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


Twitter - [https://twitter.com/ZookeeperPhy](https://twitter.com/ZookeeperPhy)

Facebook - [https://www.facebook.com/IIT.JEE.by.Prof.Subhashish/](https://www.facebook.com/IIT.JEE.by.Prof.Subhashish/)

Blog - [http://skmclasses.kinja.com](http://skmclasses.kinja.com)
A very polite request:

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

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

Random - 1

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

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

Random - 2

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

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

Random - 3

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

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

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

Random - 6

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

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.
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 upto the extent to choose the right/rich man to marry. So generally what happens in case of Divorces ? Search the net on “ most costly divorces “ and you will know. The women; ( who had no contribution at all, in setting up the business / empire ), often gets in Billions, or several Millions in divorce settlements.

Number 1

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 1978 while doing Erhard Seminars Training.

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


See http://skmclasses.kinja.com/save-the-male-1761788732
It was Boys and Men, who brought the girls / women home. The Laws are biased, completely favoring women. The men are paying for their own mistakes.

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

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

Random - 12

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

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


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/](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](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/](https://www.facebook.com/WomenCriminals/)

Some Random Examples must be known by all

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

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"Sex with my son is incredible - we're in love and we want a baby"  
Ben Ford, who dated his wife when he met his mother Kim West after 30 years, claims what the couple are doing isn't incest.

[https://www.aol.com/article/2016/12/23/british-couple-says-she-was-incestuous-love-sexy-son/20830642/](https://www.aol.com/article/2016/12/23/british-couple-says-she-was-incestuous-love-sexy-son/20830642/)

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

Edwina Louis rape...

See More

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


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Woman sent to jail for raping her four grandchildren.

A Ohio grandmother has been sentenced to four consecutive life terms after being found guilty of the rape of her own grandchildren. Edwina Louis, 51, will spend the rest of her life behind bars.

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

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

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

WOMANJUICE.COM
We must first understand the most important graph or image of Chemistry

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

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

ELECTROCHEMICAL CELLS

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

Electrochemical Cells can be classified as:

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

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

**ELECTROCHEMICAL CELLS**

**Galvanic Cell**
- Spontaneous rxn. drawn into cell
- Oxidation occurs at anode
- Reduction occurs at cathode

**Example:**
\[ \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+} \]

**Electrolytic Cell**
- Current supplied by external source
- Anode (+) and cathode (-), opposite of galvanic cell

**Example:**
\[ 2\text{Cl}^- + \text{Mg}^{2+} \rightarrow \text{Cl}_2 + \text{Mg}(\text{I}) \]
ELECTROLYSIS (Where a Positive current, of holes, is forced into the Anode. So electrons will come out of the Anode.)

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

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

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

ELECTRODES

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

**Spoon Feeding**

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

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

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

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

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

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

**What happens during electrolysis?**

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

\[ \text{NaCl(molten)} \rightarrow \text{Na}^+ + \text{Cl}^- \]

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

Reactions at cathode (reduction): \( \text{Na}^+ + \text{e}^- \rightarrow \text{Na} \)

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

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

FARADAY’S LAWS OF ELECTROLYSIS:

(i) First law of electrolysis:

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

\[ \text{W} \propto \text{Q} \]

\[ \text{W} = \text{weight liberated, Q = charge in coulomb} \]

\[ \text{w} = \text{ZQ} \]
Z = electrochemical equivalent when Q = 1 coulomb, then w = Z

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

Let 1 ampere current is passed till ‘t’ seconds.

Then, Q = I t

∴ w = Z I t or Z i t  Some teachers prefer to write current in small case “ i “

1 Faraday = 96500 coulomb = Charge of one mole electrons

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

Let ‘E’ is equivalent weight then ‘E’ gm will be liberated by 96500 coulomb.

∴ 1 Coulomb will liberate E / 96500 gm

So by definition Z = E/96500

W = I t E / 96500

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

\[ V = \frac{I t V_e}{96500} \]

where V = volume of liberated gas, V\(_e\) = equivalent volume of gas.

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

(ii) Second law of electrolysis:

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

QUALITATIVE ASPECTS OF ELECTROLYSIS

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

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

\[
E_{RP} = E^{\circ}_{RP} - \frac{RT}{nF} \ln \left( \frac{[\text{concentration of product}]}{[\text{concentration of reactant}]} \right)
\]

Where \(E_{RP}\) = Reduction potential of cation

\(E^{\circ}_{RP}\) = Standard reduction potential of cation

Thus, it is possible that a cation (A\(^+\)) with lower standard reduction potential getting discharged in preference to cation (B\(^+\)) having higher standard reduction potential because their concentration might be such that the reduction potential of A\(^+\) is higher than that of B\(^+\). When two metal ions in the solution have identical values of their reduction potentials, the simultaneous deposition of both the metals will occur in the form of an alloy.
Walther Hermann Nernst (1864 - 1941) German Physicist & Chemist received the Nobel prize in 1920 Chemistry.

Galvanic Cell

This cell converts chemical energy into electrical energy.

\[ E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.059}{n} \log \left( \frac{[\text{Products}]}{[\text{Reactants}]} \right) \text{ or } Q. \]

\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = \frac{0.059}{n} \log \left( \frac{[P]}{[R]} \right) \]

Note on Nernst Equation also uses Electrode potential

- **GALVANIC CELL**

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

Remember:

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

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

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

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

The e.m.f of the standard cell Zn | Zn<sup>2+</sup> || Ag<sup>+</sup> | Ag is 1.562 Volt

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

Solution : 
\[ E_{\text{cell}} = E_{\text{Reduction (Right)}} - E_{\text{Reduction (Left)}} \]
So \[ 1.562 = E(Ag^+ | Ag) - (-0.762) \] => \[ E_{Ag^+ | Ag} = 0.8 \text{ Volt} \]

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

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

A solution of copper sulphate put into an iron pot will damage. This is because the standard electrode potential for Fe<sup>2+</sup>/Fe is more negative than that for Cu<sup>2+</sup>/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>$\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^-(aq)$</td>
<td>+2.87</td>
</tr>
<tr>
<td>$\text{Cl}_2(g) + 2e^- \rightarrow 2\text{Cl}^-(aq)$</td>
<td>+1.36</td>
</tr>
<tr>
<td>$\text{MnO}_2(g) + 4\text{H}^+(aq) + 2e^- \rightarrow \text{Mn}^{2+}(aq) + 2\text{H}_2\text{O}(l)$</td>
<td>+1.23</td>
</tr>
<tr>
<td>$\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO}(g) + 2\text{H}_2\text{O}(l)$</td>
<td>+0.96</td>
</tr>
<tr>
<td>$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$</td>
<td>+0.80</td>
</tr>
<tr>
<td>$\text{Fe}^{3+}(aq) + e^- \rightarrow \text{Fe}^{2+}(aq)$</td>
<td>+0.77</td>
</tr>
<tr>
<td>$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightarrow 4\text{OH}^-(aq)$</td>
<td>+0.40</td>
</tr>
<tr>
<td>$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$</td>
<td>+0.34</td>
</tr>
<tr>
<td>$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$</td>
<td>0.00</td>
</tr>
<tr>
<td>$\text{N}_2(g) + 5\text{H}^+(aq) + 4e^- \rightarrow \text{N}_2\text{H}_5^+(aq)$</td>
<td>−0.23</td>
</tr>
<tr>
<td>$\text{Fe}^{2+}(aq) + 2e^- \rightarrow \text{Fe}(s)$</td>
<td>−0.44</td>
</tr>
<tr>
<td>$2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$</td>
<td>−0.83</td>
</tr>
<tr>
<td>$\text{Na}^+(aq) + e^- \rightarrow \text{Na}(s)$</td>
<td>−2.71</td>
</tr>
<tr>
<td>$\text{Li}^+(aq) + e^- \rightarrow \text{Li}(s)$</td>
<td>−3.05</td>
</tr>
</tbody>
</table>
What will happen if a solution of Magnesium sulphate put into an Copper pot ?

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

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

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

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

\[ \text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \parallel \text{Cu(s)} \]

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

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

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

(Illustration of Phase boundary)

(v) Inert electrodes are represented in the bracket

\[ \text{Zn} \mid \text{ZnSO}_4 \parallel \text{H}^+ \parallel \text{H}_2, \text{Pt} \]

Consider the following set of half-reactions

**Reduction**

\[ \text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe} \]

\[ E_{\text{red}} = -0.44 \text{ V} \]

**Oxidation**

\[ \text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^- \]

\[ E_{\text{ox}} = +0.76 \text{ V} \]
Overall \[ \text{Zn} + \text{Fe}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Fe} \quad E^\circ_{\text{cell}} = 0.32 \text{ V} \]

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.

Remember the relation: \( \Delta G = \Delta G^\circ + RT \ln Q \)  

Nernst Equation 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 again called the Nernst Equation of another form )

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

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 \( (n = 2) \).

\[E = E^\circ - \frac{RT}{nF} \times \ln \left( \frac{[\text{Zn}^{2+}]}{[\text{Fe}^{2+}]} \right)\]

\[= 0.32 \text{ V} - \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \times \ln \left( \frac{1.9}{0.1} \right)}{2 \times 96485 \text{ C \ mol}^{-1}}\]

\[= 0.28 \text{ V}\]

Although the reaction is 90% complete (from Standard Conditions initial) the cell potential has only dropped by a small amount (0.04 V). This is normal. For example, the batteries in your flashlight will put out almost full voltage until the last traces of chemical are almost used up at which point the voltage will drop off rather sharply. This is an especially useful characteristic of cells powering electronic equipment.
In general, for a redox cell reaction involving the transference of \( n \) electrons
\[ aA + bB \rightarrow cC + dD, \]
the EMF can be calculated as:
\[
E_{\text{cell}} = E_0^{\text{cell}} - \frac{0.0591}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}
\]

**Prediction and feasibility of spontaneity of a cell reaction.**

Work done by the cell = \( nFE \);

- It is equivalent to decrease in free energy \( \Delta G = -nFE \)
- Under standard state \( \Delta G^0 = -nFE^0 \)  \( \text{(i)} \)
- From thermodynamics we know, \( \Delta G \) = negative for spontaneous process. Thus from eq. (i) it is clear that the EMF should be +ve for a cell process to be feasible or spontaneous.
- When \( \Delta G = \text{positive} \), \( E = \text{negative} \) and the cell process will be non spontaneous.
- When \( \Delta G = 0 \), \( E = 0 \) and the cell will attain the equilibrium.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>( \Delta G )</th>
<th>( E )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spontaneous</td>
<td>(-)</td>
<td>(+)</td>
</tr>
<tr>
<td>Non-spontaneous</td>
<td>(+)</td>
<td>(-)</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Standard free energy change of a cell may be calculated by electrode potential data. Substituting the value of \( E0 \) (i.e., standard reduction potential of cathode - standard reduction potential of anode) in eq. (i) we may get \( \Delta G^0 \).

**THERMODYNAMIC TREATMENT OF NERNST EQUATION**

**Determination of equilibrium constant**

\[
E^0 = \frac{0.0591}{n} \log K_{\text{eq}}
\]

\( : \) We know, that \( E = \)

\[ \ldots \text{(1)} \]

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

\( : \) From Eq. (1), we have

\[ E^0 = \frac{0.0591}{n} \log K_{\text{eq}} \]

Or

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

Recall antilog is 10 to the power

**Heat of Reaction inside the cell:**

Let \( n \) Faraday charge flows out of a cell of e.m.f. \( E \), then
Gibbs Helmholtz equation (from thermodynamics) may be given as,

\[ -\Delta G = nFE \]  (i)

Thus

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

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

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

Entropy change inside the cell:

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

where

\( \Delta G = \) Free energy change
\( \Delta H = \) Enthalpy change and
\( \Delta S = \) entropy change.

According to Gibbs Helmholtz equation,

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

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

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

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

or

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

Where \( \left[ \frac{\partial E}{\partial T} \right]_p \) is called temperature coefficient of cell e.m.f.
Spoon Feeding Rule of Electrochemistry

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

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

Recall \( \Delta G = -nFE \) or \( E = -\frac{\Delta G}{nF} \)

Spoon feeding Rule of Electrochemistry

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

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

Recall Spontaneity of \( \Delta G \)
More Positive lesser spontaneous
More negative more spontaneous

So if both half cell reactions are spontaneous then we convert less spontaneous reaction into non-spontaneous reaction.
If $\Delta G^\circ$ given in the half cells then spontaneity of the reaction not determined by $\Delta G^\circ$. We convert $\Delta G^\circ$ into $\Delta G$ by following equation.

$$\Delta G = -nFE$$

Greater the reduction potential greater will be ease of reduction. Greater the oxidation potential greater will be ease of oxidation.
If the equations are given as mix of spontaneous voltage and non-spontaneous voltage, then convert them to same form

\[ A \rightarrow A^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = -0.2 \text{ Volt (non-spontaneous)} \]

\[ B \rightarrow B^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = +0.5 \text{ Volt (Spontaneous)} \]

**Same:**

\[ B \rightarrow B^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = +0.5 \text{ Volt} \]

**Change:**

\[ A^{z2} + 2e^- \rightarrow A \quad \text{E}_{\text{R,P}} = +0.2 \text{ Volt} \]

\[ B + A^{z2} \rightarrow B^{z2} + A \quad E_{\text{cell}} = E_{\text{O,P}} + E_{\text{R,P}} = 0.5 + 0.2 = 0.7 \text{ Volt} \]

Spoon Feeding

\[ A \rightarrow A^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = +0.5 \text{ Volt (more spontaneous)} \]

\[ B \rightarrow B^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = +0.3 \text{ Volt (Less spontaneous)} \]

**Same:**

\[ A \rightarrow A^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = +0.5 \text{ Volt} \]

**Change:**

\[ B^{z2} + 2e^- \rightarrow B \quad \text{E}_{\text{R,P}} = -0.3 \text{ Volt} \]

\[ A + B^{z2} \rightarrow B + A^{z2} \quad E_{\text{cell}} = E_{\text{O,P}} + E_{\text{R,P}} = +0.5 - 0.3 = +0.2 \text{ Volt} \]

Spoon Feeding

\[ A \rightarrow A^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = -0.5 \text{ Volt (more spontaneous)} \]

\[ B \rightarrow B^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = -0.2 \text{ Volt (Less spontaneous)} \]

**Same:**

\[ B \rightarrow B^{z2} + 2e^- \quad \text{E}_{\text{O,P}} = -0.2 \text{ Volt} \]

**Change:**

\[ A^{z2} + 2e^- \rightarrow A \quad \text{E}_{\text{R,P}} = +0.2 \text{ Volt} \]

\[ A + B^{z2} \rightarrow B + A^{z2} \quad E_{\text{cell}} = E_{\text{O,P}} + E_{\text{R,P}} = -0.2 + 0.5 = +0.3 \text{ Volt} \]

Spoon Feeding

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

\[
E_{O,P} = E_{O,P}^C - (0.0592/\eta)\log[A^{z2}] \\
E_{O,P} = E_{O,P}^C - (0.0592/\eta)\log[B^{z2}]
\]
Greater the O.P. greater will be ease of oxidation.

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

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

\[
A \rightarrow A^{2+} + 2e^- \quad E^\circ_{o.p.} = -0.2 \text{ Volt} \\
B \rightarrow B^{2+} + 2e^- \quad E^\circ_{o.p.} = -0.2 \text{ Volt}
\]

If you want to gain reduction half cell then

\[
A^{2+} + 2e^- \rightarrow A \quad E_{r.p.} = +0.2 \text{ Volt} \\
B^{2+} + 2e^- \rightarrow B \quad E_{r.p.} = +0.5 \text{ Volt}
\]

If you want to gain reduction half cell then

\[
B^{2+} + 2e^- \rightarrow B \quad E_{r.p.} = -0.5 \text{ Volt}
\]

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

\[
A \rightarrow A^{2+} + 2e^- \quad E_{o.p.} = 0.2 \text{ Volt} \\
B^{2+} + 2e^- \rightarrow B \quad E_{r.p.} = 0.5 \text{ Volt}
\]

$E_{cell} = (?)$

(i) Convert both reaction into oxidation half

\[
A \rightarrow A^{2+} + 2e^- \quad E_{r.p.} = -0.2 \text{ Volt} \\
B \rightarrow B^{2+} + 2e^- \quad E_{o.p.} = -0.5 \text{ Volt}
\]

(ii) Convert both reaction into reduction half cell

\[
A^{2+} + 2e^- \rightarrow A \quad E_{r.p.} = -0.2 \text{ Volt} \\
B^{2+} + 2e^- \rightarrow B \quad E_{r.p.} = 0.5 \text{ Volt}
\]

Same:

\[
B^{2+} + 2e^- \rightarrow B \quad E_{r.p.} = 0.5 \text{ Volt}
\]

Change:

\[
A \rightarrow A^{2+} + 2e^- \quad E_{o.p.} = +0.2 \text{ Volt} \\
B^{2+} + A \rightarrow A^{2+} + B \quad E_{cell} = 0.7 \text{ Volt}
\]

For following type half cell reaction hybrid reaction quotients (mixture of $Q_p$ and $Q_c$) used in place of $Q_c$ or $Q_p$
Emf is mass or mole independent property (intensive property), but free energy is mass or mole dependent property (Extensive property).

