CONH}_2
\]

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 \( \text{NaOH} \) 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. \( R = \text{C}_2\text{H}_5 \).

Hence, the compound is \( \text{C}_2\text{H}_5\text{CONH}_2 \).
Try to figure out what sequence is depicted

\[
\begin{align*}
\text{CH}_3\text{CHO} & < \text{CH}_2\text{COCH}_3 < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{COCH}_3 \\
\text{NO}_2 & > \text{F} > \text{Cl} > \text{OCH}_3 > \text{C}_6\text{H}_5 > \text{CH}_3 > \text{C}_2\text{H}_3 > (\text{CH}_3)_2\text{CH} > (\text{CH}_3)_3\text{C} \\
\text{C}_6\text{H}_5\text{COC}_6\text{H}_5 & < \text{C}_6\text{H}_5\text{COCH}_3 < \text{CH}_3\text{COCH}_3 < \text{CH}_3\text{CHO} < \text{HCHO}
\end{align*}
\]

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

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

\[
\begin{align*}
\text{CH}_3 & = \text{CH}_2 < \text{CH}_2\text{CH} = \text{CHCH}_3 < (\text{CH}_3)_2\text{C} = \text{CH}_2 \\
\text{CH}_2 & = \text{CHCH}_3 < \text{CH}_3\text{CH} = \text{CHCH}_3 < \text{CH}_2 = \text{CH} = \text{CHCH}_3 < \text{CH}_2 = \text{CH} = \text{CH} = \text{CHCH}_3 < \text{CH}_2 = \text{CH} = \text{CH} = \text{CH} = \text{CHCH}_3
\end{align*}
\]

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

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_3 & < \text{C}_6\text{H}_5\text{CH}_2\text{Cl} < \text{C}_6\text{H}_5\text{CHCl}_2 < \text{C}_6\text{H}_5\text{CCl}_3 \\
\text{tert-butanol} & < \text{sec-butanol} < \text{n-butanol} < \text{CH}_3\text{OH}. \text{ Alkyl group makes an alcohol less acidic. Bigger the alkyl group, the less acidic the alcohol. Methanol is the strongest and tertary alcohols are the weakest.}
\end{align*}
\]

\[
\begin{align*}
(\text{CH}_2)_2\text{CHCOOH} & < \text{C}_2\text{H}_5\text{COOH} < \text{CH}_3\text{COOH} < \text{C}_6\text{H}_5\text{COOH} < \text{HCOOH} < \text{CICH}_2\text{COOH}
\end{align*}
\]

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) C₆H₅N₂O  
(b) C₆H₅NO  
(c) C₆H₇NO₂  
(d) C₆H₄NO

Ans : 

\[
\begin{align*}
\text{Amount of H}_2\text{SO}_4 \text{ neutralized} & = (25 \times 10^{-3} \text{L})(0.05 \text{ M}) = 1.25 \times 10^{-3} \text{ mol} \\
\text{The neutralization reaction is} & \quad 2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4, \\
\text{Amount of NH}_3 \text{ evolved} & = 2 \times 1.25 \times 10^{-3} \text{ mol} = 2.5 \times 10^{-3} \text{ mol} \\
\text{Mass of N in the compound} & = (2.5 \times 10^{-3} \text{ mol})(14 \text{ g mol}^{-1}) = 0.035 \text{ g} \\
\text{Per cent of N in the compound} & = \frac{0.035}{0.3} \times 100 = 11.67 \\
\text{Per cent of O in the compound} & = 100 - (69.4 + 5.8 + 11.67) = 13.13 \\
\text{Ratio of atoms in the compound is} & = 69.4 : 5.8 : 11.67 : 13.13 \\
\text{Hence, empirical formula:} & \quad \text{C}_6\text{H}_5\text{NO}.
\end{align*}
\]

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 Carbonmonoxide

\[
\begin{align*}
\text{COOH} + (\text{H}_2\text{SO}_4)(l) & \rightarrow \text{H}_2\text{O} + \text{CO}_2(g) + \text{CO}_2(g) + (\text{H}_2\text{SO}_4)(l) \\
\text{COOH} & \text{Hot Concentrated Sulphuric acid} \\
\end{align*}
\]

**IMPORTANT ORDER AND FACTS OF ORGANIC CHEMISTRY**

1. RCOCl > RCOOOR > RCOOR > RCONH₂ Nucleophilic substitution reaction.
2. HI > HBr > HCl > RCOOH > C₆H₅OH > H₂O > CH≡CH > NH₃ (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.

5. Substitution Reaction

6. Nucleophilic Substitution Reaction

7. \( (\text{C}_2\text{H}_5)\text{Cl} > \text{Cl} - \text{CH}_2 - \text{CH}_2 > \text{CH}_2 > \text{C}_2\text{H}_5\text{Cl} > \text{CH}_2 = \text{Cl} \)

8. \( (\text{C}_2\text{H}_5)\text{Cl} > \text{C}_6\text{H}_5\text{CH}_2 > \text{CH}_2 - \text{CH} = \text{CH}_2 \) (Carbocation stability)

9. \( \text{CH}_2 > \text{CH}_2 - \text{CH} = \text{CH}_2 > \text{C}_2\text{H}_5\text{Cl} > \text{CH}_2 = \text{Cl} \)

10. \( (\text{CH}_3)\text{C} = \text{C}(\text{CH}_3)\text{Cl} > \text{CH}_3 - \text{CH} = \text{C} - (\text{CH}_3)\text{Cl} > \text{CH}_3 - \text{CH} = \text{CH}_3 > \text{CH}_3 - \text{CH} = \text{CH}_3 \) (Stability)

11. \( \text{CH}_2 = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 > \text{CH}_3 - \text{CH} = \text{CH}_2 \\ \text{Heat of Hydration} \)

12. \( \text{NH}_2 > \text{OH} > \text{NH}_3 > \text{H}_2\text{O} \) (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. \( \text{CHCl}_3 \) 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 \( \text{HgSO}_4 \) and \( \text{dil H}_2\text{SO}_4 \).
23. 1-alkynes forms ppt with Ag(NH₃)₂⁺ and Cu(NH₃)₄⁺.

24. Cis-2-butene reacts with Br₂ to form the 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.


26. Chloral reacts with chloro benzene in con. H₂SO₄ to form insecticide DDT.

27. NBS is used for free radical allylation.

28. Rate for S¹ reaction is 3° > 2° > 1° in protic polar solvent.

29. Rate for S² reaction is 1° > 2° > 3° in polar aprotic solvent like DMSO, DMF, HMPT.

30. Chemical reactions like Hoffmann carbylamine and Reimer Tiemann’s reaction active species is biradical CCl₂.

31. If cyclo 1,3-penta diene reacts with CHCl₃ and potassium tert. butoxide to form chlorobenzene.

32. Alkyl halides react with AgCN to form isocyanides due to ambident nature of nucleophile, other ambident nucleophiles are NO₂⁻ and SO₃²⁻.

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

\[
\text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} \xrightarrow{\text{H}^+} \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}
\]

36. Ether's reacts with HI to form alcohol and halide where fission of lower ether by S² mechanism while higher ethers like ter. butyl methyl ether or alkyl methyl ether by S¹ mechanism.

37. Quantitative estimation of ethers is done by ziesal’s method.

38. If unsym. cyclic ether undergo fission it depends upon medium weather it is acid or basic like in acidic medium some character of carbocation so nucleophile goes to carbon where more alkyl groups are there while reverse in basic medium due to steric factor.

39. Aldehydes are reducing agent while ketones are not.

40. Aldehydes and ketones are separated by tolleen’s reagent.

41. Carbonyl and noncarbonyl are separated by sodium bi sulphite and bradye’s reagent.

42. As the size of alkyl group increases steric hindrance comes into play, reactivity towards nucleophilic addition decreases.

43. Aldehydes with \(\text{H}^+\) hydrogen atom in the presence of dil base undergo enolization and form \(\text{H}_2\text{O}\).
44. If there is two-CHO group with \( \ddot{\text{O}} \) hydrogen atom to form cyclic intra aldol product.

45. Aldehydes without \(-\text{hydrogen atom}\) 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 knobengel’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 rearragant is a reaction of oximes in the presence of \( \text{H}_2\text{SO}_4 \) or \( \text{PCl}_5 \) to produce N-alkyl amide derivatives.

51. Migratory attitude of alkyl group in Pinacol-pinacolone, beckmann’s and bayer villegar oxidation is 
\[ \text{C}_6\text{H}_5 > (\text{CH}_3)_2\text{C} \rightarrow (\text{CH}_3)\text{CH} \rightarrow \text{C}_2\text{H}_5 \rightarrow \text{CH}_3 \]

52. Cyclo hexanoneoxime on beckmann’s reaction gives caprolectum which on reaction with \( \dddot{\text{O}} \) to give polymer nylon-6

53. 2-methyl propanal even contains \( \ddot{\text{O}} \)-hydrogen atom but does not give aldol reaction.

54. Diphenyl glyoxal reacts with con. KOH to form salt of benzillic acid.

55. Propanone in the presence of dry HCl gas by enolic intermediate to form diacetone alcohol undergo heating form mesityl oxide. If this again reacts with propanone to form phoron.

56. Benzaldehyde reacts with alc. KCN to form Benzoin which on oxidation form benzil.

57. By wittig reaction carbonyl compounds are converted into E-Z form of alkene.

58. Benzaldehyde do not respond to benedict’s and fehling’s solution due to less redusing power of aromatic aldehyde.

59. HCOOH respond to oxidising agent due to presence of \( \ddot{\text{O}} \) CHO group.

60. \( \text{HI} > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{RCOOH} > \text{H}_3\text{CO}_3 > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH} \equiv \text{CH} > \text{NH}_3 > \text{CH}_3 \cdot \text{C} \equiv \text{CH} > \text{CH}_2 = \text{CH}_2 > \text{H}_2 \) this is decreasing acidic nature.

61. Acids with \( \dddot{\text{O}} \)-hydrogen atom when reacts with halogen in the presence of P to form \( \dddot{\text{O}} \)-haloacid (HVZ).

62. Carboxylic acid on reaction with \( \text{PCl}_5 \), \( \text{CH}_2\text{N}_2 \) and \( \text{H}_2\text{O} \) 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 \( \text{PCl}_5 \) to form alkane nitrile.

65. Anhydride on reaction with carbonyl compound in the presence of base (carbanian) forms \( \dddot{\text{O}}, \beta \)-unsaturated carboxylic acid (perkin reaction)
66. Amide on reaction with Br₂ and alkali to form primary amine of lower homologue. Intermediate species is nitrene which undergo intra rearrangement to form RNH₂.