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

Magnitude of Emf and $\Delta G$ are same but sign is reverse.

If two half cell (no. of electron same or different) produces full cell reaction then for simplicity we add directly emf of half cell not $\Delta G$. Addition of $\Delta G$ gives same result but process is lengthy.
If no. of electron involved and apparent in reaction then reaction is half cell. But if no. of electron involved but not apparent in the reaction then reaction is full cell reaction.

\[
A \rightarrow A^{+2} + 2e^- \quad E_1 \\
B^{+2} + 2e^- \rightarrow B \quad E_2 
\]

\[
B^{+2} + A \rightarrow A^{+2} + B \quad E_{cell} = E_1 + E_2
\]

If we proceed this problem by \( \Delta G \) then:

\[
A \rightarrow A^{+2} + 2e^- \quad \Delta G_1 = -2FE_1 \\
B^{+2} + 2e^- \rightarrow B \quad \Delta G_2 = -2FE_2 
\]

\[
\Delta G_{rxn} = \Delta G_1 + \Delta G_2 \\
-2FE_{cell} = -2FE_1 - 2FE_2 \\
E_{cell} = E_1 + E_2
\]

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

**Example:**

\[
Fe \rightarrow Fe^{+3} + 3e^- \quad \text{oxidation half cell, } n=3 \\
Fe^{+3} + 1e^- \rightarrow Fe^{+2} \quad \text{reduction half cell, } n=1 \\
2Fe^{+3} + 3H^+ \rightarrow 2Fe^{+2} + 3H_2O \quad \text{full cell rxn, } n=2 \\
MnO_4^- + 4H^+ + 3e^- \rightarrow 2H_2O + MnO_2 \quad \text{reduction half cell, } n=3 \\
Fe^{+2} \rightarrow Fe^{+3} + 1e^- \quad \text{oxidation half cell, } n=1
\]

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

**Example:**

\[
2 \times (A \rightarrow A^{+3} + 3e^-) \quad E_4, \quad \Delta G_4 = -6FE_4 \\
3 \times (B^{+2} + 2e^- \rightarrow B) \quad E_2, \quad \Delta G_2 = -6FE_2
\]

\[
2A + 3B^{+2} \rightarrow 2A^{+3} + 3B, \quad \Delta G_{rxn} = -6FE_3 \\
\Delta G_{rxn} = \Delta G_1 + \Delta G_2 = -6FE_4 - 6FE_2 = -6FE_3 \\
E_3 = E_1 + E_2
\]

If two half cell produces third half cell then we should not added Emf directly. To calculate Emf of third half cell we add \( \Delta G \),
For writing shorthand notation or cell representation of electrochemical cell following conventions are used.

\[
\begin{align*}
A & \rightarrow A^{2+} + 2\sigma & E_{\text{O.P.}} &= 0.5 \text{ Volt} \\
B^{2+} + 2\sigma & \rightarrow B & E_{\text{R.P.}} &= 0.2 \text{ Volt} \\
A + B^{2+} & \rightarrow B + A^{2+} & E_{\text{cell}} &= 0.7 \text{ Volt}
\end{align*}
\]

**DIFFERENT TYPES OF HALF-CELLS AND THEIR REDUCTION POTENTIAL**

(1) Gas-Ion Half Cell:

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

\[
\text{H}^- + (\text{aq}) + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2
\]

\[
E_{\text{H}^+ / \text{H}_2} = E^0_{\text{H}^+ / \text{H}_2} - 0.0591 \log \left( \frac{[\text{H}_2]}{[\text{H}^+]} \right)
\]

\[\text{So} \]

(2) Metal-Metal Ion Half Cell:

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

\[
M^{n+} (\text{aq}) + n\text{e}^- \rightarrow M(\text{s})
\]

\[
E_{M^{n+} / M} = E^0_{M^{n+} / M} - 0.0591 \log \left( \frac{1}{[M^{n+}]} \right)
\]
(3) Metal-Insoluble Salt - Anion Half Cell:
In this half cell, a metal coated with its insoluble salt is in contact with a solution containing the anion of the insoluble salt. eg. Silver-Silver Chloride Half Cell:

This half cell is represented as Cl⁻/AgCl/Ag. The equilibrium reaction that occurs at the electrode is AgCl(s) + e⁻ → Ag(s) + Cl⁻ (aq)

\[ \Delta G = E^0 - \frac{0.0591}{1} \log \left( \frac{[\text{Cl}^-]}{[\text{AgCl}^-]} \right) \]

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

(4) Oxidation-reduction Half Cell:
This type of half cell is made by using an inert metal collector, usually platinum, immersed in a solution which contains two ions of the same element in different states of oxidation. eg. Fe²⁺ → Fe³⁺ half cell.

Fe³⁺ (aq) + e⁻ → Fe²⁺ (aq)

\[ \Delta G = E^0 \] \[
\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \] \[
\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \]

CONCENTRATION CELL

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

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

Electrode Gas concentration cell :
Pt, H₂(P₁) | H⁺(C) | H₂(P₂), Pt

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

Cell Process : \( \frac{1}{2} \text{H}_2 (P_1) -> \text{H}^+ (c) + e^- (\text{Anode Process}) \)

\[ \frac{1}{2} \text{H}_2 (P_1) \rightarrow \text{H}^+ (P_2) \]

So \( E = - \left[ \frac{2.303RT}{F} \right] \log \left( \frac{P_2}{P_1} \right) \] Recall - Log (a / b) is log (b / a)
For spontaneity of such cell reaction, $p_1 > p_2$

Electrolyte concentration cells:

$$\text{Zn}(s) \mid \text{ZnSO}_4(C_1) \parallel \text{ZnSO}_4(C_2) \mid \text{Zn}(s)$$

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

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

$$\frac{\text{Zn}^{2+}(C_2) + 2e \rightarrow \text{Zn}(s)}{\text{Zn}^{2+}(C_2) \rightarrow \text{Zn}^{2+}(C_1)}$$

∴ From Nernst equation, we have

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

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

---

**Conductance**

**Introduction:**

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

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

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

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

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

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

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

where $C =$ conductance ohm$^{-1}$ ; $K =$ specific conductance ohm$^{-1}$ cm$^{-1}$.
Mho and siemens are other units of conductance
So \[
K = \frac{LC}{A}
\]
Specific conductance = Cell constant x Conductance
Specific Conductance is conductance of 1 Cm³ of an electrolyte Solution.

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

1. Equivalent Conductance

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

\[
\wedge = K \times V
\]
\[
(\wedge = \text{ohm}^{-1} \text{cm}^{-1} \times \text{cm}^3 = \text{ohm}^{-1} \text{cm}^2)
\]

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

Thus, \( V = \frac{1000}{C} \)

Also \( \wedge = K \times \frac{1000}{C} \)

2. Molar Conductance

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

\[
\wedge_m = K \times V
\]

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

Thus, \( V = \frac{1000}{M} \)

Hence, \( \wedge_m = K \times \frac{1000}{M} \)

Relation between \( \wedge \) and \( \wedge_m \): \( \wedge_m = n \times \wedge \)

Determination of \( \wedge_m \) OR \( \wedge^0 \)

A plot of \( \wedge_m \) VS \( \sqrt{C} \) as found experimentally; is as shown below.
The plot of strong electrolyte being linear it can be extrapolated to zero concentration.

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

$\Lambda_m$ values are then plotted against $\sqrt{C}$ when a straight line is obtained. This is the extrapolated to zero concentration. The point where the straight line intersects $\Lambda_m$ axis is $\Lambda_0$ of the strong electrolyte.

However, the plot in the case weak electrolyte being non linear, shooting up suddenly at some low concentration and assuming the shape of a straight line parallel to $\Lambda_m$ axis. Hence extrapolation in this case is not possible. Thus, $\Lambda_0$ of a weak electrolyte cannot be determined experimentally. It can, however, be done with the help of Kohlrausch's law.

**Kohlrausch's Law of Independent Migration of Ions**

Kohlrausch determined $\Lambda_0$ values of pairs of some strong electrolytes containing same cation say KF and KCl, NaF and NaCl etc., and found that the difference in $\Lambda_0$ values in each case remains the same:

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

He also determined $\Lambda_0$ values of pairs of strong electrolytes containing same anion say KF and NaF, KCl and NaCl etc. and found that the difference in $\Lambda_0$ values in each case remains the same.

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

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

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

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

Application of Kohlrausch's law:

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

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

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

$\lambda^0_m$ of CH₃COOH is then given as:

$\lambda^0_m$(CH₃COOH) = $\lambda^0_m$(HCl) + $\lambda^0_m$(CH₃COONa) - $\lambda^0_m$(NaCl)

Proof:

$\lambda^0_m$(HCl) = $\lambda^0_+$(H⁺) + $\lambda^0_-$(Cl⁻)       ....(i)

$\lambda^0_m$(CH₃COONa) = $\lambda^0_+$(CH₃COO⁻) + $\lambda^0_-$(Na⁺)       ....(ii)

$\lambda^0_m$(NaCl) = $\lambda^0_+$Na⁺ + $\lambda^0_-$Cl⁻       ....(iii)

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

$\lambda^0_m$(HCl) + $\lambda^0_m$(CH₃COONa) - $\lambda^0_m$(NaCl) = $\lambda^0_+$(H⁺) + $\lambda^0_+$(CH₃COO⁻) = $\lambda^0_m$(CH₃COOH)

(2) Determination of degree of dissociation ($\alpha$):

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

(3) Determination of solubility of sparingly soluble Salt

The specific conductivity of a saturated solution of the test electrolyte (sparingly soluble) made in conductivity water is determined by the method as described above. From this the specific conductivity of conductivity water is deducted. The molar conductance of the saturated solution is taken to be equal to $\lambda^0_m$ as the saturated solution of a sparingly soluble salt is extremely dilute. Hence from equation (4).
\[ a_m^0 = \frac{1000 \kappa}{C}, \]

where \( C \) is the molarity of solution and hence the solubility.

A voltaic cell using inactive electrodes.

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

**Reduction half-reaction**
\[ \text{MnO}_4^- (aq) + 8H^+ (aq) + 5e^- \rightarrow \text{Mn}^{2+} (aq) + 4H_2O(l) \]

**Overall (cell) reaction**
\[ 2\text{MnO}_4^- (aq) + 16H^+ (aq) + 10I^- (aq) \rightarrow 2\text{Mn}^{2+} (aq) + 5I_2 (s) + 8H_2O(l) \]

The inert electrode is specified. A comma is used to show components that are in the same phase.
A voltaic cell is made of aqueous Bromine and Zinc. Given -

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

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

Solution:

\[ \text{Br}_2(aq) + 2e^- \rightarrow 2\text{Br}^-(aq) \quad \text{[reduction; cathode]} \]
\[ \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^- \quad \text{[oxidation; anode]} \quad E_{\text{zinc}} = -0.76 \text{ V} \]

\[ E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \]
\[ 1.83 = E_{\text{bromine}} - (-0.76) \]
\[ 1.83 - 0.76 = E_{\text{bromine}} = 1.07 \text{ Volt} \]

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: \( \text{Br}_2 + 2e^- \leftrightarrow 2\text{Br}^- \quad E_{\text{red}} = 1.09 \text{ V} \)

Anode: \( \text{Cu} \leftrightarrow \text{Cu}^{2+} + 2e^- \quad E_{\text{ox}} = -E_{\text{red}} = -0.34 \text{ V} \)

Cell: \( \text{Cu} + \text{Br}_2 \leftrightarrow \text{Cu}^{2+} + 2\text{Br}^- \quad E_{\text{cell}} = 0.75 \)

\[
\ln K = \frac{nF \Delta E^{\circ}}{RT} = \frac{2 \times 96485 \text{ C}}{8.3145 \text{ J/molK} \times 298.15 \text{ K}} \times 0.75 \text{ V} = 58.38 \times 10^{-20} \]

\[ K = e^{\ln K} = 2.2 \times 10^{25} \]

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

Adding of Oxygen, or Halogens (F, Cl, Br, I) or other p-Block elements which accept electrons, is oxidation. So if Potassium (K) gets Oxygen (attaches to O) to form \( \text{K}_2\text{O} \) or \( \text{K}_2\text{O}_2 \) (Superoxide), K is getting oxidized. If Cs attaches with F then Cs is getting oxidized, while F is being reduced. Cs is a reducing agent as it is loosing electrons. F is an oxidizing agent as it is gaining electrons.

Adding of Hydrogen is reduction. So if Ethene receives Hydrogen to become Ethane, then Ethene is being reduced. Raney Nickel is Nickel with molecular level pores. Raney Ni with HCl gives Hydrogen atoms, (some teachers say this as Nascent Hydrogen) locally, meaning near the molecule where the reaction is needed. So Raney Ni + HCl is a good reducing agent. Same for Zinc dust + HCl. But then what is Birch reduction?
As my experience of teaching more than 25 years, almost every student understands these. Knowing this is essential but does not ensure success in chemistry. There are many kinds of details of oxidizing agent or Reducing agent that vary from reactions / situations.

Using half reactions write the spontaneous Redox reactions

\[ \text{Sn}^{2+} (aq) + 2e^- \rightarrow \text{Sn}(s) \quad E^\circ_{\text{Sn}} = -0.14 \text{ V} \]
\[ \text{Ag}^+ (aq) + e^- \rightarrow \text{Ag}(s) \quad E^\circ_{\text{Ag}} = 0.80 \text{ V} \]

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

\[ 2\text{Ag}^+ (aq) + 2e^- \rightarrow 2\text{Ag}(s) \quad E^\circ_{\text{Ag}} = 0.80 \text{ V} \]

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

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

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

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 looses electrons in Anode.

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

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

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

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

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

Two Types of Redox Reactions

(i) Inter molecular Redox Reactions:

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

\[ \text{NO}_2^- + H_2S + H_2O + H^+ \rightarrow \text{NH}_4^+ + HSO_4^- \]

(ii) Intra molecular Redox Reactions:

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

(1) Molecular Equations:

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

Example: \( \text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2 \)

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

(2) Ionic Equation:

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

Example: \( \text{MnO}_2 + 4\text{H}^+ + 4\text{Cl}^- \rightarrow \text{Mn}^{2+} + 2\text{Cl}^2^+ + 2\text{H}_2\text{O} + \text{Cl}_2 \)
In the above example, the reactant and products have been written in ionic forms, thus the equation is termed as ionic equation.

The rules to be followed for writing ionic equations are:

- All soluble ionic compounds involved in a chemical changes are expressed in ionic symbols and covalent substances are written in molecular form. \( \text{H}_2\text{O}, \text{NH}_3, \text{NO}_2, \text{NO}, \text{SO}_2, \text{CO}, \text{CO}_2, \text{etc.}, \) are expressed in molecular form.
- The ionic compound which is highly insoluble is expressed in molecular form.
- The ions which are common and equal in number on both sides, i.e., spectator ions, are cancelled.
- Besides the atoms, the ionic charges must also be balanced on both the sides.