67. Ester’s with O-hydrogen atom in the presence of strong base to form carbanian undergo nucleophilic substitution reaction forms β-keto ester for example ethyl acetate in the presence of pot. Butoxide form aceto acetic ester (AAE). reaction is known as clesen’s ester condensation of four types

(a) Simple clesen’s ester condensation.
(b) CROSS clesen’s ester condensation.
(c) Intra CEC (Dieckmann’s condensation).
(d) mixed clesen ester condensation.

68. For a compound to be aromatic it must be cyclic, planar and obey (4n + 2) π electron rule.

69. Cyclooctatetraene is non aromatic compound while pyrrole, pyredene, furan, cyclopentadienylanion 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 NaHCO₃.

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. C₆H₅NH₂ > C₆H₅OH > C₆H₅OR > C₆H₅Br > C₆H₅NO₂ (Reactivity towards electrophilic substitution reaction

General Series - Chemistry Fact Sheet - 3

<table>
<thead>
<tr>
<th>General series</th>
<th>Order</th>
<th>Why ?</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.P. of</td>
<td>CH₃CH₂OH, CH₃OCH₃, CH₃CH₂</td>
<td>I &gt; II &gt; III</td>
</tr>
<tr>
<td>I</td>
<td>II</td>
<td>III</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>B.P. of o, m, p-nitro phenol</th>
<th>o &lt; m &lt; p</th>
</tr>
</thead>
</table>
3. Reactivity of ... with Tollen's reagent

\[ \text{HCHO, CH}_2\text{CHO, CH}_2\text{COCH}_3, \text{C}_6\text{H}_5\text{CHO} \]

\[ \text{I > II > IV > III} \]

---CHO group is easily oxidised compared to keto group due to reducing hydrogen.

4. Reactivity of ... with Fehling's solution

\[ \text{I > II > IV > III} \]

5. Extent of hydration of

\[ \text{(I) < (II) < (III) < (IV)} \]

Aldehydes are more hydrated than ketones. Halide makes C of carbonyl group more electropositive.

6. Electrophilic nature of ........ for nucleophilic attack

\[ \text{I > II > III} \]

\[ \text{CH}_3 \text{ group decreases +ve charge on C hence nucleophilic attack.} \]

7. Reactivity of isomeric 1°, 2°, 3° butyl halide towards elimination (E1 or E2)

\[ 3° < 2° < 1° \]

due to stability of intermediate carbocation

8. Dehydration of

\[ \text{(I) < (II) < (III) < (IV)} \]

Alcohol leading to increase in conjugation due to dehydration is more easily dehydrated. IV is vinylic, hence least.

9. Stability of
10. Stability of

\[ \text{I} < \text{III} < \text{II} \]

Substituted alkenes are more stable. More the alkyl groups are attached to the doubly bonded carbon atom more is the stability.

11. Stability of

\[ \text{III} > \text{II} > \text{I} > \text{IV} \]

IV is vinylc while in conjugative, II allylic.

12. Stability of

\[ \text{I} < \text{IV} < \text{II} < \text{III} \]

III is 3° allylic and II is 1° allylic

13. Dehydration of

1°, 2°, 3° isometric butyl alcohol

More the stability of intermediate, greater the reactivity of chemical reaction.

14. Boiling points of

\[ n\text{-butyl amine, } n\text{-butyl alcohol, } n\text{-pentane} \]

II > I > III

15. Formation of

\[ \text{I} > \text{II} > \text{III} > \text{IV} \]

(easiest I)

16. Reactivity of \( \text{C—H} \) bond (abstraction of H)
17. Leaving nature (tendency) of \( \text{...} \) in \( S_N \) reaction.

\[
\begin{align*}
\text{H}^+, & \quad \text{R}^+, \quad \text{MeO}^-, \quad \text{OH}^-, \quad \text{CN}^-, \quad \text{CH}_2\text{COO}^-, \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} & \quad \text{VIII} \\
\text{ROSO}_2^-, & \quad \text{ArSO}_2^- \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} & \quad \text{VIII}
\end{align*}
\]

If acid is strong, its conjugate base is weak and greater the leaving tendency.

18. Rate of esterification of the following acids with \( \text{MeOH} \)

\[
\begin{align*}
\text{MeCH}_2\text{COOH}, & \quad \text{Me}_2\text{CHCOOH}, \quad \text{MeCOCOOH}, \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} \\
\text{EtC} & \quad \text{COOH (I - Pr)}_2 \text{CHCOOH} \\
\text{IV} & \quad \text{V}
\end{align*}
\]

As the size of the substituents on the \( -\text{C} \) increases, the tetrahedrally bonded interme. diate becomes more crowded and these slower the rate.

19. Relative reactivity of \( \ldots \) with electrophile in \( S_N \) reaction

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} & \quad \text{VIII} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{OH} & \quad \text{CH}_3 & \quad \text{H}_2\text{C} \quad \text{CH}_2
\end{align*}
\]

\( -\text{CH}_3 \) is \( \sigma-, \ p- \) directing and responsible for activation.

20. Relative reactivity of these compounds with electrophile in \( S_N \) reaction

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} & \quad \text{VIII} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{NO}_2 & \quad \text{OH} & \quad \text{COOH} & \quad \text{COOH} & \quad \text{COOH}
\end{align*}
\]

\( -\text{CH}_3 \) is \( \sigma-, \ p- \) directing due to activation while \( -\text{COOH} \) is \( m- \) directing and deactivating group.

21. Relative reactivity of \( \ldots \) with electrophile in \( S_N \) reaction.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{I} & \quad \text{II} & \quad \text{III} & \quad \text{IV} & \quad \text{V} & \quad \text{VI} & \quad \text{VII} & \quad \text{VIII} \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{COOH} & \quad \text{OH} & \quad \text{COOH}
\end{align*}
\]

As the number of \( \text{sp}^3 \)-hybridised C
Atoms separating the ring from the positively charged substituent increases, deactivating effect decreases due to less electronegativity.

$I^0$ is best able to donate electrons there by giving a very stable uncharged intermediate. In

\[
\text{CH}_3\text{CO} - \text{cross conjugation diminished its ability to donate electrons to an arenium ion. Intermediates are benzyl cations. So CH}_3\text{O(electron repelling) gives greater stability through delocalisation while NO}_2\text{(electron attracting) decreases stability.}
\]

### 22. Activating effects of the following o, p-directors.

<table>
<thead>
<tr>
<th>Alkyl halide</th>
<th>Relative Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}$</td>
<td>+</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO}$</td>
<td>−</td>
</tr>
</tbody>
</table>

### 23. Relative reactivity of... towards $S_n1$ reaction

<table>
<thead>
<tr>
<th>Alkyl halide</th>
<th>Relative Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzylic chloride</td>
<td>II</td>
</tr>
<tr>
<td>$\text{CH}_3\text{O}$</td>
<td>+</td>
</tr>
<tr>
<td>$\text{CH}_3\text{CO}$</td>
<td>−</td>
</tr>
</tbody>
</table>

### 24. Relative reactivity of... towards $S_n1$ and $S_n2$ reaction

<table>
<thead>
<tr>
<th>Alkyl halide</th>
<th>Relative Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PhCH}_2\text{Cl}$</td>
<td>III</td>
</tr>
<tr>
<td>$\text{PhCH}_2\text{ClMe}$</td>
<td>II</td>
</tr>
<tr>
<td>$\text{PhCClMe}_2$</td>
<td>I</td>
</tr>
</tbody>
</table>

### 25. Relative reactivity of... with $E^+$ (electrophile) in $S_e$ reaction.

<table>
<thead>
<tr>
<th>Alkyl halide</th>
<th>Relative Reactivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PhCH}_2\text{Cl}$</td>
<td>III</td>
</tr>
<tr>
<td>$\text{PhCH}_2\text{ClMe}$</td>
<td>II</td>
</tr>
<tr>
<td>$\text{PhCClMe}_2$</td>
<td>I</td>
</tr>
</tbody>
</table>

$S_n1 : 1^+ < 2^+ < 3^+$
$S_n2 : 3^- < 2^- < 1^-$
26. Order of $\text{Sn}_2$ reactivity of alkoxide nucleophiles:

$\text{Me}_3\text{CO}^-$, $\text{MeO}^-$, $\text{MeCH}_2\text{O}^-$, $\text{Me}_2\text{CHO}^-$

$I < IV < V < III < II$

$\text{Sn}_2$ reactivity is susceptible to steric hindrance by the nucleophile as well as by the size of alkyl group.

Basic power - Chemistry Fact Sheet - 2

<table>
<thead>
<tr>
<th>Basic Power</th>
<th>Order</th>
<th>Why?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>$I &gt; III &gt; II$</td>
<td>lone pair on N is not used in resonance of $\pi$-electrons in I. In II lone pair of the ring is itself used in delocalisation while that of outside ring in III. $-\text{OCH}_3$ is strong electron donating group. This is due to ortho effect, all the aniline are less basic than $p$-substituted aniline due to steric hindrance. I (hyperconjugation and induction) II (induction) IV (ortho effect), ortho effect normally decreases basic nature.</td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>$I &gt; II &gt; III &gt; IV$</td>
<td></td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td>(I)</td>
<td>(II)</td>
<td>(III)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 \(\pi\)-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
phenyl and \(-\text{COCH}_3\) are electron-withdrawing and \(-\text{C}_6\text{H}_5 < \text{COCH}_3\)

7. III > I > II
Electron donating nature of \(\text{C}_2\text{H}_5 > \text{CH}_3\) So more basic strength.

8. I < II < III
9. 
\[
\begin{array}{c}
\text{(I)} & \text{Cl} & \text{NH}_2 \\
\text{(II)} & \text{Cl} & \text{NH}_2 \\
\text{(III)} & \text{Cl} & \text{NH}_2 \\
\end{array}
\]
\(I < II < III\) ortho effect in (I).

10. 
\[
\begin{array}{c}
\text{(I)} & \text{NH}_2 & \text{NH}_2 \\
\text{(II)} & \text{NH}_2 & \text{NH}_2 \\
\text{(III)} & \text{NH}_2 & \text{NH}_2 \\
\end{array}
\]
\(I < II < III\) ortho effect in (I).

### Acidic Powers & Their Orders - Chemistry Fact Sheet

<table>
<thead>
<tr>
<th>Acidic power</th>
<th>Order</th>
<th>Why?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 1-, 2-, 3- chlorobutanoic acid</td>
<td>I, II, III</td>
<td>(III &lt; II &lt; I) Farther the (-I) group (Cl), lesser the acidic strength</td>
</tr>
<tr>
<td>2. 1-, 2-, 3- methylpentanoic acid</td>
<td>I, II, III</td>
<td>(I &lt; II &lt; III) Farther the (+I) group, greater the acidic power</td>
</tr>
<tr>
<td>3. (\text{OH} \quad \text{OH} \quad \text{OH} \quad \text{NO}_2)</td>
<td>I, II, III</td>
<td>(II &lt; I &lt; III) (-\text{CH}_3) is electron donating and (-\text{NO}_2) is electron attracting</td>
</tr>
<tr>
<td>4. (\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3)</td>
<td>I, II, III</td>
<td>(II &lt; I &lt; III) (-\text{CH}_3) is electron repelling; decreases acidic strength of phenol</td>
</tr>
<tr>
<td>5. (\text{OCH}_3 \quad \text{OCH}_3 \quad \text{OCH}_3)</td>
<td>I, II, III</td>
<td>(III &lt; I &lt; II) (-\text{OCH}_3) group contains +M effect and decreases acidic power.</td>
</tr>
</tbody>
</table>
6. 

\[
\begin{align*}
&\text{I} \quad \text{II} \quad \text{III} \\
&\text{(OH)} \quad \text{(NO}_2\text{)} \quad \text{(OH)} \\
&\begin{array}{c}
\text{(I)} \\
\text{(II)} \\
\text{(III)}
\end{array}
\end{align*}
\]

\(\text{NO}_2\) is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative. \(\text{sp}^2\) hybridised carbon of I, II are more electronegative hence acid strength is increased. Benzylic (\(\text{C}_6\text{H}_5\text{CH}_2\)) is more stabilised than allylic (\(\text{CH}_2\text{==CHCH}_2\)). Effect of one \(-\text{COOH}\) on the other decreases as its distance between them increases, \((\text{COOH})_2\) is maximum acidic.

7. 

\[
\begin{align*}
&\text{I} \quad \text{II} \quad \text{III} \\
&\text{CH}_2\text{COOH} \quad \text{CH}_2\text{==CHCH}_2\text{COOH} \quad \text{CH}_2\text{==CHCH}_2\text{COOH} \\
&\begin{array}{c}
\text{(I)} \\
\text{(II)} \\
\text{(III)}
\end{array}
\end{align*}
\]

\text{oxalic acid, succinic acid, malonic acid, adipic acid} \\
I \quad II \quad III

\text{I > II > III}

8. 

\text{adipic acid} \quad \text{(all dibasic)} \\
\text{IV}

\text{I > II > III > IV}

9. 

\[
\begin{align*}
&\text{I} \quad \text{II} \quad \text{III} \\
&\text{o-nitrobenzoic acid} \\
&\begin{array}{c}
\text{(I)} \\
\text{(II)} \\
\text{(III)}
\end{array}
\end{align*}
\]

\text{II < III < I}

10. 

\[
\begin{align*}
&\text{I} \quad \text{II} \quad \text{III} \\
&\text{o-hydroxy benzoic acid} \\
&\begin{array}{c}
\text{(I)} \\
\text{(II)} \\
\text{(III)}
\end{array}
\end{align*}
\]

\text{III < II < I}

\text{NO}_2\text{ is electron attracting; }\text{o- isomer due to intramolecular bonding in salicylate ion is stronger than }\text{m- isomer}
11. \( o\)-m-\( p\)-methoxy benzoic acid  
\( I \) \( II \) \( III \)  
\( III < II < I \) —do—

12. \( o\)-m-\( p\)-amino benzoic acid  
\( I \) \( II \) \( III \)  
\( I < III < II \) —\( \text{NH}_2 \) is electron donating.

---

**Topic wise grouping of information kind of Dictionary of Inorganic Chemistry**

---

Given two Equations

(1) \( \text{B}_2\text{O}_3 + 6\text{NaOH} \rightarrow (\text{X}) + 3\text{H}_2\text{O} \)

(2) \( \text{B}_2\text{O}_3 + 2\text{NaOH} \rightarrow (\text{Y}) + \text{H}_2\text{O} \)

What are (\( \text{X} \)) and (\( \text{Y} \))?

Ans: \( \text{X} \) is Sodium Borate and \( \text{Y} \) is Sodium meta borate

\( \text{B}_2\text{O}_3 + 6\text{NaOH} \rightarrow 2\text{Na}_3\text{BO}_3 \) (Sodium Borate) + 3\text{H}_2\text{O}

\( \text{B}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaBO}_2 \) (Sodium metaborate) + \text{H}_2\text{O}
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)

\( \text{K}_3\text{Co(NO}_2)_6 \) is Fischer’s Salt

The brown ring test for NO\(_3^-\) is due to formation of the complex \([\text{Fe(H}_2\text{O})_5\text{NO}]^{2+}\)

Merck’s perhydrol is 30.4% \( \text{H}_2\text{O}_2 \)

\( \text{H}_2\text{SO}_3 \), \( \text{H}_2\text{S}_2\text{O}_8 \) have peroxide linkages
Bromine reacting with NaOH in cold and hot give different mix of products. Specify

\[ \text{Br}_2 + 2\text{NaOH (cold)} \rightarrow \text{NaBr} + \text{NaOBr} + \text{H}_2\text{O} \]

\[ 3\text{Br}_2 + 6\text{NaOH (hot)} \rightarrow 5\text{NaBr} + \text{NaBrO}_3 + 3\text{H}_2\text{O} \]
Malachite decomposes to give $A + CO_2 + H_2O$ and compound $A$ on reduction with Carbon gives $CO + B$

Identify $A$ and $B$

Solution : $CuCO_3, Cu(OH)_2 \rightarrow 2CuO (A) + CO_2 + H_2O$

$CuO + C \rightarrow Cu (B) + CO$

Some examples of Complex Anions

$K_2PtCl_6 \leftrightarrow 2K^+ + [PtCl_6]^{2-}$

$Na_3AlF_6 \leftrightarrow 3Na^+ + AlF_6^{-3}$

$K_2SiF_6 \leftrightarrow 2K^+ + SiF_6^{-2}$
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)**

Microcosmic Salt is $Na(NH_4)HPO_4$ Sodium ammonium hydrogen phosphate
Which of the following electrolyte will be most effective in coagulation of gold sol?

(1) NaNO₃ (2) K₄Fe(CN)₆ (3) Na₃PO₄ (4) MgCl₂

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) Mg²⁺ ion has highest valency so MgCl₂ is most effective.

Organometallic compounds are Metal atoms directly linked with Carbon. So Ti(OC₃H₇)₄ is not an organometallic compound.
IUPAC name of Diamminetetraaquacobalt III chloride

As per IUPAC nomenclature, the name of the complex \([\text{Co(H}_2\text{O})_4(\text{NH}_3)_2]\text{Cl}_3\) is

(a) Tetraaquadiminecobalt(III) chloride  
(b) Tetraaquadiminecobalt(III) chloride  
(c) Diaminetetraaquacobalt(III) chloride  
(d) Diaminetetraaquacobalt(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. \(\text{NH}_3\) is named as ammine and not as amine. Hence, the IUPAC name of the given compound is Diaminetetraaquacobalt(III) chloride.

Therefore, the choice (d) is correct.

---

Color of light absorbed by aqueous solution of \(\text{CuSO}_4\)

The colour of light absorbed by an aqueous solution of \(\text{CuSO}_4\) is

(a) orange-red  
(b) blue-green  
(c) yellow  
(d) violet

**Solution:**

An aqueous solution of \(\text{CuSO}_4\) 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.
Temperature dependent Magnetic behaviour

\( \text{NiCl}_2(\text{P(C}_2\text{H}_5)_3(\text{C}_6\text{H}_5)_2)_2 \) exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of \( \text{Ni}^{2+} \) in the paramagnetic and diamagnetic states are respectively

(a) tetrahedral and tetrahedral  (b) square planar and square planar
(c) tetrahedral and square planar  (d) square planar and tetrahedral.

**Solution:**

In the paramagnetic state, the complex will have unpaired 3d electrons in \( \text{Ni}^{2+} \) ion, whereas no such electrons (i.e. all the 3d electrons will be paired) are present in the diamagnetic state.

The electronic configuration of \( _{28}^3\text{Ni}^{2+} \) is

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\downarrow \\
\uparrow \\
\hline
3d \\
4s \\
4p
\end{array}
\]

If the two unpaired electrons remain present in the ion, it will undergo sp³ hybridization to accommodate ligands and the geometry of the complex ion will be tetrahedral.

If the two unpaired electrons are coupled, the ion will be diamagnetic and it can undergo dsp³ hybridization to accommodate ligands leading to the square planar geometry to the complex ion.

Therefore, the choice (c) is correct.
Reaction of white phosphorus with aqueous NaOH

The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type, the oxidation states of phosphorus in phosphine and the other product, respectively, are

(a) redox reaction, -3 and -5  (b) redox reaction, 3 and +5  
(c) disproportionation reaction, -3 and +5  (e) disproportionation reaction, -3 and +3

**Solution:**

$$\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$$

The salt NaH$_2$PO$_2$ undergoes the following changes on heating.

$$4\text{NaH}_2\text{PO}_2 \rightarrow \text{Na}_4\text{P}_2\text{O}_7 + 2\text{PH}_3 + \text{H}_2\text{O}$$

The reaction is disproportionation reaction and the oxidation states of phosphorus are -3 (in phosphine) and +5 in the second product.

Therefore, the choice (c) is correct.

Generally the stabilities of complexes decreases with increasing atomic number for the electropositive metals e.g. group IIA or hard Lewis acids, and increase with increasing atomic number for the noble metals (soft acids), following the general trend of ionization energy.

(a) For electropositive metals (hard acids) the order of stabilities of the Halide complexes F > Cl > Br > I but for highly polarizing soft acid metal ions such as Hg$^{+2}$, we see the reverse order.

(b) The most electropositive metals (hardest acids) show a greater tendency of forming complexes, with hard ligands such as F⁻ or Oxygen containing ligands.
Metals are classified according to their acceptor properties.