(3) Spectator Ions:

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

\[ \text{Zn} + 2\text{H}^+ + 2\text{Cl}^- \rightarrow \text{Zn}^{2+} + 2\text{Cl}^- + \text{H}_2 \]

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

(4) Oxidising agent:

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

(5) Reducing agent:

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

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

\[ \text{Au}^{3+}(\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{Au}(\text{s}) + \text{I}_2(\text{s}) \]

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

\[ \text{Au}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow \text{Au}(\text{s}) + \text{I}_2(\text{s}) \]

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

\[ \text{I}^- (aq) \rightarrow \frac{1}{2} \text{I}_2 (s) + e^- \]
\[ \text{Au}^{3+} (aq) + 3e^- \rightarrow \text{Au} (s) \]

We know that in redox reactions, the number of electrons lost by the reducing agent must be equal to the number of electrons gained by the oxidizing agent; thus, for each \( \text{Au}^{3+} \) that gains three electrons, there must be three \( \text{I}^- \) ions that each lose one electron. If we place a 3 in front of the \( \text{I}^- \) and balance the iodine atoms with a \( \frac{3}{2} \) in front of the \( \text{I}_2 \), both the atoms and the charge will be balanced.

\[ \text{Au}^{3+} (aq) + 3\text{I}^- (aq) \rightarrow \text{Au} (s) + \frac{3}{2} \text{I}_2 (s) \]

or  
\[ 2\text{Au}^{3+} (aq) + 6\text{I}^- (aq) \rightarrow 2\text{Au} (s) + 3\text{I}_2 (s) \]

**Balancing Redox Equations Using the Oxidation Number Method**

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

**General Steps**

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

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

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

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

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

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

**Step 7:** Balance the rest of the equation by inspection.
Balance the following redox equation using either the “inspection” technique or the “oxidation number” method. Be sure to check that the atoms and the charge are balanced.

\[
\text{HNO}_3(aq) + \text{H}_3\text{AsO}_3(aq) \\
\rightarrow \text{NO}(g) + \text{H}_3\text{AsO}_4(aq) + \text{H}_2\text{O}(l)
\]

**Solution:**

**Step 1:** Try to balance the atoms by inspection.

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

**Step 3:** Is the reaction redox?

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

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

As  +3 to +5  \quad \text{Net Change} = +2  
N  +5 to +2  \quad \text{Net Change} = −3

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

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

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

\[
2\text{HNO}_3(aq) + 3\text{H}_3\text{AsO}_3(aq) \\
\rightarrow 2\text{NO}(g) + \text{H}_3\text{AsO}_4(aq) + \text{H}_2\text{O}(l)
\]

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

\[
2\text{HNO}_3(aq) + 3\text{H}_3\text{AsO}_3(aq) \\
\rightarrow 2\text{NO}(g) + 3\text{H}_3\text{AsO}_4(aq) + \text{H}_2\text{O}(l)
\]
Balancing Redox Reactions Using the Oxidation Number Method:

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

\[ \text{Cu(s)} + \text{HNO}_3(aq) \rightarrow \text{Cu(NO}_3)_2(aq) + \text{NO(g)} + \text{H}_2\text{O(l)} \]

**Solution:**

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

\[ \text{Cu} \quad 0 \to +2 \quad \text{Net Change} = +2 \]

\[ \text{Some N} \quad +5 \to +2 \quad \text{Net Change} = -3 \]

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

\[ 3\text{Cu(s)} + \text{HNO}_3(aq) \rightarrow 3\text{Cu(NO}_3)_2(aq) + 2\text{NO(g)} + \text{H}_2\text{O(l)} \]

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

\[ 3\text{Cu(s)} + 8\text{HNO}_3(aq) \rightarrow 3\text{Cu(NO}_3)_2(aq) + 2\text{NO(g)} + 4\text{H}_2\text{O(l)} \]

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

\[ \text{NO}_2(g) + \text{H}_2(g) \rightarrow \text{NH}_3(g) + \text{H}_2\text{O(l)} \]

**Solution:**

The atoms in this equation can be balanced by inspection. (You might first place a 2 in front of the H\(_2\)O to balance the O’s, then 7/2 in front of the H\(_2\) to balance the H’s, and then multiply all the coefficients by 2 to get rid of the fraction.)

\[ 2\text{NO}_2(g) + 7\text{H}_2(g) \rightarrow 2\text{NH}_3(g) + 4\text{H}_2\text{O(l)} \]
We therefore proceed to Step 2. For the reaction between NO$_2$ and H$_2$, the net charge on both sides of the equation in Step 1 is zero. Because the charge and the atoms are balanced, the equation is correctly balanced.

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

Redox reactions are commonly run in acidic solution, in which case the reaction equations often include H$_2$O(l) and H$^+$ (aq). This page will show you how to write balanced equations for such reactions even when you do not know whether the H$_2$O(l) and H$^+$ (aq) are reactants or products. For example, you may know that dichromate ions, Cr$_2$O$_7^{2-}$, react with nitrous acid molecules, HNO$_2$, in acidic conditions to form chromium ions, Cr$^{3+}$, and nitrate ions, NO$_3^-$.

Because the reaction requires acidic conditions, you assume that H$_2$O(l) and H$^+$ (aq) participate in some way, but you do not know whether they are reactants or products, and you do not know the coefficients for the reactants and products. An unbalanced equation for this reaction might be written:

$$\text{Cr}_2\text{O}_7^{2-}(aq) + \text{HNO}_2(aq) \rightarrow \text{Cr}^{3+}(aq) + \text{NO}_3^-(aq) \quad \text{(acidic)}$$

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

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

**General Steps**

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

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

3. **Step 3:** Balance the oxygen atoms by adding H$_2$O molecules where needed.

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

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

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

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

8. **Step 8:** Check to make sure that the atoms and the charges balance.
EXAMPLE - Balancing Redox Equations for Reactions Run in Acidic Conditions: Balance the following redox equation using the “half-reaction” method.

\[ \text{Cr}_2\text{O}_7^{2-}(aq) + \text{HNO}_2(aq) \rightarrow \text{Cr}^{3+}(aq) + \text{NO}_3^-(aq) \text{ (acidic)} \]

Solution:

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

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

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
\[ \text{HNO}_2 \rightarrow \text{NO}_3^- \]

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

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

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} \]
\[ \text{HNO}_2 \rightarrow \text{NO}_3^- \]

Step 3: Balance the oxygen atoms by adding \( \text{H}_2\text{O} \) molecules on the side of the arrow where O atoms are needed.

The first half-reaction needs seven oxygen atoms on the right, so we add seven \( \text{H}_2\text{O} \) molecules.

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

The second half-reaction needs one more oxygen atom on the left, so we add one \( \text{H}_2\text{O} \) molecule.

\[ \text{HNO}_2 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- \]

Step 4: Balance the hydrogen atoms by adding \( \text{H}^+ \) ions on the side of the arrow where H atoms are needed.

The first half-reaction needs 14 hydrogen atoms on the left to balance the 14 hydrogen atoms in the 7 \( \text{H}_2\text{O} \) molecules, so we add 14 \( \text{H}^+ \) ions to the left.

\[ \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

The second half-reaction needs three hydrogen atoms on the right to balance the three hydrogen atoms on the left, so we add 3 \( \text{H}^+ \) ions to the right.
HNO₂ + H₂O → NO₃⁻ + 3H⁺

**Step 5:** Balance the charge by adding electrons, e⁻.

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

The sum of the charges on the left side of the chromium half-reaction is +12 (-2 for the Cr₂O₇²⁻ plus +14 for the 14 H⁺). The sum of the charges on the right side of the chromium half-reaction is +6 (for the 2 Cr³⁺). If we add six electrons to the left side, the sum of the charges on each side of the equation becomes +6.

6e⁻ + Cr₂O₇²⁻ + 14H⁺ → 2Cr³⁺ + 7H₂O

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

HNO₂ + H₂O → NO₃⁻ + 3H⁺ + 2e⁻

(Although it is not necessary, you can check that you have added the correct number of electrons by looking to see whether the net change in oxidation number for each half-reaction is equal to the number of electrons gained or lost. Because the two Cr atoms in Cr₂O₇²⁻ are changing from +6 to +3, the net change in oxidation number is 2(−3) or −6. This would require six electrons, so we have added the correct number of electrons to the first half-reaction. The N atom in HNO₂ changes from +3 to +5, so the net change is +2. Two electrons would be lost in this change, so we have added the correct number of electrons to the second half-reaction.)

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

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

6e⁻ + Cr₂O₇²⁻ + 14H⁺ → 2Cr³⁺ + 7H₂O

3(HNO₂ + H₂O → NO₃⁻ + 3H⁺ + 2e⁻)

or

6e⁻ + Cr₂O₇²⁻ + 14H⁺ → 2Cr³⁺ + 7H₂O

3HNO₂ + 3H₂O → 3NO₃⁻ + 9H⁺ + 6e⁻

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

The 3 H₂O in the second half-reaction cancel three of the 7 H₂O in the first half-reaction to yield 4 H₂O on the right of the final equation.
The 9 H⁺ on the right of the second half-reaction cancel nine of the 14 H⁺ on the left of the first half-reaction leaving 5 H⁺ on the left of the final equation.

\[ \text{Cr}_2\text{O}_7^{2-} + 3\text{HNO}_2 + 5\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{NO}_3^- + 4\text{H}_2\text{O} \]

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

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

\[ \text{Cr}_2\text{O}_7^{2-} (aq) + 3\text{HNO}_2 (aq) + 5\text{H}^+ (aq) \rightarrow 2\text{Cr}^{3+} (aq) + 3\text{NO}_3^- (aq) + 4\text{H}_2\text{O}(l) \]

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

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

\[ \text{Cr(OH)}_3(s) + \text{ClO}_3^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}^-(aq) \quad \text{(basic)} \]

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

**Balancing Redox Equations Run in Basic Conditions Using the Half-reaction Technique**

To balance a redox equation and told that it takes place in a basic solution, you can use the following procedure.

**General Steps**

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

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

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

**Step 10:** Cancel or combine the H₂O molecules.
Step 11: Check to make sure that the atoms and the charge balance. If they do balance, you are done. If they do not balance, re-check your work in Steps 1-10.

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

\[
\text{Cr(OH)}_3(s) + \text{ClO}_3^-(aq) \rightarrow \text{CrO}_4^{2-}(aq) + \text{Cl}^-(aq) \quad \text{(basic)}
\]

**Solution:**

**Step 1:**

\[
\begin{align*}
\text{Cr(OH)}_3 & \rightarrow \text{CrO}_4^{2-} \\
\text{ClO}_3^- & \rightarrow \text{Cl}^-
\end{align*}
\]

**Step 2:** (Not necessary for this example)

\[
\begin{align*}
\text{Cr(OH)}_3 & \rightarrow \text{CrO}_4^{2-} \\
\text{ClO}_3^- & \rightarrow \text{Cl}^- \quad \text{3H}_2\text{O}
\end{align*}
\]

**Step 3:**

\[
\begin{align*}
\text{Cr(OH)}_3 + \text{H}_2\text{O} & \rightarrow \text{CrO}_4^{2-} \\
\text{ClO}_3^- & \rightarrow \text{Cl}^- + \text{3H}_2\text{O}
\end{align*}
\]

**Step 4:**

\[
\begin{align*}
\text{Cr(OH)}_3 + \text{H}_2\text{O} & \rightarrow \text{CrO}_4^{2-} + 5\text{H}^+ \\
\text{ClO}_3^- + 6\text{H}^+ & \rightarrow \text{Cl}^- + \text{3H}_2\text{O}
\end{align*}
\]

**Step 5:**

\[
\begin{align*}
\text{Cr(OH)}_3 + \text{H}_2\text{O} & \rightarrow \text{CrO}_4^{2-} + 5\text{H}^+ + 3\text{e}^- \\
\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{Cl}^- + \text{3H}_2\text{O}
\end{align*}
\]

**Step 6:**

\[
\begin{align*}
2(\text{Cr(OH)}_3 + \text{H}_2\text{O} & \rightarrow \text{CrO}_4^{2-} + 5\text{H}^+ + 3\text{e}^-) \\
\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{Cl}^- + \text{3H}_2\text{O}
\end{align*}
\]

or
2Cr(OH)₃ + 2H₂O → 2CrO₄²⁻ + 10H⁺ + 6e⁻

ClO₃⁻ + 6H⁺ + 6e⁻ → Cl⁻ + 3H₂O

Step 7:
2Cr(OH)₃(s) + ClO₃⁻(aq) → 2CrO₄²⁻(aq) + Cl⁻(aq) + H₂O(l) + 4H⁺(aq)

Step 8: Because there are 4 H⁺ on the right side of our equation above, we add 4 OH⁻ to each side of the equation.
2Cr(OH)₃ + ClO₃⁻ + 4OH⁻ → 2CrO₄²⁻ + Cl⁻ + H₂O + 4H⁺ + 4OH⁻

Step 9: Combine the 4 H⁺ ions and the 4 OH⁻ ions on the right of the equation to form 4 H₂O.
2Cr(OH)₃ + ClO₃⁻ + 4OH⁻ → 2CrO₄²⁻ + Cl⁻ + H₂O + 4H₂O

Step 10: Cancel or combine the H₂O molecules.
2Cr(OH)₃(s) + ClO₃⁻(aq) + 4OH⁻(aq) → 2CrO₄²⁻(aq) + Cl⁻(aq) + 5H₂O(l)

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

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

Example: ClO₃⁻ + SO₂ --> SO₄²⁻ + Cl⁻

Solution:
1) Split into unbalanced half-reactions:
ClO₃⁻ --> Cl⁻
SO₂ --> SO₄²⁻

2) Balance the half-reactions:
6e⁻ + 6H⁺ + ClO₃⁻ --> Cl⁻ + 3H₂O
2H₂O + SO₂ --→ SO₄²⁻ + 4H⁺ + 2e⁻
3) Make the number of electrons equal:

\[ 6e^- + 6H^+ + ClO_3^- \rightarrow Cl^- + 3H_2O \]

\[ 6H_2O + 3SO_2 \rightarrow 3SO_4^{2-} + 12H^+ + 6e^- \quad \text{multiplied through by a factor of 3} \]

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

\[ ClO_3^- + 3H_2O + 3SO_2 \rightarrow 3SO_4^{2-} + Cl^- + 6H^+ \]

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

**Example**: \( H_2S + NO_3^- \rightarrow S_8 + NO \)

**Solution**:

1) The unbalanced half-reactions:

\[ H_2S \rightarrow S_8 \]

\[ NO_3^- \rightarrow NO \]

2) balance each half-reaction:

\[ 8H_2S \rightarrow S_8 + 16H^+ + 16e^- \]

\[ 3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O \]

3) Make the number of electrons equal:

\[ 24H_2S \rightarrow 3S_8 + 48H^+ + 48e^- \quad \text{multiplied by a factor of 3} \]

\[ 48e^- + 64H^+ + 16NO_3^- \rightarrow 16NO + 32H_2O \quad \text{multiplied by a factor of 16} \]

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

4) Add:

\[ 24H_2S + 16H^+ + 16NO_3^- \rightarrow 3S_8 + 16NO + 32H_2O \]

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

**Example**: \( MnO_4^- + H_2S \rightarrow Mn^{2+} + S_8 \)

**Solution**:

1) Half-reactions:

\[ H_2S \rightarrow S_8 \]

\[ MnO_4^- \rightarrow Mn^{2+} \]

\[ 24H_2S + 16H^+ + 16NO_3^- \rightarrow 3S_8 + 16NO + 32H_2O \]
2) Balance:

\[ 8H_2S \rightarrow S_8 + 16H^+ + 16e^- \]
\[ 5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \]

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

\[ 40H_2S \rightarrow 5S_8 + 80H^+ + 80e^- \quad \text{factor of 5} \]
\[ 80e^- + 128H^+ + 16MnO_4^- \rightarrow 16Mn^{2+} + 64H_2O \quad \text{factor of 16} \]

4) The final answer:

\[ 40H_2S + 48H^+ + 16MnO_4^- \rightarrow 5S_8 + 16Mn^{2+} + 64H_2O \]

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

**Example:** \( Cu + SO_4^{2-} \rightarrow Cu^{2+} + SO_2 \)

1) The unbalanced half-reactions:

\( Cu \rightarrow Cu^{2+} \]
\( SO_4^{2-} \rightarrow SO_2 \]

2) The balanced half-reactions:

\( Cu \rightarrow Cu^{2+} + 2e^- \]
\( 2e^- + 4H^+ + SO_4^{2-} \rightarrow SO_2 + 2H_2O \]

3) The final answer:

\( Cu + 4H^+ + SO_4^{2-} \rightarrow Cu^{2+} + SO_2 + 2H_2O \]

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

**Example:** \( MnO_4^- + CH_3OH \rightarrow HCOOH + Mn^{2+} \)

1) The balanced half-reactions:

\( 5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \]
\( H_2O + CH_3OH \rightarrow HCOOH + 4H^+ + 4e^- \]

2) Equalize electrons:

\[ 20e^- + 32H^+ + 4MnO_4^- \rightarrow 4Mn^{2+} + 16H_2O \quad \text{factor of 4} \]
\[ 5H_2O + 5CH_3OH \rightarrow 5HCOOH + 20H^+ + 20e^- \quad \text{factor of 5} \]
3) The final answer:

\[ 12H^+ + 5CH_3OH + 4MnO_4^- \rightarrow 5HCOOH + 4Mn^{2+} + 11H_2O \]

**Example:** \[ Cr_2O_7^{2-} + SO_2 + H^+ \rightarrow Cr^{3+} + HSO_4^- + H_2O \]

**Solution:**

1) Half-reactions:

\[ Cr_2O_7^{2-} \rightarrow Cr^{3+} \]
\[ SO_2 \rightarrow HSO_4^- \]

2) Balance in acidic solution:

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]
\[ 2H_2O + SO_2 \rightarrow HSO_4^- + 3H^+ + 2e^- \]

3) Equalize electrons:

\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]
\[ 6H_2O + 3SO_2 \rightarrow 3HSO_4^- + 9H^+ + 6e^- \]

4) Add:

\[ 5H^+ + Cr_2O_7^{2-} + 3SO_2 \rightarrow 2Cr^{3+} + 3HSO_4^- + H_2O \]

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

Since the equation is in acidic solution, you can use HCl or HNO_3. I’ll use HCl. The most common dichromate that is soluble is potassium dichromate, so we will use that. Using those, we find this:

\[ 5HCl + K_2Cr_2O_7 + 3SO_2 \rightarrow 2CrCl_3 + 3KHSO_4 + H_2O \]

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

\[ KCl + 5HCl + K_2Cr_2O_7 + 3SO_2 \rightarrow 2CrCl_3 + 3KHSO_4 + H_2O \]

You can write the equation using HNO_3 and the nitrate would simply replace the chloride.

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

If you don’t have a net ionic equation to balance, that means you have what is usually called a molecular equation (or a complete molecular equation). These are harder to balance because the elements being oxidized and reduced are mixed in with substances that are not being reduced or oxidized.
The solution is to, as much as possible, remove the "extraneous" substances: the ones that are neither oxidized or reduced. This gives you an unbalanced net ionic equation, which you proceed to balance. You then add back in the substances you had removed.

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

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

\[ \text{CuCl}_2 + \text{KI} \rightarrow \text{CuI} + \text{I}_2 + \text{KCl} \]

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

\[ \text{Cu}^{2+} + \text{I}^- \rightarrow \text{Cu}^+ + \text{I}_2 \]

and eventually this:

\[ 2\text{Cu}^{2+} + 2\text{I}^- \rightarrow 2\text{Cu}^+ + \text{I}_2 \]

**Example:** \( \text{NaCl} + \text{H}_2\text{SO}_4 + \text{MnO}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2 \)

**Solution:**

1) What to remove?

\( \text{NaCl}: \) sodium ion is a classic spectator ion and it will be removed.
\( \text{H}_2\text{SO}_4: \) notice how only sulfate is present on the right-hand side. It will be removed.
\( \text{MnO}_2: \) this stays since Mn is reduced in the reaction.
\( \text{Cl}_2: \) it stays since the chloride from the left-hand side is oxidized.

Here is what remains: \( \text{Cl}^- + \text{H}^+ + \text{MnO}_2 \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} + \text{Cl}_2 \)

That's the net ionic.

Notice I kept the \( \text{MnO}_2 \) intact.

2) Now for the half-reactions:

\( \text{Cl}^- \rightarrow \text{Cl}_2 \)
\( \text{MnO}_2 \rightarrow \text{Mn}^{2+} \)

3) Balance them:

\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]
\[ 2\text{e}^- + 4\text{H}^+ + \text{MnO}_2 \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \]
4) Since the electrons are already balanced, we add:

\[2\text{Cl}^- + 4\text{H}^+ + \text{MnO}_2 \rightarrow \text{Cl}_2 + \text{Mn}^{2+} + 2\text{H}_2\text{O}\]

5) We add in two more chloride to make \(\text{MnCl}_2\):

\[4\text{Cl}^- + 4\text{H}^+ + \text{MnO}_2 \rightarrow \text{Cl}_2 + \text{MnCl}_2 + 2\text{H}_2\text{O}\]

6) We add in 4 sodium ion to make \(\text{NaCl}\):

\[4\text{Na}^+ + 4\text{H}^+ + \text{MnO}_2 \rightarrow 4\text{Na}^+ + \text{Cl}_2 + \text{MnCl}_2 + 2\text{H}_2\text{O}\]

7) Add in four sulfate ions:

\[4\text{Na}^+ + 2\text{H}_2\text{SO}_4 + \text{MnO}_2 \rightarrow 2\text{Na}_2\text{SO}_4 + \text{Cl}_2 + \text{MnCl}_2 + 2\text{H}_2\text{O}\]

**Example:** \(\text{SeCl}_2 \rightarrow \text{H}_2\text{SeO}_3 + \text{Se} + \text{HCl}\)

**Solution:**

1) Here is what can be removed:

a) the \(\text{SeCl}_2\) can be changed to \(\text{Se}^{2+}\)

b) the \(\text{H}_2\text{SeO}_3\) can be changed to \(\text{SeO}_3^{2-}\)

c) the HCl.

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

I will discuss the \(\text{SeO}_3^{2-}\) a bit more below. Also, the HCl tells me that this solution is to be balanced in acidic solution.

2) We now have this unbalanced net ionic equation:

\(\text{Se}^{2+} \rightarrow \text{SeO}_3^{2-} + \text{Se}\)

3) Here are the two half-reactions:

\(\text{Se}^{2+} \rightarrow \text{SeO}_3^{2-}\)

\(\text{Se}^{2+} \rightarrow \text{Se}\)

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

\[3\text{H}_2\text{O} + \text{Se}^{2+} \rightarrow \text{SeO}_3^{2-} + 6\text{H}^+ + 2\text{e}^-\]

\(\text{Se}^{2+} + 2\text{e}^- \rightarrow \text{Se}\)
5) Add the two half-reactions and eliminate electrons:

\[ 3\text{H}_2\text{O} + 2\text{Se}^{2+} \rightarrow \text{Se} + \text{SeO}_3^{2-} + 6\text{H}^+ \]

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

a) \[ 3\text{H}_2\text{O} + 2\text{SeCl}_2 \rightarrow \text{Se} + \text{SeO}_3^{2-} + 4\text{HCl} + 2\text{H}^+ \]

b) \[ 3\text{H}_2\text{O} + 2\text{SeCl}_2 \rightarrow \text{Se} + \text{H}_2\text{SeO}_3 + 4\text{HCl} \]

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

\[ \text{Se}^{2+} \rightarrow \text{Se}^{4+} + 2e^- \]

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

\[ 2\text{Se}^{2+} \rightarrow \text{Se}^{4+} + \text{Se} \]

However, it seems to me to be a bit of a hassle to get back to the final answer. You might wish to try that on your own. Also, \( \text{H}_2\text{SeO}_3 \) is a weak acid. You might want to keep the full formula in its half-reaction and then balance. You can also get to the correct answer that way.

**Example** : \( \text{H}_2\text{SO}_3 + \text{KMnO}_4 \rightarrow \text{MnSO}_4 + \text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \)

**Solution:**

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

1) Here is what I will remove:

a) the \( \text{H}_2\text{O} \) (it will get back in via both half-reactions)

b) the H in \( \text{H}_2\text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \)

c) the potassium ion

Here is the unbalanced net-ionic equation that results:

\[ \text{SO}_3^{2-} + \text{MnO}_4^- \rightarrow \text{MnSO}_4 \]

In order to make the half-reactions, I going to allow the \( \text{MnSO}_4 \) to ionize. Why?

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

Also, suppose I keep the \( \text{MnSO}_4 \) unionized. That means I would have to include the permanganate in the equation, to keep Mn present on both sides. That means I have to balance the net-ionic equation.
2) Here are the half-reactions that result:

\[ \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} \]
\[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \]

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

\[ 5 \left[ \text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2e^- \right] \]
\[ 2 \left[ 5e^- + 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \right] \]

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

\[ 5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 5\text{SO}_4^{2-} + 2\text{Mn}^{2+} + 3\text{H}_2\text{O} \]

5) Make some MnSO₄:

\[ 5\text{SO}_3^{2-} + 2\text{MnO}_4^- + 6\text{H}^+ \rightarrow 3\text{SO}_4^{2-} + 2\text{MnSO}_4 + 3\text{H}_2\text{O} \]

6) Make some potassium permanganate:

\[ 5\text{SO}_3^{2-} + 2\text{KMnO}_4 + 6\text{H}^+ \rightarrow 2\text{SO}_4^{2-} + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{SO}_4 \]

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

7) Make some H₂SO₃:

\[ 2\text{SO}_3^{2-} + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_3 \rightarrow 2\text{SO}_4^{2-} + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{SO}_4 \]

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

\[ 2\text{KMnO}_4 + 5\text{H}_2\text{SO}_3 \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{SO}_4 \]

Example

\[ \text{HCl} + \text{KMnO}_4 \rightarrow \text{H}_2\text{O} + \text{KCl} + \text{MnCl}_2 + \text{Cl}_2 \]

And \[ \text{KMnO}_4 + \text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Cl}_2 + \text{H}_2\text{O} \]

We can eliminate the following:

\[ \text{H}^+ \text{ from the HCl} \]
\[ \text{H}_2\text{O} \]
\[ \text{K}^+ \]
\[ \text{Cl}^- \text{, but only from the right-hand side} \]

Why only from the right-hand side? It is because the Cl¯ will be oxidized. I know this because there is Cl₂ on the right-hand side as well. This tells me the chlorine is going from a -1 oxidation state to zero. It is being oxidized. So, I need Cl¯ on the left-hand side, but not the right-hand side.
Here is the net-ionic equation:

\[ \text{Cl}^- + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 \]

From this, we get the half-reactions:

\[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \]
\[ \text{Cl}^- \rightarrow \text{Cl}_2 \]

The balanced half-reactions:

\[ 2 \left[ 5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \right] \]
\[ 5 \left[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \right] \]

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

The balanced equation, in net-ionic form:

\[ 16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

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

\[ 6\text{H}^+ + 2\text{MnO}_4^- + 10\text{HCl} \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

Next, add potassium ion back in:

\[ 6\text{H}^+ + 2\text{KMnO}_4 + 10\text{HCl} \rightarrow 2\text{Mn}^{2+} + 2\text{K}^+ + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

To both sides, add in six chlorine ions:

\[ 2\text{KMnO}_4 + 16\text{HCl} \rightarrow 2\text{MnCl}_2 + 2\text{KCl} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \]

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

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

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

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

- \( \text{K}^+ \) (from the KMnO4 AND the KCl)
- \( \text{H}_2\text{SO}_4 \)
- \( \text{K}_2\text{SO}_4 \)
- \( \text{SO}_4^{2-} \) (from the MnSO4)
- \( \text{H}_2\text{O} \)
That leaves this:

\[ \text{MnO}_4^- + \text{Cl}^- \rightarrow \text{Mn}^{2+} + \text{Cl}_2 \]

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

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

\[ \begin{align*}
\text{MnO}_4^- & \rightarrow \text{Mn}^{2+} \\
\text{Cl}^- & \rightarrow \text{Cl}_2 \\
5e^- + 8\text{H}^+ + \text{MnO}_4^- & \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \\
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^- \\
16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Cl}^- & \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 8\text{H}_2\text{O} \quad \text{(this is the balanced, net ionic equation)}
\end{align*} \]

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

a) add back in 8 sulfates:

\[ 8\text{H}_2\text{SO}_4 + 2\text{MnO}_4^- + 10\text{Cl}^- \rightarrow 2\text{MnSO}_4 + 5\text{Cl}_2 + 8\text{H}_2\text{O} + 6\text{K}_2\text{SO}_4 \]

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

\[ 8\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 + 10\text{KCl} \rightarrow 2\text{MnSO}_4 + 5\text{Cl}_2 + 8\text{H}_2\text{O} + 6\text{K}_2\text{SO}_4 \]

The last equation is the balanced, molecular equation.

Or

\[ \text{KMnO}_4 + \text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Cl}_2 + \text{H}_2\text{O} \]

1) identify the atoms being oxidized and reduced:

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

2) write the two half-reactions:

\[ \begin{align*}
\text{Mn}^{7+} + 5e^- & \rightarrow \text{Mn}^{2+} \\
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^-
\end{align*} \]

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

\[ 2\text{Mn}^{7+} + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 \]

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

\[ 2\text{KMnO}_4 + 10\text{KCl} + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Cl}_2 + \text{H}_2\text{O} \]

5) balancing the other atoms can be done easily now by 'trial and error' method
Example: \( \text{Fe(s)} + \text{NO}_3^-(aq) \rightarrow \text{Fe}^{3+}(aq) + \text{NO}_2(g) \)

Solution:

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

Balance by half-reactions in acidic solution:

\[
\begin{align*}
\text{Fe(s)} & \rightarrow \text{Fe}^{3+}(aq) + 3e^- \\
2e^- + 2H^+ + \text{NO}_3^-(aq) & \rightarrow \text{NO}_2(g) + H_2O
\end{align*}
\]

\[
\begin{align*}
3e^- + 6H^+ + 3\text{NO}_3^-(aq) & \rightarrow 3\text{NO}_2(g) + 3H_2O \\
6H^+ + \text{Fe(s)} + 3\text{NO}_3^-(aq) & \rightarrow \text{Fe}^{3+}(aq) + 3\text{NO}_2(g) + 3H_2O
\end{align*}
\]

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

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

\[
3H^+ + \text{Fe(s)} + 3\text{HNO}_3(aq) \rightarrow \text{Fe(NO}_3)_3(aq) + 3\text{NO}_2(g) + 3H_2O
\]

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

\[
\text{Fe(s)} + 6\text{HNO}_3(aq) \rightarrow \text{Fe(NO}_3)_3(aq) + 3\text{NO}_2(g) + 3H_2O
\]

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

Example: \( \text{HBr} + \text{NaMnO}_4 \rightarrow \text{NaBr} + \text{Br}_2 + \text{MnBr}_2 + \text{H}_2\text{O} \)

1) Half-reactions:

\[
\begin{align*}
\text{Br}^- & \rightarrow \text{Br}_2 \\
\text{MnO}_4^- & \rightarrow \text{Mn}^{2+}
\end{align*}
\]

2) Balance them:

\[
\begin{align*}
2\text{Br}^- & \rightarrow \text{Br}_2 + 2e^- \\
5e^- + 8H^+ + \text{MnO}_4^- & \rightarrow \text{Mn}^{2+} + 4H_2O
\end{align*}
\]

3) Equalize electrons, then combine half-reactions:

\[
16H^+ + 10\text{Br}^- + 2\text{MnO}_4^- \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} + 8H_2O
\]

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

\[
16H^+ + 12\text{Br}^- + 2\text{NaMnO}_4 \rightarrow 2\text{NaBr} + 5\text{Br}_2 + 2\text{Mn}^{2+} + 8H_2O
\]
5) Add four bromide ions to each side:

\[16\text{HBr} + 2\text{NaMnO}_4 \rightarrow 2\text{NaBr} + 5\text{Br}_2 + 2\text{MnBr}_2 + 8\text{H}_2\text{O}\]

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

**Example** \(\text{HNO}_3 + \text{KI} \rightarrow \text{KNO}_3 + \text{I}_2 + \text{NO} + \text{H}_2\text{O}\)

1) Half-reactions:

\[\text{NO}_3^- \rightarrow \text{NO}\]
\[\text{I}^- \rightarrow \text{I}_2\]