**Class A** - Hard Acids. Show affinities to ligands whose basicity is proportional to protons.

**Class B** - Soft acids form stable olefin complexes.

**Class C** - Borderline metals
cyanide extraction process of silver from argentite ore

In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are
(a) $O_2$ and CO, respectively  
(b) $O_2$ and Zn dust, respectively
(c) HNO₃ and Zn, respectively  
(d) HNO₃ and CO, respectively

Solution:
The argentite ore contains Ag₂S. After crushing and concentration by froth flotation process, the ore is leached with 0.4 – 7% solution of sodium cyanide kept agitated with a current of air.
Silver passes into the solution as argentocyanide. \[ \text{Ag}_2\text{S} + 4\text{NaCN} \rightleftharpoons 2\text{Na} \left[ \text{Ag(CN)}_2 \right] + \text{Na}_2\text{S} \]
The air blown removes Na$_2$S as Na$_2$S$_2$O$_3$ and Na$_2$SO$_4$ causing the above reaction to proceed to completion. Silver is recovered by adding zinc into argentocyanide. \[ 2\text{Ag(CN)}_2^- + \text{Zn} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2\text{Ag} \]
Thus, oxidizing agent is O$_2$ (from air) and the reducing agent is Zn.
Therefore, the choice (b) is correct.
<table>
<thead>
<tr>
<th>Common Name</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>acetone</td>
<td>dimethyl ketone; 2-propanone (usually known as acetone)</td>
</tr>
<tr>
<td>acid potassium sulfate</td>
<td>potassium bisulfate</td>
</tr>
<tr>
<td>acid of sugar</td>
<td>oxalic acid</td>
</tr>
<tr>
<td>ackey</td>
<td>nitric acid</td>
</tr>
<tr>
<td>alcali volatil</td>
<td>ammonium hydroxide</td>
</tr>
<tr>
<td>alcohol, grain</td>
<td>ethyl alcohol</td>
</tr>
<tr>
<td>alcohol sulfuris</td>
<td>carbon disulfide</td>
</tr>
<tr>
<td>alcohol, wood</td>
<td>methyl alcohol</td>
</tr>
<tr>
<td>alum</td>
<td>aluminum potassium sulfate</td>
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<tr>
<td>alumina</td>
<td>aluminum oxide</td>
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<tr>
<td>antichlor</td>
<td>sodium thiosulfate</td>
</tr>
<tr>
<td>antimony black</td>
<td>antimony trisulfide</td>
</tr>
<tr>
<td>antimony bloom</td>
<td>antimony trioxide</td>
</tr>
<tr>
<td>antimony glance</td>
<td>antimony trisulfide</td>
</tr>
<tr>
<td>antimony red (vermillion)</td>
<td>antimony oxysulfide</td>
</tr>
<tr>
<td>aqua ammonia</td>
<td>aqueous solution of ammonium hydroxide</td>
</tr>
<tr>
<td>aqua fortis</td>
<td>nitric acid</td>
</tr>
<tr>
<td>aqua regia</td>
<td>nitrohydrochloric acid</td>
</tr>
<tr>
<td>aromatic spirit of ammonia</td>
<td>ammonia in alcohol</td>
</tr>
<tr>
<td>arsenic glass</td>
<td>arsenic trioxide</td>
</tr>
<tr>
<td>azurite</td>
<td>mineral form of basic copper carbonate</td>
</tr>
<tr>
<td>asbestos</td>
<td>magnesium silicate</td>
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<tr>
<td>aspirin</td>
<td>acetylsalicylic acid</td>
</tr>
<tr>
<td>baking soda</td>
<td>sodium bicarbonate</td>
</tr>
<tr>
<td>banana oil (artificial)</td>
<td>isoamyl acetate</td>
</tr>
<tr>
<td>barium white</td>
<td>barium sulfate</td>
</tr>
<tr>
<td>benzol</td>
<td>benzene</td>
</tr>
<tr>
<td>bicarbonate of soda</td>
<td>sodium hydrogen carbonate or sodium bicarbonate</td>
</tr>
<tr>
<td>bichloride of mercury</td>
<td>mercuric chloride</td>
</tr>
<tr>
<td>bichrome</td>
<td>potassium dichromate</td>
</tr>
<tr>
<td>bitter salt</td>
<td>magnesium sulfate</td>
</tr>
<tr>
<td>black ash</td>
<td>crude form of sodium carbonate</td>
</tr>
<tr>
<td>Black Copper Oxide</td>
<td>Cupric Oxide</td>
</tr>
<tr>
<td>---------------------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Black Lead</td>
<td>Graphite (Carbon)</td>
</tr>
<tr>
<td>Blanc-Fixe</td>
<td>Barium Sulfate</td>
</tr>
<tr>
<td>Bleaching Powder</td>
<td>Chlorinated Lime; Calcium Hypochlorite</td>
</tr>
<tr>
<td>Blue Copperas</td>
<td>Copper Sulfate (Crystals)</td>
</tr>
<tr>
<td>Blue Lead</td>
<td>Lead Sulfate</td>
</tr>
<tr>
<td>Blue Salts</td>
<td>Nickel Sulfate</td>
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<tr>
<td>Blue Stone</td>
<td>Copper Sulfate (Crystals)</td>
</tr>
<tr>
<td>Blue Vitriol</td>
<td>Copper Sulfate</td>
</tr>
<tr>
<td>Bluestone</td>
<td>Copper Sulfate</td>
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<tr>
<td>Bone Ash</td>
<td>Crude Calcium Phosphate</td>
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<tr>
<td>Bone Black</td>
<td>Crude Animal Charcoal</td>
</tr>
<tr>
<td>Boracic Acid</td>
<td>Boric Acid</td>
</tr>
<tr>
<td>Borax</td>
<td>Sodium Borate; Sodium Tetraborate</td>
</tr>
<tr>
<td>Bremen Blue</td>
<td>Basic Copper Carbonate</td>
</tr>
<tr>
<td>Brimstone</td>
<td>Sulfur</td>
</tr>
<tr>
<td>Burnt Alum</td>
<td>Anhydrous Potassium Aluminum Sulfate</td>
</tr>
<tr>
<td>Burnt Lime</td>
<td>Calcium Oxide</td>
</tr>
<tr>
<td>Burnt Ochre</td>
<td>Ferric Oxide</td>
</tr>
<tr>
<td>Burnt Ore</td>
<td>Ferric Oxide</td>
</tr>
<tr>
<td>Brine</td>
<td>Aqueous Sodium Chloride Solution</td>
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<tr>
<td>Butter of Antimony</td>
<td>Antimony Trichloride</td>
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<tr>
<td>Butter of Tin</td>
<td>Anhydrous Stannic Chloride</td>
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<tr>
<td>Butter of Zinc</td>
<td>Zinc Chloride</td>
</tr>
<tr>
<td>Calomel</td>
<td>Mercury Chloride; Mercurous Chloride</td>
</tr>
<tr>
<td>Carbolic Acid</td>
<td>Phenol</td>
</tr>
<tr>
<td>Carbonic Acid Gas</td>
<td>Carbon Dioxide</td>
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<tr>
<td>Caustic Lime</td>
<td>Calcium Hydroxide</td>
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<tr>
<td>Caustic Potash</td>
<td>Potassium Hydroxide</td>
</tr>
<tr>
<td>Caustic Soda</td>
<td>Sodium Hydroxide</td>
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<tr>
<td>Chalk</td>
<td>Calcium Carbonate</td>
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<tr>
<td>Chile Saltpeter</td>
<td>Sodium Nitrate</td>
</tr>
<tr>
<td>Chile Nitre</td>
<td>Sodium Nitrate</td>
</tr>
</tbody>
</table>
Chinese red basic lead chromate
Chinese white zinc oxide
chloride of soda sodium hypochlorite
chloride of lime calcium hypochlorite
chrome alum chromic potassium sulfate
chrome green chromium oxide
chrome yellow lead (VI) chromate
chromic acid chromium trioxide
copperas ferrous sulfate
corrosive sublimate mercury (II) chloride
corundum (ruby, sapphire) chiefly aluminum oxide
cream of tartar potassium bitartrate
crocus powder ferric oxide
crystal carbonate sodium carbonate
dechlor sodium thiophosphate
diamond carbon crystal
emery powder impure aluminum oxide
epsom salts magnesium sulfate
ethanol ethyl alcohol
farina starch
ferro prussiate potassium ferricyanide
ferrum iron
flores martis anhydride iron (III) chloride
fluorspar natural calcium fluoride
fixed white barium sulfate
flowers of sulfur sulfur
'flowers of' any metal oxide of the metal
formalin aqueous formaldehyde solution
French chalk natural magnesium silicate
French vergidris basic copper acetate
galena natural lead sulfide
Glauber's salt sodium sulfate
green verditer basic copper carbonate
green vitriol    ferrous sulfate crystals
 gypsum         natural calcium sulfate
 hard oil       boiled linseed oil
 heavy spar     barium sulfate
 hydrocyanic acid hydrogen 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 sulfured potash
 lye or soda lye sodium hydroxide
 magnesia       magnesium oxide
 manganese black manganese dioxide
 marble         mainly calcium carbonate
 mercury oxide, black mercurous oxide
 methanol       methyl alcohol
 methylated spirits methyl alcohol
 milk of lime   calcium hydroxide
 milk of magnesium magnesium hydroxide
 milk of sulfur precipitated sulfur
 "muriate" of a metal chloride of the metal
 muriatic acid  hydrochloric acid
natron  sodium carbonate
nitre  potassium nitrate
nordhausen acid  fuming sulfuric acid
oil of mars  deliquescent anhydrous iron (III) chloride
oil of vitriol  sulfuric acid
oil of wintergreen (artificial)  methyl salicylate
orthophosphoric acid  phosphoric acid
Paris blue  ferric ferrocyanide
Paris green  copper acetoarsenite
Paris white  powdered calcium carbonate
pear oil (artificial)  isoamyl acetate
pearl ash  potassium carbonate
permanent white  barium sulfate
plaster of Paris  calcium sulfate
plumbago  graphite
potash  potassium carbonate
potassa  potassium hydroxide
precipitated chalk  calcium carbonate
Prussic acid  hydrogen cyanide
pyro  tetrasodium pyrophosphate
quicklime  calcium oxide
quicksilver  mercury
red lead  lead tetraoxide
red liquor  aluminum acetate solution
red prussiate of potash  potassium ferrocyanide
red prussiate of soda  sodium ferrocyanide
Rochelle salt  potassium sodium tartrate
rock salt  sodium chloride
rouge, jeweler's  ferric oxide
rubbing alcohol  isopropyl alcohol
sal ammoniac  ammonium chloride
sal soda  sodium carbonate
salt, table  sodium chloride
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<thead>
<tr>
<th>Substance</th>
<th>Chemical Formula</th>
</tr>
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<tbody>
<tr>
<td>salt of lemon</td>
<td>potassium binoxalate</td>
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<tr>
<td>salt of tartar</td>
<td>potassium carbonate</td>
</tr>
<tr>
<td>saltpeter</td>
<td>potassium nitrate</td>
</tr>
<tr>
<td>silica</td>
<td>silicon dioxide</td>
</tr>
<tr>
<td>slaked lime</td>
<td>calcium hydroxide</td>
</tr>
<tr>
<td>soda ash</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>soda nitre</td>
<td>sodium nitrate</td>
</tr>
<tr>
<td>soda lye</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>soluble glass</td>
<td>sodium silicate</td>
</tr>
<tr>
<td>sour water</td>
<td>dilute sulfuric acid</td>
</tr>
<tr>
<td>spirit of hartshorn</td>
<td>ammonium hydroxide solution</td>
</tr>
<tr>
<td>spirit of salt</td>
<td>hydrochloric acid</td>
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<td>spirit of wine</td>
<td>ethyl alcohol</td>
</tr>
<tr>
<td>spirits of nitrous ether</td>
<td>ethyl nitrate</td>
</tr>
<tr>
<td>sugar, table</td>
<td>sucrose</td>
</tr>
<tr>
<td>sugar of lead</td>
<td>lead acetate</td>
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<tr>
<td>sulfuric ether</td>
<td>ethyl ether</td>
</tr>
<tr>
<td>talc or talcum</td>
<td>magnesium silicate</td>
</tr>
<tr>
<td>tin crystals</td>
<td>stannous chloride</td>
</tr>
<tr>
<td>trona</td>
<td>natural sodium carbonate</td>
</tr>
<tr>
<td>unslaked lime</td>
<td>calcium oxide</td>
</tr>
<tr>
<td>Venetian red</td>
<td>ferric oxide</td>
</tr>
<tr>
<td>verdigris</td>
<td>basic copper acetate</td>
</tr>
<tr>
<td>Vienna lime</td>
<td>calcium carbonate</td>
</tr>
<tr>
<td>vinegar</td>
<td>impure dilute acetic acid</td>
</tr>
<tr>
<td>vitamin C</td>
<td>ascorbic acid</td>
</tr>
<tr>
<td>vitriol</td>
<td>sulfuric acid</td>
</tr>
<tr>
<td>washing soda</td>
<td>sodium carbonate</td>
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<td>water glass</td>
<td>sodium silicate</td>
</tr>
<tr>
<td>white caustic</td>
<td>sodium hydroxide</td>
</tr>
<tr>
<td>white lead</td>
<td>basic lead carbonate</td>
</tr>
<tr>
<td>white vitriol</td>
<td>zinc sulfate crystals</td>
</tr>
<tr>
<td>yellow prussiate of potash</td>
<td>potassium ferrocyanide</td>
</tr>
</tbody>
</table>
yellow prussiate of soda  sodium ferrocyanide
zinc vitriol        zinc sulfate
zinc white         zinc oxide

Westron - A refrigerant. $\text{C}_2\text{H}_2\text{Cl}_4$

Colours of Compounds

**Cr}_2(\text{SO}_4)_3 - green**

![Cr2(SO4)3](image)

**PbS - Black**

![PbS](image)

**[Fe(H2O)5NO]SO4 - brown**

![Fe(H2O)5NO]SO4](image)

**(CH3COO)3Fe - blood red**

![Fe(C2H3O2)3](image)
NH₄Cl - white fumes

AgCl - curdy white precipitate

AgCl + NH₄OH → Ag(NH₃)₂Cl + H₂O

CrO₃ + HCl → CrO₂Cl₂ (deep red fumes) + H₂O
NaOH + CrO₂Cl₂ → Na₂CrO₄ (yellow) + NaCl + H₂O

Na₂CrO₄ (yellow) + Pb(CH₃COO)₂ → PbCrO₄ (yellow) + CH₃COONa

NaBr + AgNO₃ → AgBr (pale yellow) + NaNO₃
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.
NaI + AgNO₃ → AgI (yellow ppt) + NaNO₃

Cu + HNO₃ → Cu(NO₃)₂ + NO₂ + H₂O

Cu(NO₃)₂

NO₂

H₃BO₃ + C₂H₅OH → (C₂H₅)₃BO₃ + H₂O (greenish flame)

H₃PO₄ + 12(NH₄)₂MoO₄ + HNO₃ → (NH₄)₃.PO₄.12MoO₃ (canary yellow) + 21 NH₄NO₃ + 12 H₂O
In the presence of Arsenic, we get yellow precipitate of (NH₄)₃.AsO₄.12MoO₃ (ammonium arsenomolybdate)

Mo₃O₈.xH₂O - molybdenum blue

SiF₄ + H₂O → H₄SiO₄ (silicic acid - white) + H₂SiO₄
Na₂S + Na₂[Fe(CN)₅NO] → Na₄[Fe(CN)₅NOS) - violet colour

Na₂S + CdCO₃ → CdS (yellow) + Na₂CO₃

Na₃[Co(NO₂)₆] + KCl → K₃[Co(NO₂)₆] (potassium cobalt nitrate - yellow ppt) + NaCl

AgCl, PbCl₂, Hg₂Cl₂ - white
PbCl$_2$ is white

Hg$_2$Cl$_2$ is white

H$_2$S, PbS, Bi$_2$S$_3$, CuS - black

H$_2$S is Black
PbS is Black

Bi₂S₃ is Black

CuS - black

CdS, As₂S₃, SnS₂ - Yellow

CdS is Yellow

As₂S₃ is Yellow
SnS₂ is Yellow

Sb₂S₃ is orange
SnS is Brown

Cr(OH)₃ is green

Chromium (III) Oxide is Green

CoS, NiS - black

CoS is black
NiS is Black Mineral Millerite

Cobalt Oxide is Black

Cobalt Sulphate is deep red brown
Cobalt Nitrate is deep red brown

Cobalt Chloride is deep Brown red

Cobalt Acetate is deep Brown

Azulene - Deep Bue

Iodoform - CHI₃ Yellow

Iron Phenol complex - Violet - [ Fe ( OC₆H₅)₉ ]³⁻

6 C₆H₂OH + FeCl₃ → [ Fe ( OC₆H₅)₉ ]³⁻ + 3 H⁺ + Cl⁻

Ammonium Phosphomolybdate - Yellow - (NH₄)₃PO₄.12MoO₃ (Yellow)

Prussian Blue - Fe₄[Fe(CN)₆]₃.xH₂O

[Fe(CN)₃NOS ]⁴⁻ - Violet

[Fe(SCN)]²⁺ Blood Red

[Co(NH₃)₅Br]²⁺ SO₄²⁻ - Violet - Pentaaminebromocobalt(III)sulphate
Test for Halogen:

Halogens present in an organic compound form 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. HNO₃.

If chlorine is present, a white curdy precipitate soluble in ammonium hydroxide solution is formed.

\[
\text{Na} + \text{Cl} \rightarrow \text{NaCl}
\]

\[
\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3
\]

If bromine is present, an yellowish white precipitate sparingly soluble in ammonium hydroxide solution is formed.

\[
\text{Na} + \text{Br} \rightarrow \text{NaBr}
\]

\[
\text{NaBr} + \text{AgNO}_3 \rightarrow \text{AgBr} + \text{NaNO}_3
\]

If iodine is present, an yellow precipitate insoluble in ammonium hydroxide solution is formed.

\[
\text{Na} + \text{I} \rightarrow \text{NaI}
\]

\[
\text{NaI} + \text{AgNO}_3 \rightarrow \text{AgI} + \text{NaNO}_3
\]

Test for Nitrogen:

The carbon and nitrogen present in the organic compound on fusion with sodium metal gives sodium cyanide (NaCN) soluble in water. This is converted into 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.

\[
\text{Na} + \text{C} + \text{N} \rightarrow \text{NaCN}
\]

\[
6\text{NaCN} + \text{FeSO}_4 \rightarrow \text{Na}_4[\text{Fe(CN)}_6] + \text{Na}_2\text{SO}_4
\]

**Sodium ferrocyanide**

\[
\text{Na}_4[\text{Fe(CN)}_6] + \text{Fe}^{3+} \rightarrow \text{Fe}_3[\text{Fe(CN)}_6]_3
\]

**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.

\[
\text{Na} + \text{S} \rightarrow \text{Na}_2\text{S}
\]

\[
\text{Na}_2\text{S} + \text{Na}_2\text{[Fe(CN)NO]} \rightarrow \text{Na}_4\text{[Fe(CN)NOS]}
\]

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 \(\text{Fe}^{3+}\) to form blood colour complex \([\text{Fe(SCN)}]^2+\)

\[
\text{Na} + \text{C} + \text{N} + \text{S} \rightarrow \text{NaSCN}
\]

\[
\text{Fe}^{3+} + 2\text{Na} \rightarrow [\text{Fe(SCN)}]^2+
\]

Note: If the Lassaigne's extract containing excess of sodium metal, sodium cyanide and sulphides are formed instead of sodium thiocyanate.

\[
\text{NaSCN} + 2\text{Na} \rightarrow \text{NaCN} + \text{Na}_2\text{S}
\]

Here in this type of cases, both sulphur and nitrogen are to be identified in separate tests.
BaCO₃, SrCO₃, CaCO₃, Mg(NH₄)PO₄ - white

BaCO₃ is white

SrCO₃ is white

CaCO₃ powder is white
Mg(NH₄)PO₄ is white

Pentaamminechlorocobalt(III)Bromide

\[
[\text{Co(NH₃)₅Cl}] Cl₂
\]

Pentaamminechlorocobalt(III)chloride

Pentaamminesulphatocobalt(III)Bromide

- Dark Yellow
- Pale Yellow
The hapticity of a ligand is described with the Greek letter η ('eta'). For example, η2 describes a ligand that coordinates through 2 contiguous atoms. In general the η-notation only applies when multiple atoms are coordinated (otherwise the κ-notation is used). In addition, if the ligand coordinates through multiple atoms that are not contiguous then this is considered denticity (not hapticity), and the κ-notation is used once again. Lastly, bridging ligands are described with the μ ('mu') notation.

Ferrocene - bis(η5-cyclopentadienyli)ron

Uranocene - bis(η8-1,3,5,7-cyclooctatetraene)uranium
W(CO)₃(PPri₃)₂(η₂-H₂) - the first compound to be synthesized with a dihydrogen ligand (also known as Dihydrogen Complexes).

IrCl(CO)[P(C₆H₅)₃]₂(η₂-O₂) - the dioxygen derivative which forms reversibly upon oxygenation of Vaska’s complex.

Chromium (III) chloride is purple.