2) Balance them:

\[3e^- + 4\text{H}^+ + \text{NO}_3^- \rightarrow \text{NO} + 2\text{H}_2\text{O}\]
\[2\text{I}^- \rightarrow \text{I}_2 + 2e^-\]

3) Equalize electrons, then combine half-reactions:

\[8\text{H}^+ + 2\text{NO}_3^- + 6\text{I}^- \rightarrow 3\text{I}_2 + 2\text{NO} + 4\text{H}_2\text{O}\]

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

\[8\text{HNO}_3 + 6\text{KI} \rightarrow 6\text{KNO}_3 + 3\text{I}_2 + 2\text{NO} + 4\text{H}_2\text{O}\]

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

**Example** \(\text{KOH} + \text{Zn} + \text{H}_2\text{O} + \text{KNO}_3 \rightarrow \text{K}_2\text{Zn(OH)}_4 + \text{NH}_3\)

1) Half-reactions:

\[\text{Zn} \rightarrow \text{Zn(OH)}_4^{2^-}\]
\[\text{NO}_3^- \rightarrow \text{NH}_3\]

2) Balance:

\[4\text{OH}^- + \text{Zn} \rightarrow \text{Zn(OH)}_4^{2^-} + 2e^-\]
\[8e^- + 6\text{H}_2\text{O} + \text{NO}_3^- \rightarrow \text{NH}_3 + 9\text{OH}^-\]

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

3) Equalize electrons, then combine half-reactions:

\[7\text{OH}^- + 4\text{Zn} + 6\text{H}_2\text{O} + \text{NO}_3^- \rightarrow 4\text{Zn(OH)}_4^{2^-} + \text{NH}_3\]

4) Add eight potassium ions to each side:

\[7\text{KOH} + 4\text{Zn} + 6\text{H}_2\text{O} + \text{KNO}_3 \rightarrow 4\text{K}_2\text{Zn(OH)}_4^{2^-} + \text{NH}_3\]
Example \(\text{KNO}_2 + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{KNO}_3 + \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}\)

1) Write the net ionic equation:
\[\text{NO}_2^- + \text{MnO}_4^- \longrightarrow \text{NO}_3^- + \text{Mn}^{2+}\]

2) Half-reactions and balance:
\[\text{NO}_2^- \longrightarrow \text{NO}_3^-\]
\[\text{MnO}_4^- \longrightarrow \text{Mn}^{2+}\]
\[\text{H}_2\text{O} + \text{NO}_2^- \longrightarrow \text{NO}_3^- + 2\text{H}^+ + 2\text{e}^-\]
\[5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^- \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}\]

Top half-reaction by 5, bottom by 2; then add and eliminate water and hydrogen ion.
\[6\text{H}^+ + 5\text{NO}_2^- + 2\text{MnO}_4^- \longrightarrow 5\text{NO}_3^- + 2\text{Mn}^{2+} + 3\text{H}_2\text{O}\]

3) Add sulfate to the \(\text{Mn}^{2+}\):
\[2\text{H}^+ + 5\text{NO}_2^- + 2\text{MnO}_4^- + 2\text{H}_2\text{SO}_4 \longrightarrow 5\text{NO}_3^- + 2\text{MnSO}_4 + 3\text{H}_2\text{O}\]

4) Add seven potassium ions:
\[2\text{H}^+ + 5\text{KNO}_2 + 2\text{KMnO}_4 + 2\text{H}_2\text{SO}_4 \longrightarrow 5\text{KNO}_3 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + 2\text{K}^+\]

5) Add one more sulfate:
\[5\text{KNO}_2 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \longrightarrow 5\text{KNO}_3 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} + \text{K}_2\text{SO}_4\]

Example \(\text{K}_2\text{Cr}_2\text{O}_7 + \text{K}_2\text{C}_2\text{O}_4 + \text{H}_2\text{C}_2\text{O}_4 \longrightarrow \text{K}_3\text{Cr}(_2\text{C}_2\text{O}_4)_3 + \text{CO}_2 + \text{H}_2\text{O}\)

1) Write the net ionic equation:
\[\text{Cr}_2\text{O}_7^{2-} + \text{C}_2\text{O}_4^{2-} \longrightarrow \text{Cr}^{3+} + \text{CO}_2\]

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

2) Half-reactions and balance:
\[\text{Cr}_2\text{O}_7^{2-} \longrightarrow \text{Cr}^{3+}\]
\[\text{C}_2\text{O}_4^{2-} \longrightarrow \text{CO}_2\]
\[6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}\]
\[\text{C}_2\text{O}_4^{2-} \longrightarrow 2\text{CO}_2 + 2\text{e}^-\]
3) Equalize electrons and add:

\[ 14H^+ + Cr_2O_7^{2-} + 3C_2O_4^{2-} \rightarrow 2Cr^{3+} + 6CO_2 + 7H_2O \]

4) Add six oxalate ions to each side:

\[ 14H^+ + Cr_2O_7^{2-} + 9C_2O_4^{2-} \rightarrow 2Cr(C_2O_4)_3^{3-} + 6CO_2 + 7H_2O \]

5) Make seven oxalic acids:

\[ Cr_2O_7^{2-} + 2C_2O_4^{2-} + 7H_2C_2O_4 \rightarrow 2Cr(C_2O_4)_3^{3-} + 6CO_2 + 7H_2O \]

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

\[ K_2Cr_2O_7 + K_2C_2O_4 + 7H_2C_2O_4 \rightarrow 2K_3Cr(C_2O_4)_3 + 6CO_2 + 7H_2O \]

Example \( K_2MnF_6 + SbF_5 \rightarrow K_SbF_6 + MnF_3 + F_2 \)

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

\[ Mn^{4+} + F^- \rightarrow Mn^{3+} + F_2 \]

\[ e^- + Mn^{4+} \rightarrow Mn^{3+} \]

\[ 2F^- \rightarrow F_2 + 2e^- \]

\[ 2Mn^{4+} + 2F^- \rightarrow 2Mn^{3+} + F_2 \]

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

add 12 \( F^- \) to left side: \( 2MnF_6^{2-} + 2F^- \rightarrow 2Mn^{3+} + F_2 \)

add 12 \( F^- \) and one \( Sb^{5+} \) to the right side: \( 2MnF_6^{2-} + 2F^- \rightarrow SbF_6^- + 2MnF_3 + F_2 \)

add one \( Sb^{5+} \) to the left: \( 2MnF_6^{2-} + Sb^{5+} + 2F^- \rightarrow SbF_6^- + 2MnF_3 + F_2 \)

3) Add 4 potassium ions to the left:

\[ 2K_2MnF_6 + Sb^{5+} + 2F^- \rightarrow SbF_6^- + 2MnF_3 + F_2 \]

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

\[ 2K_2MnF_6 + Sb^{5+} + 2F^- \rightarrow 4K_SbF_6 + 2MnF_3 + F_2 \]

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

\[ 2K_2MnF_6 + 4Sb^{5+} + 20F^- \rightarrow 4K_SbF_6 + 2MnF_3 + F_2 \]

6) Combine ions for the final answer:

\[ 2K_2MnF_6 + 4SbF_5 \rightarrow 4K_SbF_6 + 2MnF_3 + F_2 \]
Example \( \text{Ca(OH)}_2 + \text{NaOH} + \text{ClO}_2 + \text{C} \rightarrow \text{NaClO}_2 + \text{CaCO}_3 + \text{H}_2\text{O} \)

1) Half-reactions:
\[
\begin{align*}
\text{C} \rightarrow & \text{CO}_3^{2-} \\
\text{ClO}_2 \rightarrow & \text{ClO}_2^- \\
\end{align*}
\]

2) Balance using acid solution & write net-ionic in basic solution:
\[
\begin{align*}
3\text{H}_2\text{O} + \text{C} \rightarrow & \text{CO}_3^{2-} + 6\text{H}^+ + 4\text{e}^- \\
\text{e}^- + \text{ClO}_2 \rightarrow & \text{ClO}_2^- \\
3\text{H}_2\text{O} + \text{C} + 4\text{ClO}_2 \rightarrow & \text{CO}_3^{2-} + 4\text{ClO}_2^- + 6\text{H}^+ \\
6\text{OH}^- + \text{C} + 4\text{ClO}_2 \rightarrow & \text{CO}_3^{2-} + 4\text{ClO}_2^- + 3\text{H}_2\text{O} \\
\end{align*}
\]

3) Add one calcium ion back in:
\[
\text{Ca(OH)}_2 + 4\text{OH}^- + \text{C} + 4\text{ClO}_2 \rightarrow \text{CaCO}_3 + 4\text{ClO}_2^- + 3\text{H}_2\text{O}
\]

4) Add 4 sodium ions:
\[
\text{Ca(OH)}_2 + 4\text{NaOH} + \text{C} + 4\text{ClO}_2 \rightarrow \text{CaCO}_3 + 4\text{NaClO}_2 + 3\text{H}_2\text{O}
\]

Example \( \text{K}_2\text{S} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{S}_8 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \)

1) Write the net ionic equation:
\[
\text{S}^{2-} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{S}_8 + \text{Cr}^{3+}
\]

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

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

2) Write the half-reactions and balance:
\[
\begin{align*}
\text{S}^{2-} \rightarrow & \text{S}_8 \\
\text{Cr}_2\text{O}_7^{2-} \rightarrow & \text{Cr}^{3+} \\
8\text{S}^{2-} \rightarrow & \text{S}_8 + 16\text{e}^- \\
6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow & 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\
\end{align*}
\]

Use a factor of three for the first half-reaction and eight for the second half-reaction.
\[
112\text{H}^+ + 8\text{Cr}_2\text{O}_7^{2-} + 24\text{S}^{2-} \rightarrow 3\text{S}_8 + 16\text{Cr}^{3+} + 56\text{H}_2\text{O}
\]
3) Add this to the left-hand side: 56 sulfate + 16 K⁺ + 48 K⁺

\[ 56\text{H}_2\text{SO}_4 + 8\text{K}_2\text{Cr}_2\text{O}_7 + 24\text{K}_2\text{S} \rightarrow 3\text{S}_8 + 16\text{Cr}^{3+} + 56\text{H}_2\text{O} \]

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

\[ 56\text{H}_2\text{SO}_4 + 8\text{K}_2\text{Cr}_2\text{O}_7 + 24\text{K}_2\text{S} \rightarrow 3\text{S}_8 + 8\text{Cr}_2(\text{SO}_4)_3 + 56\text{H}_2\text{O} \]

Note how the coefficient went from 16 to 8.

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

\[ 56\text{H}_2\text{SO}_4 + 8\text{K}_2\text{Cr}_2\text{O}_7 + 24\text{K}_2\text{S} \rightarrow 3\text{S}_8 + 8\text{Cr}_2(\text{SO}_4)_3 + 56\text{H}_2\text{O} + 32\text{K}_2\text{SO}_4 \]

**Example**

\[ \text{KMnO}_4 + \text{FeSO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} \]

1) Write the net ionic equation:

\[ \text{MnO}_4^- + \text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + \text{Fe}^{3+} \]

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

\[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \]

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]

\[ 8\text{H}^+ + \text{MnO}_4^- + 5\text{Fe}^{2+} \rightarrow 2\text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O} \]

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

The problem has to do with adding the potassium back in to make the molecular equation. One the left-hand side we have potassium permanganate (with only one potassium per formula unit) and on the right-hand side, the only place to add potassium is with potassium sulfate (with two potassium per formula unit). I can never balance the potassium with the net ionic as written above. (Yes, I could put a 2 in front of KMnO₄. Try it and see what happens. It will probably be much harder to figure out than what I'm going to do below.)

So, how to solve?

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

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

\[ 16\text{H}^+ + 2\text{MnO}_4^- + 10\text{Fe}^{2+} \rightarrow 2\text{Mn}^{2+} + 10\text{Fe}^{3+} + 8\text{H}_2\text{O} \]

Notice that I will now use 2KMnO₄ (and one K₂SO₄) to balance the potassium. So, let's do that:
3) Balance the potassium:

\[ 16H^+ + 2K MnO_4 + 10Fe^{2+} \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O + K_2SO_4 \]

I balance the sulfate introduced on the right like this:

\[ H_2SO_4 + 14H^+ + 2K MnO_4 + 10Fe^{2+} \rightarrow 2Mn^{2+} + 10Fe^{3+} + 8H_2O + K_2SO_4 \]

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

\[ H_2SO_4 + 14H^+ + 2K MnO_4 + 10FeSO_4 \rightarrow 2Mn^{2+} + 5Fe^{2+}(SO_4)_3 + 8H_2O + K_2SO_4 \]

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

\[ 6H_2SO_4 + 4H^+ + 2K MnO_4 + 10FeSO_4 \rightarrow 2Mn^{2+} + 5Fe^{2+}(SO_4)_3 + 8H_2O + K_2SO_4 \]

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

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

\[ 8H_2SO_4 + 2K MnO_4 + 10FeSO_4 \rightarrow 2MnSO_4 + 5Fe^{2+}(SO_4)_3 + 8H_2O + K_2SO_4 \]

**Example** \( CH_3CH_2OH + K_2Cr_2O_7 + H_2SO_4 \rightarrow HC_2H_3O_2 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O \)

1) Write the net ionic equation:

\[ CH_3CH_2OH + Cr_2O_7^{2-} \rightarrow Cr^{3+} + HC_2H_3O_2 \]

2) Half-reactions and balance:

\[ CH_3CH_2OH \rightarrow HC_2H_3O_2 \]
\[ Cr_2O_7^{2-} \rightarrow Cr^{3+} \]

\[ H_2O + CH_3CH_2OH \rightarrow HC_2H_3O_2 + 4H^+ + 4e^- \]
\[ 6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O \]

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

\[ 16H^+ + 3CH_3CH_2OH + 2Cr_2O_7^{2-} \rightarrow 4Cr^{3+} + 3HC_2H_3O_2 + 11H_2O \]

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

\[ 12H^+ + 2H_2SO_4 + 3CH_3CH_2OH + 2K_2Cr_2O_7 \rightarrow 4Cr^{3+} + 3HC_2H_3O_2 + 11H_2O + 2K_2SO_4 \]

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

\[ 8H_2SO_4 + 3CH_3CH_2OH + 2K_2Cr_2O_7 \rightarrow 2Cr_2(SO_4)_3 + 3HC_2H_3O_2 + 11H_2O + 2K_2SO_4 \]
Example

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

Solution:

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

\[
\text{Ti} + \text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Ti(SO}_4)_2 + \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]

2) Convert it to net ionic:

\[
\text{Ti} + \text{CrO}_4^{2-} \rightarrow \text{Ti}^{4+} + \text{Cr}^{3+}
\]

3) Write and balance half-reactions:

\[
\begin{align*}
\text{Ti} & \rightarrow \text{Ti}^{4+} \\
\text{CrO}_4^{2-} & \rightarrow \text{Cr}^{3+}
\end{align*}
\]

\[
\begin{align*}
3\text{e}^- + 8\text{H}^+ + \text{CrO}_4^{2-} & \rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O}
\end{align*}
\]

4) Balance net ionic equation:

\[
32\text{H}^+ + 3\text{Ti} + 4\text{CrO}_4^{2-} \rightarrow 3\text{Ti}^{4+} + 4\text{Cr}^{3+} + 16\text{H}_2\text{O}
\]

5) Make chromium(III) sulfate:

\[
20\text{H}^+ + 6\text{H}_2\text{SO}_4 + 3\text{Ti} + 4\text{CrO}_4^{2-} \rightarrow 3\text{Ti}^{4+} + 2\text{Cr}_2(\text{SO}_4)_3 + 16\text{H}_2\text{O}
\]

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

6) Make titanium(IV) sulfate:

\[
8\text{H}^+ + 12\text{H}_2\text{SO}_4 + 3\text{Ti} + 4\text{CrO}_4^{2-} \rightarrow 3\text{Ti(SO}_4)_2 + 2\text{Cr}_2(\text{SO}_4)_3 + 16\text{H}_2\text{O}
\]

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

7) Make potassium chromate:

\[
8\text{H}^+ + 12\text{H}_2\text{SO}_4 + 3\text{Ti} + 4\text{K}_2\text{CrO}_4 \rightarrow 3\text{Ti(SO}_4)_2 + 2\text{Cr}_2(\text{SO}_4)_3 + 16\text{H}_2\text{O} + 4\text{K}_2\text{SO}_4
\]

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

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

\[
16\text{H}_2\text{SO}_4 + 3\text{Ti} + 4\text{K}_2\text{CrO}_4 \rightarrow 3\text{Ti(SO}_4)_2 + 2\text{Cr}_2(\text{SO}_4)_3 + 16\text{H}_2\text{O} + 4\text{K}_2\text{SO}_4
\]
Did you see what I did? I simply introduced 4 more sulfuric acids. I took the 8 hydrogen ion already there and combined them with 4 sulfate ions I needed to add to the left-hand side. Notice that the coefficient of the sulfuric acid went from 12 to 16.