HgCl₂ + NH₄OH → (Hg + Hg(NH₂)Cl) + NH₄Cl + H₂O
black ppt

BiCl₃ + H₂O → BiOCl (white) + HCl

Bi(OH)₃ Bismuth Hydroxide is white
Oxidation of Phenol

**Test of Phenol**

With Neutral FeCl₃, Phenol on reaction with neutral ferric chloride gives violet colour of ferric phenoxide

\[
\text{C₆H₅OH} + \text{FeCl₃} \rightarrow \text{(C₆H₅O)₃Fe} \quad \text{Violet colour}
\]

\[
\text{Cu(NO₃)₂} + \text{K₄[Fe(CN)₆]} \rightarrow \text{Cu₂[Fe(CN)₆]} \quad \text{(Chocolate brown)} + \text{KNO₃}
\]

\[
\text{Cd(NH₃)₄(NO₃)₂} + \text{H₂S} \rightarrow \text{CdS} \quad \text{(yellow)} + \text{NH₄NO₃} + \text{NH₃}
\]
HgCl₂ + SnCl₂ → Hg₂Cl₂ (white) + SnCl₄

SbCl₃ + H₂O → SbOCl (white) + HCl

SbOCl Antimony oxychloride
**Antimony Trioxide** is white

![Antimony Trioxide](image1)

**Antimony Pentoxide** is gray

![Antimony Pentoxide](image2)

**Antimony Trichloride** is white

![Antimony Trichloride](image3)
Potassium antimonate white

FeCl₃ + KSCN -> Fe(CNS)₃ (blood red) + KCN

Can Test
Treat a few drops of ceric ammonium nitrate with 3-4 ml of hot aqueous solution of the organic compound. A green or brown precipitate is formed.

\[
\text{(NH}_4\text{)}_2\text{[Ce(NO}_3\text{)}_4] + 2\text{C}_6\text{H}_5\text{OH} \rightarrow [\text{Ce(NO}_3\text{)}_4(\text{C}_6\text{H}_5\text{OH})_2] + 2\text{NH}_4\text{NO}_3
\]

Phenol green or brown ppt.
Phenol gives blue colour with ammonia and sodium hypo chlorite.

ZnCl₂ + 2NaOH -> Zn(OH)₂ (white ppt) + 2NaCl
Zn(OH)₂ + NaOH → Na₂ZnO₂ (soluble) + H₂O

Na₂ZnO₂ + H₂S → ZnS (white) + NaOH

Mn(NO₃)₂ + Pb₃O₄ + HNO₃ → HMnO₄ (pink) + Pb(NO₃)₂ + H₂O
Co(NO₂)₃ + KNO₂ → K₃[Co(NO₂)₆] (yellow)

Na₄Co(CO₃)₂ + H₂O + [O] → Na₃Co(CO₃)₂ (green coloration) + NaOH
NiCO₃ + [O] → Ni₂O₃ (black) + CO₂

MgCl₂ + Na₂HPO₄ + NH₄OH → Mg(NH₄)PO₄ (white) + NaCl + H₂O

magnesium ammonium phosphate
K₂HgI₄ + NH₄Cl + KOH → NH₂HgOHgI (Iodide of millon’s base, brown ppt) + KCl + H₂O

Chromium oxide powder is green

Bismuth oxide is Yellow

KI Potassium iodide is white
Tin reacts with conc. HNO$_3$ forming metastannic acid (H$_2$SnO$_3$).

Tin is not attacked by organic acids and hence is used for tinning of utensils to resist corrosion. Tin foils are used for wrapping cigarettes, confectionary items and for making tooth-paste tubes.

SnO$_2$ is an amphoteric oxide.

Stannous chloride (SnCl$_2$) acts as a good reducing agent. It reduces HgCl$_2$ to first Hg$_2$Cl$_2$ and then to Hg. It also reduces FeCl$_3$ to FeCl$_2$.

Stannic chloride (SnCl$_4$) is a liquid and fumes in air due to hydrolysis. It acts as a Lewis acid and dissolves in concentrated HCl forming H$_2$SnCl$_6$.

SnCl$_4$.5H$_2$O is called butter of tin.

SnS dissolves in yellow ammonium sulphide.

Aluminum Oxide is white

Mercuric Iodide Hgl$_2$ : It is a yellow solid below 400K but changes to red solid above 400K.

\[
\text{Hgl}_2 \underset{\text{Red}}{\overset{400K}{\rightleftharpoons}} \text{Hgl}_2^+ \quad \text{Yellow}
\]

It dissolves in excess of KI forming K$_2$Hgl$_4$:

\[
\text{Hgl}_2 + 2\text{KI} \rightarrow \text{K}_2\text{Hgl}_4
\]

Alkaline solution of K$_2$Hgl$_4$ is called Nessler’s reagent.
Add NH4OH excess and dimethylglyoxime to NiCl2 then a rosy red ppt of nickel appears.

CuO + B2O3 (Glassy bead) -> Cu(BO2)2 (Copper metabolite - 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), ZnSO4. 7H2O: 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,

\[ \text{ZnSO}_4.7\text{H}_2\text{O} \xrightarrow{375K} \text{ZnSO}_4.\text{H}_2\text{O} \xrightarrow{725K} \text{ZnSO}_4 \xrightarrow{1075K} \text{ZnO} + \text{SO}_2 + \text{O}_2 \]
Verdigris - basic copper acetate

This pigment was used in 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, $\text{HgO}$: It is obtained as a red solid by heating mercury in air or oxygen for a long time at 673 K

$$2\text{Hg} + \text{O}_2 \rightarrow 2\text{HgO} \text{ (red)}$$ or by heating mercuric nitrate alone or in the presence of $\text{Hg}$

Heat

$$2\text{Hg} \ (\text{NO}_3 \ )_2 \rightarrow 2\text{HgO} + 4\text{NO}_2 + \text{O}_2$$

red
When NaOH is added to a solution of HgCl$_2$, yellow precipitate of HgO are obtained.

$$\text{Hg}_2\text{Cl}_2 + 2\text{NaOH} \rightarrow \text{HgO} \downarrow + \text{H}_2\text{O} + 2\text{NaCl}$$

(yellow)

Red and yellow forms of HgO differ only in their particle size. On heating to 673 K, yellow form changes to red form.

$$\text{HgO} \rightarrow \text{HgO}$$

(673K)

Yellow

Red

Mercury Oxide

Powder

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

$$\text{HgSO}_4 + 2\text{NaCl} \rightarrow \text{HgCl}_2 + \text{Na}_2\text{SO}_4$$

MnO$_2$
HgCl₂ is a white crystalline solid and is commonly known as corrosive sublimate. It is a covalent compound since it dissolves in organic solvents like ethanol and ether.

It is extremely poisonous and causes death. Its best antidote is white of an egg.

When treated with stannous chloride, it is first reduced to white ppt. of mercurous chloride and then to mercury (black).

\[ 2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4 \]

white ppt.

\[ \text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow 2\text{Hg} + \text{SnCl}_4 \]

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 HgCl₂ is used as an antiseptic.

(3) Mercuric iodide, Hgl₂: It is obtained when a required amount of KI solution is added to a solution of HgCl₂. HgCl₂ + 2KI → Hgl₂ + 2KCl

Below 400 K, Hgl₂ is red but above 400 K, it turns yellow.

\[ \text{Hgl}_2 \text{ readily dissolves in excess of KI solution to form the } (\text{Hgl}_4)^2- \text{complex ion.} \]

\[ \text{Hgl}_2 + 2\text{KI} \rightarrow \text{K}_2\text{Hgl}_4 \text{ Red ppt. soluble colourless solution} \]

An alkaline solution of K₂ [Hgl₄] is called Nessler's reagent and is used to test NH₄⁺ ions.

It gives a brown ppt. of NH₃ - Hg - O Hg - I (Iodide of Millon's base) with NH₄⁺ ions.

\[ 2\text{K}_2 [\text{Hgl}_4] + \text{NH}_3 + 3\text{KOH} \rightarrow \text{NH}_2 \text{O. Hgl} + 7\text{KI} + 2\text{H}_2 \text{O} \]

It is used in ointments for treating skin infections.

(4) Mercurous chloride, Hg₂Cl₂: It is obtained as under:

(a) Hg₂ (NO₃) + 2NaCl → Hg₂Cl₂ + 2NaNO₃

white ppt.

Heating in an iron retort
(b) \( \text{HgCl}_2 + \text{Hg} \rightarrow \text{Hg}_2 \text{Cl}_2 \) (condenses on cooling)

It is purified by sublimation.

Mercurous chloride is also called calomel. It is a white powder insoluble in \( \text{H}_2\text{O} \). On heating, it decomposes to give \( \text{HgCl}_2 \) and \( \text{Hg} \).

\[ \text{Heat} \]
\[ \text{Hg}_2 \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Hg} \]

It dissolves in chlorine water forming mercuric chloride.

\( \text{Hg}_2\text{Cl}_2 + \text{Cl}_2 \rightarrow 2\text{HgCl}_2 \)

With ammonia, it turns black due to the formation of a mixture of finely divided black \( \text{Hg} \) and mercuric amino chloride.

\( \text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{Hg} + \text{NH}_2\text{HgCl} + \text{NH}_4\text{Cl} \)

(black)

It is used to prepare standard calomel electrode and as a purgative in medicine.

(5) Mercuric sulphide, \( \text{HgS} \): The solubility product of \( \text{HgS} \) is lower than that of \( \text{ZnS} \) and hence it gets precipitated as black solid when \( \text{H}_2\text{S} \) is passed through an acidic solution of any mercury (II) salt.

\( \text{HgCl}_2 + \text{H}_2\text{S} \rightarrow \text{HgS} + 2\text{HCl} \)

It is insoluble in water and \( \text{HCl} \) but dissolves in aqua regia (1 part conc. \( \text{HNO}_3 \) + 3 parts conc. \( \text{HCl} \))

\[ 3\text{HCl} + \text{HNO}_3 \rightarrow \text{NOCl} + 2\text{H}_2\text{O} + 2[\text{Cl}] \]

Aqua regia Nitrosyl chloride Nacent chlorine

\( \text{HgS} + 2[\text{Cl}] \rightarrow \text{HgCl}_2 + \text{S} \downarrow \)

(Soluble)

On sublimation, its colour changes to red and hence it is used as a red pigment.

(6) Mercuric sulphate, \( \text{HgSO}_4 \): It is obtained when \( \text{HgS} \) is treated with conc. \( \text{H}_2\text{SO}_4 \).

\( \text{Hg} + 2\text{H}_2\text{SO}_4 \rightarrow \text{HgSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O} \)

It is a white solid which decomposes on heating to give mercurous sulphate.

\[ \Delta \]
\[ 3\text{HgSO}_4 \rightarrow \text{Hg}_2\text{SO}_4 + \text{Hg} + 2\text{SO}_2 + 2\text{O}_2 \]
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.

The common Anions are divided into 3 groups for the purpose of identification:

Those which evolve gases with dilute hydrochloric acid:

- Carbonate (CO\(_{3}^{2-}\))
- bicarbonate(HCO\(_{3}^{-}\))
- Nitrite(NO\(_{2}^{-}\))
- Sulphide (S\(^2\))
- Sulphite(SO\(_{3}^{2-}\))
- Thiosulphate(S\(_2\)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 (B\(_4\)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 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 hydracid. When the nonmetal is combined with H and O, the compound is called a ternary (i.e. composed of three or more elements) acid, or an oxyacid; and the characteristic name of the acid is formed by adding the termination -ic to the name of the nonmetal to denote more oxygen, or the termination -ous to denote less. Examples: 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, FeCl3, Co(NO3)2, Ba(NO3)2, NaCl.

Take about 2 c.c. of each solution, and add HC1.*

Points to be Observed Whether a precipitate is formed.

Whether the precipitate is soluble in an excess of the reagent.

* Always use dilute acids unless otherwise directed.

GROUPING THE BASES

The color of each precipitate.

Whether there is change in color of the precipitate.

Change in color of solutions.

Chemical equations.

Tabulate all results carefully in your notebook, according to the following scheme:

HC1 was added to the seven solutions with the following results:
Typical of Gr. I AgNO₃ + HCl = AgCl w. pp. + HNO₃ (aq) 8.
Typical of Gr. II A Cu(NO₃)₂ + II Cl = No change.
Typical of Gr. II B AgCl 3 + HCl = No change.
Typical of Gr. III Fe 2 Cl 6 + HCl = No change.
Typical of Gr. IV Co(NO₃)₂ + II Cl = No change.
Typical of Gr. V Ba(NO₃)₂ + HCl = No change.
Typical of Gr. VI NaCl + HCl = No change.

1) Anions which react with dilute hydrochloric acid

<table>
<thead>
<tr>
<th>Carbonates (CO₃²⁻)</th>
<th>Bicarbonates (HCO₃⁻)</th>
<th>Nitrates (NO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All carbonates except those of alkali metals and ammonium are very slightly or difficulty soluble in water. Accordingly reactions in solution are only carried out in case of the soluble salts.</td>
<td>All bicarbonates are water soluble.</td>
<td>Most nitrates are water soluble except that of silver.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solid salt + dil. HCl</th>
<th>Effervescence and a colourless odourless gas is evolved, Carbon dioxide(CO₂).</th>
<th>Effervescence and a colourless odourless gas is evolved, Carbon dioxide(CO₂).</th>
<th>Pungent brown fumes are evolved consisting mainly of nitrogen dioxide (NO₂), which is produced by the combination of nitric oxide (NO) with the oxygen of the air:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂CO₃ + 2HCl → 2NaCl + H₂O + CO₂</td>
<td>Na₂HCO₃ + HCl → NaCl + H₂O + CO₂</td>
<td>NaN₃ + HCl → NaCl + HNO₂</td>
<td>NaN₃ → HNO₂ → HNO₃ + H₂O + 2NO</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carbonate</th>
<th>Bicarbonate</th>
<th>Nitrites</th>
</tr>
</thead>
<tbody>
<tr>
<td>To differentiate between CO₃²⁻ and HCO₃⁻:</td>
<td>Confirmatory tests of nitrates:</td>
<td></td>
</tr>
<tr>
<td>1) Salt solution + magnesium sulphate solution</td>
<td>1) The brown ring test:</td>
<td></td>
</tr>
<tr>
<td>White precipitate of magnesium carbonate</td>
<td>To a dilute solution of the nitrite, add two drops of freshly prepared ferric nitrate solution (Fe(NO₃)₃), and then add dil. H₂SO₄ very carefully drop by drop inside the test tube. A brown ring forms due to the formation of (Fe₂(SO₄)₃).</td>
<td></td>
</tr>
<tr>
<td>Na₂CO₃ + MgSO₄ → MgCO₃↓ + Na₂SO₄</td>
<td>Note:</td>
<td></td>
</tr>
<tr>
<td>No ppt. in the cold, as magnesium bicarbonate is soluble. But on heating, a white ppt. of magnesium carbonate is obtained:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2NaHCO₃ + MgSO₄ → Na₂SO₄ + Mg(HCO₃)₂</td>
<td>If the addition of dil. H₂SO₄ is not down the inside of the test tube, the solution becomes brown color (we can not note the ring).</td>
<td></td>
</tr>
<tr>
<td>soluble in water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg(HCO₃)₂ → MgCO₃↓ + CO₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ppt.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No ppt. in the cold, but on heating a reddish brown ppt. of mercuric carbonate is obtained:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 NaHCO₃ + HgCl₂ → 2 NaCl + Hg(HCO₃)₂</td>
<td>(The nitrite solution is an oxidizing agent):</td>
<td></td>
</tr>
<tr>
<td>soluble in water</td>
<td>2NO₂ → 2H₂O + SO₃₂⁻ + 2H⁺</td>
<td></td>
</tr>
<tr>
<td>Hg(HCO₃)₂ → HgCO₃↓ + CO₂</td>
<td>2H₂SO₃ + 2K⁺ + 2Cl⁻</td>
<td></td>
</tr>
<tr>
<td>ppt.</td>
<td>2H₂O + 2Cl⁻</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2) Salt solution + mercuric chloride solution | 2) Solution of nitrite acidified solution of potassium permanganate KMnO₄ (i.e. KMnO₄ + dil. H₂SO₄): the purple color of the permanganate disappears (the nitrite solution is a reducing agent): |
| Reddish brown precipitate of mercuric carbonate | 5KNO₂ + 2KMnO₄ + 3H₂SO₄ → |
| Na₂CO₃ + HgCl₂ → HgCO₃↓ + 2NaCl | 5KNO₂ + K₂SO₄ + 3MnSO₄ + 3H₂O |
Is HgCO₃ reddish Brown?

<table>
<thead>
<tr>
<th>Sulphites (SO₄²⁻)</th>
<th>Thiosulphates (S₂O₃²⁻)</th>
<th>Sulphides (S²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All sulphates are slightly soluble in water except the alkali metal sulphates and the ammonium salt.</td>
<td>Sodium thiosulphate is readily soluble in water, other thiosulphates are slightly soluble.</td>
<td>All sulphides, except those of alkali, alkali earth metals and the ammonium ion are slightly soluble in water.</td>
</tr>
</tbody>
</table>

Solid salt + dilute HCl

Sulphur dioxide gas (SO₂) is evolved, which is recognizable by its pungent smell.

\[ \text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 \]

Test for sulphur dioxide:

Dip a small piece of paper into an acidic solution of potassium dichromate, and hold it over the mouth of the test tube. The paper will turn green, because the sulphur dioxide reduces the dichromate to a chromic sulphate.

\[ 3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]

Orange Green solution

Colourless gas, hydrogen sulphide (H₂S), is evolved which is recognizable by its bad smell.

\[ \text{Na}_2\text{S} + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{H}_2\text{S} \]

Test for hydrogen sulphide:

Dip a piece of paper in a solution of lead nitrate, and hold it over the mouth of the test tube in which the H₂S is being generated. The paper will turn black due to the formation of lead sulphide.

\[ \text{H}_2\text{S} + 2\text{Pb}^{2+}(\text{CH}_3\text{COO})_2 \rightarrow 2\text{PbS} + 2\text{CH}_3\text{COOH} \]

K₂SO₄ is white

Cr₂(SO₄)₃ is green
### Sulphites

<table>
<thead>
<tr>
<th>Confirmatory test:</th>
<th>Sulphites</th>
<th>Thiosulphates</th>
<th>Sulphites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Salt solution + silver nitrate solution (AgNO₃)</td>
<td>A white precipitate forms (silver sulphate Ag₂SO₄) which dissolves in excess of sulphite due to the formation of soluble complex. Na₂SO₃ + 2AgNO₃ → Ag₂SO₄ + 2NaNO₃</td>
<td>A white precipitate forms (silver thiosulphate Ag₂S₂O₇) which is insoluble in excess of the thiosulphate due to the formation of complex, which is unstable it changes to yellow, brown and finally to black Ag₂S₂O₇. Na₂S₂O₇ → 2AgNO₃ → Ag₂S₂O₇ + 2NaNO₃</td>
<td>A black precipitate of silver sulphide (Ag₂S) is formed. Na₂S + 2AgNO₃ → Ag₂S + 2NaNO₃</td>
</tr>
<tr>
<td>2) Salt solution + lead acetate solution (Pb(CH₃COO)₂)</td>
<td>A white ppt. of lead sulphate (PbSO₄) is formed. Na₂SO₃ + Pb(CH₃COO)₂ → PbSO₄↓ + 2CH₃COONa</td>
<td>A white ppt. of lead thiosulphate (PbS₂O₇) is formed, the ppt. turns black (PbS) on boiling. Na₂S₂O₇ + Pb(CH₃COO)₂ → PbS₂O₇↓ + 2CH₃COONa</td>
<td>A black ppt. of lead sulphide (PbS) is formed. Na₂S + Pb(CH₃COO)₂ → PbS↓ + 2CH₃COONa</td>
</tr>
<tr>
<td><em>Salt solution + drops of acidified solution of KMnO₄</em></td>
<td>The purple colour of the permanganate will disappear. The sulphite reduces the permanganate ion to (Mn⁷⁺) which is almost colourless. 5Na₂SO₃ + 2KMnO₄ + 3H₂SO₄ → 5Na₂SO₄ + K₂SO₄ + 2MnSO₄ + 3H₂O</td>
<td><em>Salt solution + Sodium nitroprusside solution:</em> A violet color is formed.</td>
<td></td>
</tr>
</tbody>
</table>

### Thiosulphates

<table>
<thead>
<tr>
<th>Sulphites</th>
<th>Thiosulphates</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Salt solution + 2 drops of dil. H₂SO₄ + iodine solution (I₂)</strong></td>
<td>The brown colour of the iodine solution disappears. Na₂S₂O₇ + I₂ + H₂O → Na₂S₄O₆ + 2HI</td>
</tr>
</tbody>
</table>
2) Anions which react with concentrated sulphuric acid