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

Example

\[ \text{K}_2\text{Cr}_2\text{O}_7 + \text{SnCl}_2 + \text{HCl} \rightarrow \text{CrCl}_3 + \text{SnCl}_4 + \text{KCl} + \text{H}_2\text{O} \]

Solution:

1) Write the net ionic equation:

\[ \text{Cr}_2\text{O}_7^{2-} + \text{Sn}^{2+} \rightarrow \text{Cr}^{3+} + \text{Sn}^{4+} \]

2) Break into half-reactions and balance:

\[ \begin{align*}
\text{Cr}_2\text{O}_7^{2-} & \rightarrow \text{Cr}^{3+} \\
\text{Sn}^{2+} & \rightarrow \text{Sn}^{4+}
\end{align*} \]

\[ \begin{align*}
6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \\
\text{Sn}^{2+} & \rightarrow \text{Sn}^{4+} + 2\text{e}^-
\end{align*} \]

\[ \begin{align*}
14\text{H}^+ + 3\text{Sn}^{2+} + \text{Cr}_2\text{O}_7^{2-} & \rightarrow 2\text{Cr}^{3+} + 3\text{Sn}^{4+} + 7\text{H}_2\text{O}
\end{align*} \]

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

\[ 2\text{H}^+ + 12 \text{HCl} + 3\text{SnCl}_2 + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{CrCl}_3 + 3\text{SnCl}_4 + 7\text{H}_2\text{O} \]

4) Add potassium ion:

\[ 2\text{H}^+ + 12\text{HCl} + 3\text{SnCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 2\text{CrCl}_3 + 3\text{SnCl}_4 + 7\text{H}_2\text{O} + 2\text{KCl} \]

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

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

\[ 14\text{HCl} + 3\text{SnCl}_2 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 2\text{CrCl}_3 + 3\text{SnCl}_4 + 7\text{H}_2\text{O} + 2\text{KCl} \]
Example

$$K_2Cr_2O_7 + FeSO_4 + H_2SO_4 \rightarrow K_2SO_4 + Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + H_2O$$

Solution:

1) Write the net ionic equation:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Fe_2^{6+} + Cr_2^{6+}$$

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

2) Write the half-reactions and balance them:

$$Cr_2O_7^{2-} \rightarrow Cr_2^{6+}$$
$$Fe^{2+} \rightarrow Fe_2^{6+}$$

$$6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow Cr_2^{6+} + 7H_2O$$
$$2Fe^{2+} \rightarrow Fe_2^{6+} + 2e^-$$

3) The balanced net ionic equation:

$$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \rightarrow Cr_2^{6+} + 7H_2O + 3Fe_2^{6+}$$

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

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 \rightarrow Cr_2^{6+} + 7H_2O + 3Fe_2^{6+}$$

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

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

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

That's three (of thirteen).

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

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$$

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

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

$$6FeSO_4 + 7H_2SO_4 + K_2Cr_2O_7 \rightarrow Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3 + K_2SO_4$$
Example

\[ \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + \text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7 \rightarrow \text{CO}_2 + \text{Cr}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 \]

Solution:

1) Write the net ionic equation:

\[ \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{CO}_2 + \text{Cr}^{3+} \]

2) Write the half-reactions and balance them:

\[ \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} \rightarrow \text{CO}_2 \]
\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]
\[ 13\text{H}_2\text{O} + \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} \rightarrow 12\text{CO}_2 + 48\text{H}^+ + 48\text{e}^- \]
\[ 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]

3) The balanced net ionic equation:

\[ 64\text{H}^+ + \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + 8\text{Cr}_2\text{O}_7^{2-} \rightarrow 12\text{CO}_2 + 16\text{Cr}^{3+} + 43\text{H}_2\text{O} \]

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

\[ 16\text{H}^+ + 24\text{H}_2\text{SO}_4 + \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + 8\text{Cr}_2\text{O}_7^{2-} \rightarrow 12\text{CO}_2 + 8\text{Cr}_2(\text{SO}_4)_3 + 43\text{H}_2\text{O} \]

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

5) Add potassium ion to the dichromate:

\[ 16\text{H}^+ + 24\text{H}_2\text{SO}_4 + \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + 8\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 12\text{CO}_2 + 8\text{Cr}_2(\text{SO}_4)_3 + 43\text{H}_2\text{O} + 8\text{K}_2\text{SO}_4 \]

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

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

\[ 32\text{H}_2\text{SO}_4 + \text{C}_\text{12}\text{H}_\text{22}\text{O}_{11} + 8\text{K}_2\text{Cr}_2\text{O}_7 \rightarrow 12\text{CO}_2 + 8\text{Cr}_2(\text{SO}_4)_3 + 43\text{H}_2\text{O} + 8\text{K}_2\text{SO}_4 \]

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

Example

\[ \text{Na}_2\text{HAsO}_3 + \text{KBrO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{KBr} + \text{H}_3\text{AsO}_4 \]

Solution:

1) Write the net ionic equation:

\[ \text{HAsO}_3^{2-} + \text{BrO}_3^- \rightarrow \text{AsO}_4^{3-} + \text{Br}^- \]

2) Write the half-reactions and balance:
HAsO$_3^{2-}$ $\rightarrow$ AsO$_4^{3-}$
BrO$_3^-$ $\rightarrow$ Br$^-$

H$_2$O $+$ HAsO$_3^{2-}$ $\rightarrow$ AsO$_4^{3-}$ $+$ 3H$^+$ $+$ 2e$^-$
6e$^-$ $+$ 6H$^+$ $+$ BrO$_3^-$ $\rightarrow$ Br$^-$ $+$ 3H$_2$O

3HAsO$_3^{2-}$ $+$ BrO$_3^-$ $+$ 6H$^+$ $\rightarrow$ 3H$_3$AsO$_4$ $+$ Br$^-$

3) Add one potassium to each side:
3HAsO$_3^{2-}$ $+$ KBrO$_3$ $+$ 6H$^+$ $\rightarrow$ 3H$_3$AsO$_4$ $+$ KBr

4) Add six sodium and six chloride to the left-hand side:
3Na$_2$HAsO$_3$ $+$ KBrO$_3$ $+$ 6HCl $\rightarrow$ 3H$_3$AsO$_4$ $+$ KBr

5) Add six sodium chloride to the right-hand side:
3Na$_2$HAsO$_3$ $+$ KBrO$_3$ $+$ 6HCl $\rightarrow$ 3H$_3$AsO$_4$ $+$ KBr $+$ 6NaCl

Example

K$_2$Cr$_2$O$_7$ $+$ H$_2$C$_2$O$_4$ $+$ 2H$_2$O $\rightarrow$ K[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$] $+$ 2H$_2$O $+$ CO$_2$ $+$ H$_2$O

Solution:

1) Strip out spectator ions:
Cr$_2$O$_7^{2-}$ $+$ C$_2$O$_4^{2-}$ $\rightarrow$ Cr$^{3+}$ $+$ CO$_2$

2) Balance in acidic solution (because of the oxalic acid):
Cr$_2$O$_7^{2-}$ $\rightarrow$ Cr$^{3+}$
C$_2$O$_4^{2-}$ $\rightarrow$ CO$_2$
6e$^-$ $+$ 14H$^+$ $+$ Cr$_2$O$_7^{2-}$ $\rightarrow$ 2Cr$^{3+}$ $+$ 7H$_2$O
C$_2$O$_4^{2-}$ $\rightarrow$ 2CO$_2$ $+$ 2e$^-$
6e$^-$ $+$ 14H$^+$ $+$ Cr$_2$O$_7^{2-}$ $\rightarrow$ 2Cr$^{3+}$ $+$ 7H$_2$O
3C$_2$O$_4^{2-}$ $\rightarrow$ 6CO$_2$ $+$ 6e$^-$
14H$^+$ $+$ Cr$_2$O$_7^{2-}$ $+$ 3C$_2$O$_4^{2-}$ $\rightarrow$ 2Cr$^{3+}$ $+$ 6CO$_2$ $+$ 7H$_2$O

3) To restore the molecular equation the trick, to me, is to restore the right-hand side and then deal with the left:
14H$^+$ $+$ Cr$_2$O$_7^{2-}$ $+$ 3C$_2$O$_4^{2-}$ $\rightarrow$ 2K[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$] $+$ 6CO$_2$ $+$ 3H$_2$O
Notice how I also reduced the water on the right-hand side. I will also ignore the water of hydration for the moment.

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

$$14H^+ + K_2Cr_2O_7 + 7C_2O_4^{2-} \rightarrow 2K[Cr(C_2O_4)_2(H_2O)_2] + 6CO_2 + 3H_2O$$

5) Reform the oxalic acid:

$$K_2Cr_2O_7 + 7H_2C_2O_4 \rightarrow 2K[Cr(C_2O_4)_2(H_2O)_2] + 6CO_2 + 3H_2O$$

6) When I add in the water of hydration, keep in mind that there is a 7 in front of the oxalic acid. That means 14 waters will be added to the left-hand side. On the right, the waters of hydration will only add 4, so I have to add 10 more to the $3H_2O$:

$$K_2Cr_2O_7 + 7H_2C_2O_4 \cdot 2H_2O \rightarrow 2K[Cr(C_2O_4)_2(H_2O)_2] \cdot 2H_2O + 6CO_2 + 13H_2O$$

7) Check the balance and find this:

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

Example

$$NaCl + H_3PO_4 + MnO_2 \rightarrow Na_3PO_4 + Mn_3(PO_4)_2 + H_2O + Cl_2$$

Solution:

1) Write the net ionic equation:

$$Cl^- + MnO_2 \rightarrow Cl_2 + Mn^{2+}$$

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

2) Separate into half-reactions and balance:

$$Cl^- \rightarrow Cl_2$$

$$MnO_2 \rightarrow Mn^{2+}$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

$$2e^- + 4H^+ + MnO_2 \rightarrow Mn^{2+} + 2H_2O$$

3) Add:

$$4H^+ + 2Cl^- + MnO_2 \rightarrow Mn^{2+} + Cl_2 + 2H_2O$$

4) Notice the formula $Mn_3(PO_4)_2$. It requires three manganese and we have only one in the net ionic. Multiply through by three:
12H⁺ + 6Cl⁻ + 3MnO₂⁻→ 3Mn²⁺ + 3Cl₂ + 6H₂O

5) I will make the Mn₃(PO₄)₂ by adding in two phosphates:

6H⁺ + 2H₃PO₄ + 6Cl⁻ + 3MnO₂⁻→ Mn₃(PO₄)₂ + 3Cl₂ + 6H₂O

Notice how I also made two phosphoric acids.

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

4H₃PO₄ + 6NaCl + 3MnO₂⁻→ Mn₃(PO₄)₂ + 2Na₃PO₄ + 3Cl₂ + 6H₂O

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

Example

NaCl(aq) + H₂SO₄(aq) + MnO₂(s) ---> Na₂SO₄(aq) + MnSO₄(aq) + H₂O(l) + Cl₂(g)

Solution:

1) Half-reactions:

MnO₂ ----> Mn²⁺
Cl⁻ ----> Cl₂

2) Balanced:

2e⁻ + 4H⁺ + MnO₂ ----> Mn²⁺ + 2H₂O
2Cl⁻ ----> Cl₂ + 2e⁻

3) Add them:

4H⁺ + MnO₂ + 2Cl⁻ ----> Mn²⁺ + 2H₂O + Cl₂

4) Add in one sulfate:

2H⁺ + H₂SO₄ + MnO₂ + 2Cl⁻ ----> MnSO₄ + 2H₂O + Cl₂

5) Add in two Na⁺:

2H⁺ + H₂SO₄ + MnO₂ + 2NaCl ----> MnSO₄ + 2H₂O + Cl₂ + 2Na⁺

6) Add in one more sulfate:

2H₂SO₄ + MnO₂ + 2NaCl ----> MnSO₄ + 2H₂O + Cl₂ + Na₂SO₄
Example

Fe(NO$_3$)$_2$(aq) + K$_2$Cr$_2$O$_7$(aq) + HNO$_3$(aq) ---> Fe(NO$_3$)$_3$(aq) + Cr(NO$_3$)$_3$(aq) + KNO$_3$ + H$_2$O

Solution:

1) Net ionic:

Fe$^{2+}$ + Cr$_2$O$_7^{2-}$ ---> Fe$^{3+}$ + Cr$^{3+}$

2) Half-reactions and balance:

Fe$^{2+}$ ---> Fe$^{3+}$
Cr$_2$O$_7^{2-}$ ---> Cr$^{3+}$

Fe$^{2+}$ ---> Fe$^{3+}$ + e$^-$
6e$^-$ + 14H$^+$ + Cr$_2$O$_7^{2-}$ ---> 2Cr$^{3+}$ + 7H$_2$O

3) Equalize electrons and add:

6Fe$^{2+}$ ---> 6Fe$^{3+}$ + 6e$^-$
6e$^-$ + 14H$^+$ + Cr$_2$O$_7^{2-}$ ---> 2Cr$^{3+}$ + 7H$_2$O

14H$^+$ + 6Fe$^{2+}$ + Cr$_2$O$_7^{2-}$ ---> 6Fe$^{3+}$ + 2Cr$^{3+}$ + 7H$_2$O

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

14HNO$_3$ + 6Fe(NO$_3$)$_2$ + K$_2$Cr$_2$O$_7$ ---> 6Fe(NO$_3$)$_3$ + 2Cr(NO$_3$)$_3$ + 7H$_2$O

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

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

14HNO$_3$ + 6Fe(NO$_3$)$_2$ + K$_2$Cr$_2$O$_7$ ---> 6Fe(NO$_3$)$_3$ + 2Cr(NO$_3$)$_3$ + 7H$_2$O

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

14HNO$_3$ + 6Fe(NO$_3$)$_2$ + K$_2$Cr$_2$O$_7$ ---> 6Fe(NO$_3$)$_3$ + 2Cr(NO$_3$)$_3$ + 2KNO$_3$ + 7H$_2$O

Example

Na$_2$S$_2$O$_3$ + KBrO$_3$ + H$_2$SO$_4$ ---> Na$_2$S$_4$O$_6$ + K$_2$SO$_4$ + Na$_2$SO$_4$ + Br$_2$ + H$_2$O

Solution:

1) Write balanced net ionic half-reactions:

2S$_2$O$_3^{2-}$ ---> S$_2$O$_6^{2-}$ + 2e$^-$
10e$^-$ + 12H$^+$ + 2BrO$_3^-$ ---> Br$_2$ + 6H$_2$O
2) Equalize electrons and add:
\[10S^{2-} \rightarrow 5S_2O_6^{2-} + 10e^-\]
\[10e^- + 12H^+ + 2BrO_3^- \rightarrow Br_2 + 6H_2O\]
\[12H^+ + 10S^{2-} \rightarrow 5S_2O_6^{2-} + Br_2 + 6H_2O\]

3) Add six sulfates, 20 sodium ions and two potassium ions to the left-hand side only:
\[6H_2SO_4 + 10Na_2S_2O_3 + 2KBrO_3 \rightarrow \]

4) Only 10 sodium ions can be accounted for by making 5Na_2S_2O_3. Everything else is accounted for in the spectator ions:
\[10Na_2S_2O_3 + 2KBrO_3 + 6H_2SO_4 \rightarrow 5Na_2S_2O_3 + K_2SO_4 + 5Na_2SO_4 + Br_2 + 6H_2O\]