**Note:** Do these tests in fuming room 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.

<table>
<thead>
<tr>
<th>Chlorides (Cl⁻)</th>
<th>Bromides (Br⁻)</th>
<th>Iodides (I⁻)</th>
<th>Nitrate (NO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All chlorides are water soluble except the chlorides of silver, mercury and cuprous.</td>
<td>Bromides resemble chlorides in their solubility. Iodides resemble chlorides and bromides in their solubility. However, bisulphite iodide is insoluble.</td>
<td>All nitrates are soluble in water except some basic nitrates.</td>
<td></td>
</tr>
</tbody>
</table>

**Solid salt + conc. H₂SO₄**: Effervescence with evolution of colourless gas. Hydrogen chloride (HCl). $2NaCl + H₂SO₄ → Na₂SO₄ + 2HCl$

**Test for HCl gas**: Dip a clean glass rod into a bottle of cone. ammonium solution, and hold it close to the mouth of the test tube in which the HCl is being produced. Dense white fumes of ammonium chloride will be formed: $HCl → NH₃ + HNO₃$

<table>
<thead>
<tr>
<th>Chlorides</th>
<th>Bromides</th>
<th>Iodides</th>
<th>Nitrate (NO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A dense white ppt. of silver chloride (AgCl) slowly turns a violet colour when exposed to bright light: NaCl $→$ AgNO₃ + AgCl $→$ NaNO₃ ppt.</td>
<td>A yellow precipitate of silver bromide (AgBr) is formed. NaBr $→$ AgNO₃ + AgBr $→$ NaNO₃ ppt.</td>
<td>A yellow precipitate of silver iodide (AgI) is formed. KI $→$ AgNO₃ + AgI $→$ KNO₃ ppt.</td>
<td>( \times )</td>
</tr>
</tbody>
</table>

**2) Salt solution + silver nitrate (AgNO₃)**: A white precipitate of lead chloride (PbCl₂) is formed which is soluble in hot water, and reprecipitates on cooling. 2NaCl + Pb(CH₃COO)₂ → PbCl₂ + 2Na(CH₃COO)²⁻

<table>
<thead>
<tr>
<th>Chlorides</th>
<th>Bromides</th>
<th>Iodides</th>
<th>Nitrate (NO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A white precipitate of lead bromide (PbBr₂) appears which is soluble in boiling water and reprecipitates on cooling. 2NaBr + Pb(CH₃COO)₂ → PbBr₂ + 2Na(CH₃COO)²⁻</td>
<td>A yellow precipitate of lead iodide (PbI₂) is formed which dissolves in boiling water and recrystallizes on cooling. 2KI + Pb(CH₃COO)₂ → PbI₂ + 2CH₃COOH</td>
<td>A brown ring test. The nitrate solution is mixed with freshly prepared Fe₃O₄ solution, then conc. H₂SO₄ is added and allowed to flow cautiously on the side of the test tube. A brown ring (Fe₂(NO₃)₃SO₄) is formed at the interface of the two layers. The brown ring disappears on shaking the solution.</td>
<td></td>
</tr>
</tbody>
</table>

**Salt solution + copper sulphate (CuSO₄)**: A brown ppt. of copperous iodide CuI and iodine I₂ is formed: 2KI + CuSO₄ → 2KCl + CuI₂ + I₂
AgCl is white

Cul Cuprous Iodide

Brown Ring Test
### 3) Anions which do not react with acids:

<table>
<thead>
<tr>
<th>Phosphates (H$_3$PO$_4$, HPO$_4^{2-}$, PO$_4^{3-}$)</th>
<th>Borates (BO$_3^{3-}$, BO$_2^{−}$, B$_2$O$_4^{−}$)</th>
<th>Sulphates (SO$_4^{2-}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most phosphates are insoluble in water except those of ammonium and alkali metals.</td>
<td>Ammonium and alkali metal borates are water soluble while other borates are slightly soluble in water.</td>
<td>All sulphates are soluble in water except those of some divalent metals e.g. calcium, strontium, barium and lead.</td>
</tr>
<tr>
<td><strong>Salt solution + Barium chloride solution (BaCl$_2$)</strong></td>
<td><strong>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.</strong>&lt;br&gt;Na$_2$HPO$_4$ + BaCl$_2$ → BaHPO$_4$↓ + 2NaCl</td>
<td><strong>A white precipitate of barium sulphate (BaSO$_4$) is formed, which is insoluble in dilute acids and in excess of barium chloride.</strong>&lt;br&gt;Na$_2$SO$_4$ + BaCl$_2$ → BaSO$_4$↓ + 2NaCl</td>
</tr>
<tr>
<td><strong>Confirmatory test:</strong>&lt;br&gt;1) Salt solution + silver nitrate (AgNO$_3$)</td>
<td><strong>A yellow precipitate of silver phosphate (Ag$_2$PO$_4$) is formed, which is readily soluble in dil. HNO$_3$ and ammonia.</strong>&lt;br&gt;N$_2$HPO$_4$ + 3H$_2$O + 2AgNO$_3$ → 2Ag$_2$PO$_4$↓ + 2H$_3$PO$_4$ + 2NaCl</td>
<td><strong>A white precipitate of silver sulphate (Ag$_2$SO$_4$) is formed with concentrated solution.</strong>&lt;br&gt;N$_2$SO$_4$ + 2AgNO$_3$ → Ag$_2$SO$_4$↓ + 2NaCl</td>
</tr>
</tbody>
</table>

BaSO$_4$ is white
For phosphates:

0.5 ml of salt solution + 1 ml of ammonium molybdate solution + 0.5 ml of conc. HNO₃

Form a canary yellow precipitate of ammonium phosphomolybdate \((\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3 \cdot \text{H}_2\text{O}\) in the cold or by gentle warming.

(Uses the volume needed in this test).

For sulphates:

Salt solution + lead acetate:

A white precipitate of lead sulphate is formed, which is slightly soluble in hot concentrated ammonium acetate or conc. H₂SO₄.

| Reaction | 
|----------|------|
| \(\text{K}_2\text{SO}_4 + \text{Pb(CH}_3\text{COO)}_2 \rightarrow \text{PbSO}_4 + 2\text{CH}_3\text{COOK}\) | 
| \(\text{PbSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Pb(HSO}_4)_2\) |
### Scheme for the identification of acid radicals

<table>
<thead>
<tr>
<th>Observation</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effervescence and a colourless gas evolved.</td>
<td>The gas is ( \text{CO}_2 ). The anion is bicarbonate.</td>
</tr>
<tr>
<td>Pungent brown fumes are evolved.</td>
<td>The gas is ( \text{NO}_2 ). The anion is nitrate</td>
</tr>
<tr>
<td>Colourless gas with pungent odour, which turns an acidified dichromate paper green, is evolved.</td>
<td>The gas is ( \text{SO}_2 ) and the green colour is ( \text{Cr}_2(\text{SO}_4)_3 ). The anion is sulphite.</td>
</tr>
<tr>
<td>Colourless gas is evolved which is characterized by its bad odour and turning a lead acetate paper black.</td>
<td>The gas is ( \text{H}_2\text{S} ), the black colour is ( \text{PbS} ). The anion is thiosulphate.</td>
</tr>
</tbody>
</table>

To differentiate between carbonate and bicarbonate:

1. **Salt solution - magnesium sulphate solution**
   - **For carbonate:** White precipitate of magnesium carbonate \( (\text{MgCO}_3) \).
   - **For bicarbonate:** No ppt in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained.

2. **Solid salt + conc. \( \text{H}_2\text{SO}_4 \):**
   - **Observation**
     - Effervescence with the evolution of a colourless gas which forms white fumes with \( \text{NH}_3\text{OH} \).
     - Reddish fumes evolve and the solution turns orange.
     - Violet fumes are evolved, and a brown or black precipitate is formed in the test tube.
   - **Results**
     - The gas is \( \text{HCl} \) and the white fumes are \( \text{NH}_3\text{Cl} \). The anion is chloride.
     - The gas is \( \text{Br}_2 \). The anion is bromide.
     - The gas is \( \text{I}_2 \). The anion is iodide.
     - The gas is \( \text{NO}_2 \); The anion is nitrate.
     - The salt does not react with conc. \( \text{H}_2\text{SO}_4 \).

3. **Salt solution - \( \text{BaCl}_2 \):**
   - **Observation**
     - A white precipitate is produced, soluble in dilute acids e.g. \( \text{HNO}_3 \) or \( \text{HCl} \) 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 \( (\text{BaHPO}_4) \). The anion is phosphate.
     - The white ppt. is barium borate \( \text{Ba(BO}_3\text{)}_2 \). The anion is borate.
     - A white precipitate is barium sulphate \( (\text{BaSO}_4) \). The anion is sulphate.
To differentiate between phosphate, borate and sulphate:

Salt solution + AgNO₃ (silver nitrate):

<table>
<thead>
<tr>
<th></th>
<th>phosphate</th>
<th>borate</th>
<th>Sulphate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observation</td>
<td>A yellow precipitate is formed, which is readily soluble in dil. HNO₃ and ammonia.</td>
<td>A white ppt. is formed from concentrated solution, which gives brown ppt. after boiling. (Also, a brown ppt. is formed with diluted solution.)</td>
<td>A white ppt. is formed, with concentrated solution</td>
</tr>
<tr>
<td>Results</td>
<td>The yellow ppt. is silver phosphate (Ag₃PO₄). The anion is phosphate.</td>
<td>The white ppt. is silver borate (AgBO₃). The anion is borate.</td>
<td>The white ppt. is silver sulphate (Ag₂SO₄). The anion is sulphate.</td>
</tr>
</tbody>
</table>
## Oxidation States and Colors

<table>
<thead>
<tr>
<th>Metal</th>
<th>+1</th>
<th>+2</th>
<th>+3</th>
<th>+4</th>
<th>+5</th>
<th>+6</th>
<th>+7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>V</td>
<td>Violet</td>
<td>Green</td>
<td>blue</td>
<td>Yellow (CrO$_2^-$) orange (Cr$_2$O$_7^{2-}$)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>Blue</td>
<td>Green</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>Pale pink</td>
<td>Brown</td>
<td></td>
<td>Dark green (MnO$_2^+$)</td>
<td>Intense purple (MnO$_4^-$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>Pale green</td>
<td>Yellow or brown</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>Pink</td>
<td>Orange/yellow</td>
<td></td>
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<tr>
<td>Ni</td>
<td>Green</td>
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<tr>
<td>Cu</td>
<td>Blue</td>
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<tr>
<td>Zn</td>
<td>colorless</td>
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</tbody>
</table>
Good Luck to you for your Preparations, References, and Exams

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Professor Subhashish Chattopadhyay

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