Example

\[K_2Cr_2O_7 + NaCl + H_2SO_4 \rightarrow Cl_2 + H_2O + K_2SO_4 + Na_2SO_4 + CrSO_4\]

Solution:

1) Write the net ionic:
\[Cr_2O_7^{2-} + Cl^- \rightarrow Cl_2 + Cr^{3+}\]

2) Write half-reactions and balance:
\[Cr_2O_7^{2-} \rightarrow Cr^{3+}\]
\[Cl^- \rightarrow Cl_2\]

\[8e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{2+} + 7H_2O\]
\[2Cl^- \rightarrow Cl_2 + 2e^-\]

3) Equalize electrons and write balanced net ionic:
\[8e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{2+} + 7H_2O\]
\[8Cl^- \rightarrow 4Cl_2 + 8e^-\]

\[14H^+ + Cr_2O_7^{2-} + 8Cl^- \rightarrow 4Cl_2 + 2Cr^{2+} + 7H_2O\]

4) Add everything to the left-hand side:
\[7H_2SO_4 + K_2Cr_2O_7 + 8NaCl \rightarrow 4Cl_2 + 2Cr^{2+} + 7H_2O\]

I added two potassium ions, eight sodium ions and seven sulfate ions.
5) Add two potassium ions and one sulfate to the RHS:

\[7\text{H}_2\text{SO}_4 + K_2\text{Cr}_2\text{O}_7 + 8\text{NaCl} \rightarrow 4\text{Cl}_2 + 2\text{Cr}^{2+} + 7\text{H}_2\text{O} + K_2\text{SO}_4\]

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

\[7\text{H}_2\text{SO}_4 + K_2\text{Cr}_2\text{O}_7 + 8\text{NaCl} \rightarrow 4\text{Cl}_2 + 2\text{Cr}^{2+} + 7\text{H}_2\text{O} + K_2\text{SO}_4 + 4\text{Na}_2\text{SO}_4\]

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

\[7\text{H}_2\text{SO}_4 + K_2\text{Cr}_2\text{O}_7 + 8\text{NaCl} \rightarrow 4\text{Cl}_2 + 2\text{CrSO}_4 + 7\text{H}_2\text{O} + K_2\text{SO}_4 + 4\text{Na}_2\text{SO}_4\]

Example

\[\text{H}_3\text{AsO}_4 + \text{Zn} + \text{HNO}_3 \rightarrow \text{AsH}_3 + \text{Zn(NO}_3)_2 + \text{H}_2\text{O}\]

1) Write the net ionic half-reactions:

\[
\begin{align*}
\text{H}_3\text{AsO}_4 & \rightarrow \text{AsH}_3 \\
\text{Zn} & \rightarrow \text{Zn}^{2+}
\end{align*}
\]

I could have written \(\text{AsO}_4^{3-}\) if I had wanted to. I would have just re-formed \(\text{H}_3\text{AsO}_4\) at the end.

2) Balance in acidic solution:

\[
\begin{align*}
8\text{e}^- + 8\text{H}^+ + \text{H}_3\text{AsO}_4 & \rightarrow \text{AsH}_3 + 4\text{H}_2\text{O} \\
\text{Zn} & \rightarrow \text{Zn}^{2+} + 2\text{e}^-
\end{align*}
\]

3) Equalize electrons:

\[
\begin{align*}
8\text{e}^- + 8\text{H}^+ + \text{H}_3\text{AsO}_4 & \rightarrow \text{AsH}_3 + 4\text{H}_2\text{O} \\
4\text{Zn} & \rightarrow 4\text{Zn}^{2+} + 8\text{e}^-
\end{align*}
\]

4) Add:

\[8\text{H}^+ + \text{H}_3\text{AsO}_4 + 4\text{Zn} \rightarrow \text{AsH}_3 + 4\text{Zn}^{2+} + 4\text{H}_2\text{O}\]

5) Bring back to molecular:

\[8\text{HNO}_3 + \text{H}_3\text{AsO}_4 + 4\text{Zn} \rightarrow \text{AsH}_3 + 4\text{Zn(NO}_3)_2 + 4\text{H}_2\text{O}\]
Example

\[
\text{KMnO}_4 + \text{CH}_3\text{OH} \rightarrow \text{MnO}_2 + \text{H}_2\text{O} + \text{HCHO} + \text{KOH}
\]

Solution:

1) Half-reactions:

\[
\text{CH}_3\text{OH} \rightarrow \text{HCHO} \\
\text{MnO}_4^- \rightarrow \text{MnO}_2
\]

2) Balance in acidic solution:

\[
\text{CH}_3\text{OH} \rightarrow \text{HCHO} + 2\text{H}^+ + 2\text{e}^- \\
3\text{e}^- + 4\text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O}
\]

3) Equalize electrons:

\[
3\text{CH}_3\text{OH} \rightarrow 3\text{HCHO} + 6\text{H}^+ + 6\text{e}^- \\
6\text{e}^- + 8\text{H}^+ + 2\text{MnO}_4^- \rightarrow 2\text{MnO}_2 + 4\text{H}_2\text{O}
\]

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

\[
2\text{H}^+ + 2\text{MnO}_4^- + 3\text{CH}_3\text{OH} \rightarrow 2\text{MnO}_2 + 4\text{H}_2\text{O} + 3\text{HCHO}
\]

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

\[
2\text{MnO}_4^- + 3\text{CH}_3\text{OH} \rightarrow 2\text{MnO}_2 + 2\text{H}_2\text{O} + 3\text{HCHO} + 2\text{OH}^-
\]

6) Add in two potassium ions:

\[
2\text{KMnO}_4 + 3\text{CH}_3\text{OH} \rightarrow 2\text{MnO}_2 + 2\text{H}_2\text{O} + 3\text{HCHO} + 2\text{KOH}
\]

Example

\[
\text{MnSO}_4 + (\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} \rightarrow \text{MnO}_2 + \text{H}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4
\]

Solution:

1) Half-reactions:

\[
\text{Mn}^{2+} \rightarrow \text{MnO}_2 \\
\text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-}
\]

2) Balance:

\[
2\text{H}_2\text{O} + \text{Mn}^{2+} \rightarrow \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \\
2\text{e}^- + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{SO}_4^{2-}
\]
3) Add:

\[ 2H_2O + Mn^{2+} + S_2O_8^{2-} \rightarrow MnO_2 + 2SO_4^{2-} + 4H^+ \]

4) Add one sulfate:

\[ 2H_2O + MnSO_4 + S_2O_8^{2-} \rightarrow MnO_2 + 3SO_4^{2-} + 4H^+ \]

5) Add two ammonium ions:

\[ 2H_2O + MnSO_4 + (NH_4)_2S_2O_8 \rightarrow MnO_2 + (NH_4)_2SO_4 + 2H_2SO_4 \]

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

**Example**

\[ U(SO_4)_2 + KMnO_4 + H_2O \rightarrow H_2SO_4 + K_2SO_4 + MnSO_4 + UO_2SO_4 \]

**Solution:**

1) Half-reactions:

\[ U^{4+} \rightarrow UO_2^{2+} \]
\[ MnO_4^{-} \rightarrow Mn^{2+} \]

2) Balance:

\[ 2H_2O + U^{4+} \rightarrow UO_2^{2+} + 4H^+ + 2e^- \]
\[ 5e^- + 8H^+ + MnO_4^{-} \rightarrow Mn^{2+} + 4H_2O \]

3) Make electrons equal:

\[ 10H_2O + 5U^{4+} \rightarrow 5UO_2^{2+} + 20H^+ + 10e^- \]
\[ 10e^- + 16H^+ + 2MnO_4^{-} \rightarrow 2Mn^{2+} + 8H_2O \]

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

\[ 2H_2O + 5U^{4+} + 2MnO_4^- \rightarrow 5UO_2^{2+} + 2Mn^{2+} + 4H^+ \]

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

\[ 2H_2O + 5U(SO_4)_2 + 2KMnO_4 \rightarrow 5UO_2SO_4 + 2MnSO_4 + 2H_2SO_4 \]

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

\[ 2H_2O + 5U(SO_4)_2 + 2KMnO_4 \rightarrow 5UO_2SO_4 + 2MnSO_4 + 2H_2SO_4 \]

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

\[ 2H_2O + 5U(SO_4)_2 + 2KMnO_4 \rightarrow 5UO_2SO_4 + 2MnSO_4 + 2H_2SO_4 + K_2SO_4 \]
Example

\[ \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{K}_2\text{CrO}_4(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{CrCl}_3(\text{aq}) + \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\ell) + \text{CO}_2(\text{g}) \]

Solution:

1) The half-reactions are these:

\[
\begin{align*}
\text{CrO}_4^{2-} &\rightarrow \text{Cr}^{3+} \\
\text{C}_2\text{O}_4^{2-} &\rightarrow \text{CO}_2
\end{align*}
\]

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

\[
\begin{align*}
\text{CrO}_4^{2-} &\rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \\
\text{C}_2\text{O}_4^{2-} &\rightarrow 2\text{CO}_2
\end{align*}
\]

3) Balance for H:

\[
\begin{align*}
8\text{H}^+ + \text{CrO}_4^{2-} &\rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \\
\text{C}_2\text{O}_4^{2-} &\rightarrow 2\text{CO}_2
\end{align*}
\]

4) Balance for charge:

\[
\begin{align*}
3\text{e}^- + 8\text{H}^+ + \text{CrO}_4^{2-} &\rightarrow \text{Cr}^{3+} + 4\text{H}_2\text{O} \\
\text{C}_2\text{O}_4^{2-} &\rightarrow 2\text{CO}_2 + 2\text{e}^-
\end{align*}
\]

5) Equalize charge:

\[
\begin{align*}
6\text{e}^- + 16\text{H}^+ + 2\text{CrO}_4^{2-} &\rightarrow 2\text{Cr}^{3+} + 8\text{H}_2\text{O} \\
3\text{C}_2\text{O}_4^{2-} &\rightarrow 6\text{CO}_2 + 6\text{e}^-
\end{align*}
\]

6) Add:

\[
\begin{align*}
16\text{H}^+ + 3\text{C}_2\text{O}_4^{2-} + 2\text{CrO}_4^{2-} &\rightarrow 2\text{Cr}^{3+} + 6\text{CO}_2 + 8\text{H}_2\text{O}
\end{align*}
\]

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

\[
\begin{align*}
10\text{HCl} + 3\text{H}_2\text{C}_2\text{O}_4 + 2\text{K}_2\text{CrO}_4 &\rightarrow 2\text{CrCl}_3 + 6\text{CO}_2 + 8\text{H}_2\text{O}
\end{align*}
\]

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

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

\[
\begin{align*}
10\text{HCl} + 3\text{H}_2\text{C}_2\text{O}_4 + 2\text{K}_2\text{CrO}_4 &\rightarrow 2\text{CrCl}_3 + 4\text{KCl} + 6\text{CO}_2 + 8\text{H}_2\text{O}
\end{align*}
\]

Six Cl\(^{-}\) went to make the 2CrCl\(_3\) and the other four Cl\(^{-}\) paired with the four K\(^{+}\) to make 4KCl.
Example

\[ \text{Mn(NO}_3)_2 + \text{PbO}_2 + \text{HNO}_3 \rightarrow \text{HMnO}_4 + \text{Pb(NO}_3)_2 + \text{H}_2\text{O} \]

Solution:

1) Half-reactions:

\[ \text{Mn}^{2+} \rightarrow \text{MnO}_4^- \]
\[ \text{PbO}_2 \rightarrow \text{Pb}^{2+} \]

2) Balance:

\[ 4\text{H}_2\text{O} + \text{Mn}^{2+} \rightarrow 2\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \]
\[ 2\text{e}^- + 4\text{H}^+ + \text{PbO}_2 \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O} \]

3) Equalize electrons:

\[ 8\text{H}_2\text{O} + 2\text{Mn}^{2+} \rightarrow 2\text{MnO}_4^- + 16\text{H}^+ + 10\text{e}^- \]
\[ 10\text{e}^- + 20\text{H}^+ + 5\text{PbO}_2 \rightarrow 5\text{Pb}^{2+} + 10\text{H}_2\text{O} \]

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

\[ 4\text{H}^+ + 2\text{Mn}^{2+} + 5\text{PbO}_2 \rightarrow 5\text{Pb}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \]

5) What needs to be added in is mostly nitrate. The only other item would be two hydrogens intended to make \( \text{HMnO}_4 \). Add them in before adding the nitrates:

\[ 6\text{H}^+ + 2\text{Mn}^{2+} + 5\text{PbO}_2 \rightarrow 5\text{Pb}^{2+} + 2\text{HMnO}_4 + 2\text{H}_2\text{O} \]

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

6) Ten nitrates finish the problem:

\[ 6\text{HNO}_3 + 2\text{Mn(NO}_3)_2 + 5\text{PbO}_2 \rightarrow 5\text{Pb(NO}_3)_2 + 2\text{HMnO}_4 + 2\text{H}_2\text{O} \]

You are welcome to add some nitrate in first and then add in two hydrogens. What will happen is that you'll have two unattached nitrates on the left that will become \( \text{HNO}_3 \) when you add in the two hydrogen.
Example

\[ \text{Sb}_2\text{O}_5 + \text{Kl} + \text{HCl} \rightarrow \text{SbCl}_3 + \text{KCl} + \text{I}_2 + \text{H}_2\text{O} \]

**Solution:**

1) Half-reactions:

\[ \text{Sb}_2\text{O}_5 \rightarrow \text{Sb}^{3+} \]

\[ \text{I}^- \rightarrow \text{I}_2 \]

2) Balance:

\[ 4\text{e}^- + 10\text{H}^+ + \text{Sb}_2\text{O}_5 \rightarrow 2\text{Sb}^{3+} + 5\text{H}_2\text{O} \]

\[ 2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^- \]

3) Equalize electrons:

\[ 4\text{e}^- + 10\text{H}^+ + \text{Sb}_2\text{O}_5 \rightarrow 2\text{Sb}^{3+} + 5\text{H}_2\text{O} \]

\[ 4\text{I}^- \rightarrow 2\text{I}_2 + 4\text{e}^- \]

4) Add:

\[ 10\text{H}^+ + \text{Sb}_2\text{O}_5 + 4\text{I}^- \rightarrow 2\text{Sb}^{3+} + 2\text{I}_2 + 5\text{H}_2\text{O} \]

5) Add 10 chlorides to each side:

\[ 10\text{HCl} + \text{Sb}_2\text{O}_5 + 4\text{I}^- \rightarrow 2\text{SbCl}_3 + 4\text{Cl}^- + 2\text{I}_2 + 5\text{H}_2\text{O} \]

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

6) Add four potassium ions to each side:

\[ 10\text{HCl} + \text{Sb}_2\text{O}_5 + 4\text{KI} \rightarrow 2\text{SbCl}_3 + 4\text{KCl} + 2\text{I}_2 + 5\text{H}_2\text{O} \]

Example

\[ \text{Bi(OH)}_3 + \text{K}_2\text{SnO}_2 \rightarrow \text{Bi} + \text{K}_2\text{SnO}_3 + \text{H}_2\text{O} \]

**Solution:**

1) Half-reactions:

\[ \text{Bi(OH)}_3 \rightarrow \text{Bi} \]

\[ \text{SnO}_2^{2-} \rightarrow \text{SnO}_3^{2-} \]
2) Balance:

\[3e^- + Bi(OH)_3 \rightarrow Bi + 3OH^-\]
\[H_2O + SnO_2^{2-} \rightarrow SnO_3^{2-} + 2H^+ + 2e^-\]

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

3) Equalize electrons:

\[6e^- + 2Bi(OH)_3 \rightarrow 2Bi + 6OH^-\]
\[3H_2O + 3SnO_2^{2-} \rightarrow 3SnO_3^{2-} + 6H^+ + 6e^-\]

4) Add:

\[3H_2O + 2Bi(OH)_3 + 3SnO_2^{2-} \rightarrow 2Bi + 3SnO_3^{2-} + 6H^+ + 6OH^-\]

\[6H^+ + 6OH^- = 6H_2O\] and then cancel three H_2O.

\[2Bi(OH)_3 + 3SnO_2^{2-} \rightarrow 2Bi + 3SnO_3^{2-} + 3H_2O\]

5) Add six potassium ions to each side:

\[2Bi(OH)_3 + 3K_2SnO_2 \rightarrow 2Bi + 3K_2SnO_3 + 3H_2O\]

Example

\[C_{14}H_{12} + Na_2Cr_2O_7 + H_2SO_4 \rightarrow C_{14}H_8O_2 + Cr_2(SO_4)_3\]

Solution:

1) Half-reactions:

\[C_{14}H_{12} \rightarrow C_{14}H_8O_2\]
\[Cr_2O_7^{2-} \rightarrow Cr^{3+}\]

2) Balance:

\[2H_2O + C_{14}H_{12} \rightarrow C_{14}H_8O_2 + 8H^+ + 8e^-\]
\[6e^- + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O\]

3) Equalize electrons:

\[6H_2O + 3C_{14}H_{12} \rightarrow 3C_{14}H_8O_2 + 24H^+ + 24e^-\]
\[24e^- + 56H^+ + 4Cr_2O_7^{2-} \rightarrow 8Cr^{3+} + 28H_2O\]

4) Add:

\[32H^+ + 3C_{14}H_{12} + 4Cr_2O_7^{2-} \rightarrow 3C_{14}H_8O_2 + 8Cr^{3+} + 22H_2O\]
5) Add 12 sulfates to both sides (to make the $\text{Cr}_2(\text{SO}_4)_3$):

$$8\text{H}^+ + 12\text{H}_2\text{SO}_4 + 3\text{C}_6\text{H}_4\text{O}_2 + 4\text{Cr}_2\text{O}_7^{2-} \rightarrow 3\text{C}_4\text{H}_6\text{O}_2 + 4\text{Cr}_2(\text{SO}_4)_3 + 22\text{H}_2\text{O}$$

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

$$8\text{H}^+ + 12\text{H}_2\text{SO}_4 + 3\text{C}_6\text{H}_4\text{O}_2 + 4\text{Na}_2\text{Cr}_2\text{O}_7 \rightarrow 3\text{C}_4\text{H}_6\text{O}_2 + 4\text{Cr}_2(\text{SO}_4)_3 + 22\text{H}_2\text{O} + 8\text{Na}^+$$

7) Add four more sulfates:

$$16\text{H}_2\text{SO}_4 + 3\text{C}_6\text{H}_4\text{O}_2 + 4\text{Na}_2\text{Cr}_2\text{O}_7 \rightarrow 3\text{C}_4\text{H}_6\text{O}_2 + 4\text{Cr}_2(\text{SO}_4)_3 + 22\text{H}_2\text{O} + 4\text{Na}_2\text{SO}_4$$

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

Example

$$\text{C}_6\text{H}_6\text{O}_2 + \text{Na}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{C}_6\text{H}_4\text{O}_2 + \text{Cr}_2(\text{SO}_4)_3$$

Solution:

1) Half-reactions:

$$\text{C}_6\text{H}_6\text{O}_2 \rightarrow \text{C}_6\text{H}_4\text{O}_2$$  
$$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$$

2) Balance:

$$\text{C}_6\text{H}_6\text{O}_2 \rightarrow \text{C}_6\text{H}_4\text{O}_2 + 2\text{H}^+ + 2e^-$$  
$$6e^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

3) Equalize electrons:

$$3\text{C}_6\text{H}_6\text{O}_2 \rightarrow 3\text{C}_6\text{H}_4\text{O}_2 + 6\text{H}^+ + 6e^-$$  
$$6e^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

4) Add:

$$8\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 3\text{C}_6\text{H}_6\text{O}_2 \rightarrow 3\text{C}_6\text{H}_4\text{O}_2 + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$

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

$$2\text{H}^+ + 3\text{H}_2\text{SO}_4 + \text{Cr}_2\text{O}_7^{2-} + 3\text{C}_6\text{H}_6\text{O}_2 \rightarrow 3\text{C}_6\text{H}_4\text{O}_2 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O}$$

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

$$4\text{H}_2\text{SO}_4 + \text{Na}_2\text{Cr}_2\text{O}_7 + 3\text{C}_6\text{H}_6\text{O}_2 \rightarrow 3\text{C}_6\text{H}_4\text{O}_2 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$$

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

\[ C_6H_{10}O + HNO_3 \rightarrow C_6H_{10}O_4 + NO_2 \]

Solution:

1) Half-reactions:

\[ C_6H_{10}O \rightarrow C_6H_{10}O_4 \]

\[ NO_3^- \rightarrow NO_2 \]

2) Balance:

\[ 3H_2O + C_6H_{10}O \rightarrow C_6H_{10}O_4 + 6H^+ + 6e^- \]

\[ e^- + 2H^+ + NO_3^- \rightarrow NO_2 + H_2O \]

3) Equalize electrons:

\[ 3H_2O + C_6H_{10}O \rightarrow C_6H_{10}O_4 + 6H^+ + 6e^- \]

\[ 6e^- + 12H^+ + 6NO_3^- \rightarrow 6NO_2 + 6H_2O \]

4) Add:

\[ 6HNO_3 + C_6H_{10}O \rightarrow 6NO_2 + C_6H_{10}O_4 + 3H_2O \]

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

\[ 6HNO_3 + C_6H_{10}O \rightarrow 6NO_2 + C_6H_{10}O_4 + 3H_2O \]

Example

\[ KMnO_4 + Na_2SO_3 + NaOH \rightarrow K_2MnO_4 + Na_2MnO_4 + Na_2SO_4 + H_2O \]

Solution:

1) Half-reactions:

\[ MnO_4^- \rightarrow MnO_4^{2-} \]

\[ SO_3^{2-} \rightarrow SO_4^{2-} \]

2) Balance:

\[ e^- + MnO_4^- \rightarrow MnO_4^{2-} \]

\[ H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^- \]

3) Equalize electrons:

\[ 2e^- + 2MnO_4^- \rightarrow 2MnO_4^{2-} \]

\[ H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^- \]
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4) Add and convert to basic:

\[ H_2O + 2MnO_4^- + SO_3^{2-} \rightarrow 2MnO_4^{2-} + SO_4^{2-} + 2H^+ \]
\[ 2OH^- + 2MnO_4^- + SO_3^{2-} \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O \]

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

First, add to the left-hand side:

\[ 2NaOH + 2KMnO_4 + Na_2SO_3 \rightarrow 2MnO_4^{2-} + SO_4^{2-} + H_2O \]

Now, to the RHS:

\[ 2NaOH + 2KMnO_4 + Na_2SO_3 \rightarrow K_2MnO_4 + Na_2MnO_4 + Na_2SO_4 + H_2O \]

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

\[ 2NaOH + 2KMnO_4 + Na_2SO_3 \rightarrow 2Na_2MnO_4 + K_2SO_4 + H_2O \]

or

\[ 2NaOH + 2NaMnO_4 + Na_2SO_3 \rightarrow 2Na_2MnO_4 + Na_2SO_4 + H_2O \]

Example

\[ KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O \]

Solution:

1) Half-reactions:

\[ MnO_4^- \rightarrow Mn^{2+} \]
\[ C_2O_4^{2-} \rightarrow CO_2 \]

2) Balance:

\[ 5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \]
\[ C_2O_4^{2-} \rightarrow 2CO_2 + 2e^- \]

3) Equalize electrons:

\[ 10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O \]
\[ 5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^- \]

4) Add:

\[ 16H^+ + 5C_2O_4^{2-} + 2MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \]
5) Make five undissociated oxalic acids:

\[ 6H^+ + 5H_2C_2O_4 + 2MnO_4^- \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \]

6) Add two sulfates to each side:

\[ 2H^+ + 2H_2SO_4 + 5H_2C_2O_4 + 2MnO_4^- \rightarrow 2MnSO_4 + 10CO_2 + 8H_2O \]

7) Add two potassium ions and one more sulfate:

\[ 3H_2SO_4 + 5H_2C_2O_4 + 2KMnO_4 \rightarrow 2MnSO_4 + 10CO_2 + K_2SO_4 + 8H_2O \]

8) The same problem with nitric acid:

\[ KMnO_4 + H_2C_2O_4 + HNO_3 \rightarrow CO_2 + Mn(NO_3)_2 + KNO_3 + H_2O \]

balanced:

\[ 2KMnO_4 + 5H_2C_2O_4 + 6HNO_3 \rightarrow 10CO_2 + 2Mn(NO_3)_2 + 2KNO_3 + 8H_2O \]

Example

\[ KMnO_4 + H_2SO_3 \rightarrow K_2SO_4 + MnSO_4 + H_2SO_4 + H_2O \]

Solution:

1) Half-reactions:

\[ MnO_4^- \rightarrow Mn^{2+} \]

\[ SO_3^{2-} \rightarrow SO_4^{2-} \]

2) Balance:

\[ 5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O \]

\[ H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^- \]

3) Equalize electrons:

\[ 10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O \]

\[ 5H_2O + 5SO_3^{2-} \rightarrow 5SO_4^{2-} + 10H^+ + 10e^- \]

4) Add:

\[ 6H^+ + 2MnO_4^- + 5SO_3^{2-} \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O \]

5) Add four hydrogen ion to each side:

\[ 2MnO_4^- + 5H_2SO_3 \rightarrow 2MnSO_4 + 2H_2SO_4 + SO_4^{2-} + 3H_2O \]
Two sulfates went to sulfuric acid, two sulfates went to MnSO$_4$ and one sulfate is still to be dealt with.

6) Add two potassium ions to finish it:

$$2\text{KMnO}_4 + 5\text{H}_2\text{SO}_3 \rightarrow 2\text{MnSO}_4 + 2\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + 3\text{H}_2\text{O}$$

**Example**

$$\text{KMnO}_4(\text{aq}) + \text{NaHSO}_3(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{MnSO}_4(\text{aq}) + \text{K}_2\text{SO}_4(\text{aq}) + \text{Na}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\ell)$$

**Solution:**

1) Half-reactions:

- $$\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$$
- $$\text{HSO}_3^- \rightarrow \text{SO}_4^{2-}$$

2) Balance:

- $$5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- $$\text{H}_2\text{O} + \text{HSO}_3^- \rightarrow \text{SO}_4^{2-} + 3\text{H}^+ + 2\text{e}^-$$

3) Equalize electrons:

- $$10\text{e}^- + 16\text{H}^+ + 2\text{MnO}_4^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$$
- $$5\text{H}_2\text{O} + 5\text{HSO}_3^- \rightarrow 5\text{SO}_4^{2-} + 15\text{H}^+ + 10\text{e}^-$$

4) Add:

- $$\text{H}^+ + 2\text{MnO}_4^- + 5\text{HSO}_3^- \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}$$

5) We know that there will be at least one H$_2$SO$_4$, but we have only one H$^+$ on the left-hand side. Double everything to get two H$^+$:

- $$2\text{H}^+ + 4\text{MnO}_4^- + 10\text{HSO}_3^- \rightarrow 4\text{Mn}^{2+} + 10\text{SO}_4^{2-} + 6\text{H}_2\text{O}$$

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

- $$\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 + 10\text{NaHSO}_3 \rightarrow 4\text{Mn}^{2+} + 10\text{SO}_4^{2-} + 6\text{H}_2\text{O}$$

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

- $$\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 + 10\text{NaHSO}_3 \rightarrow 4\text{MnSO}_4 + 7\text{SO}_4^{2-} + 6\text{H}_2\text{O}$$

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

- $$\text{H}_2\text{SO}_4 + 4\text{KMnO}_4 + 10\text{NaHSO}_3 \rightarrow 4\text{MnSO}_4 + 2\text{K}_2\text{SO}_4 + 5\text{Na}_2\text{SO}_4 + 6\text{H}_2\text{O}$$
Example

\[\text{KMnO}_4 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{MnSO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}\]

**Solution:**

1) Half-reactions:

\[\text{MnO}_4^{2-} \rightarrow \text{Mn}^{2+}\]
\[\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}\]

2) Balance:

\[5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 4\text{H}_2\text{O}\]
\[\text{H}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-\]

3) Equalize electrons:

\[10\text{e}^- + 16\text{H}^+ + 2\text{MnO}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O}\]
\[5\text{H}_2\text{O} + 5\text{SO}_3^{2-} \rightarrow 5\text{SO}_4^{2-} + 10\text{H}^+ + 10\text{e}^-\]

4) Add:

\[6\text{H}^+ + 2\text{MnO}_4^{2-} + 5\text{SO}_3^{2-} \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}\]

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

\[3\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 + 5\text{Na}_2\text{SO}_3 \rightarrow 2\text{Mn}^{2+} + 5\text{SO}_4^{2-} + 3\text{H}_2\text{O}\]

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

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

\[3\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 + 5\text{Na}_2\text{SO}_3 \rightarrow 2\text{Mn}^{2+} + 5\text{Na}_2\text{SO}_4 + 3\text{H}_2\text{O}\]

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

7) Now, the three sulfate ions:

\[3\text{H}_2\text{SO}_4 + 2\text{KMnO}_4 + 5\text{Na}_2\text{SO}_3 \rightarrow \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 5\text{Na}_2\text{SO}_4 + 3\text{H}_2\text{O}\]

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

As$_2$O$_3$ + Cl$_2$ + H$_2$O ---> H$_3$AsO$_4$ + HCl

Solution:

1) Half-reactions:
   
   As$_2$O$_3$ ---> AsO$_4^{3-}$
   Cl$_2$ ---> Cl$^-$

2) Balance:

   5H$_2$O + As$_2$O$_3$ ---> 2AsO$_4^{3-}$ + 10H$^+$ + 4e$^-$
   2e$^-$ + Cl$_2$ ---> 2Cl$^-$

3) Equalize electrons:

   5H$_2$O + As$_2$O$_3$ ---> 2AsO$_4^{3-}$ + 10H$^+$ + 4e$^-$
   4e$^-$ + 2Cl$_2$ ---> 4Cl$^-$

4) Add:

   5H$_2$O + As$_2$O$_3$ + 2Cl$_2$ ---> 2H$_3$AsO$_4$ - 4HCl

5) Reunite ions on the right-hand side:

   5H$_2$O + As$_2$O$_3$ + 2Cl$_2$ ---> 2H$_3$AsO$_4$ + 4HCl

Note that no spectator ions needed to be added in.

Example

H$_2$O(ℓ) + P$_4$(s) + KOH(aq) ---> KH$_2$PO$_2$(aq) + PH$_3$(g)

Solution:

1) Half-reactions:

   P$_4$ ---> H$_3$PO$_2$$^-$
   P$_4$ ---> PH$_3$

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

   8H$_2$O + P$_4$ ---> 4H$_3$PO$_2$$^-$ + 8H$^+$ + 4e$^-$
   12e$^-$ + 12H$^+$ + P$_4$ ---> 4PH$_3$
3) Equalize electrons (still in acid):

\[
24H_2O + 3P_4 \rightarrow 12H_3PO_2^- + 24H^+ + 12e^-
\]
\[
12e^- + 12H^+ + P_4 \rightarrow 4PH_3
\]

4) Add (then change to basic):

\[
24H_2O + 4P_4 \rightarrow 12H_3PO_2^- + 4PH_3 + 12H^+
\]

Add 12 hydroxide:

\[
12OH^- + 24H_2O + 4P_4 \rightarrow 12H_3PO_2^- + 4PH_3 + 12H_2O
\]

Remove 12 waters:

\[
12OH^- + 12H_2O + 4P_4 \rightarrow 12H_3PO_2^- + 4PH_3
\]

5) Remove factor of 4:

\[
3OH^- + 3H_2O + P_4 \rightarrow 3H_3PO_2^- + PH_3
\]

6) Add thee potassium ions:

\[
3KOH + 3H_2O + P_4 \rightarrow 3KH_2PO_2 + PH_3
\]

**Example**

\[
K_2CrO_4 + Na_2SO_3 + HCl \rightarrow KCl + Na_2SO_4 + CrCl_3 + H_2O
\]

**Solution:**

1) Half-reactions:

\[
CrO_4^{2-} \rightarrow Cr^{3+}
\]
\[
SO_3^{2-} \rightarrow SO_4^{2-}
\]

2) Balance:

\[
3e^- + 8H^+ + CrO_4^{2-} \rightarrow Cr^{3+} + 4H_2O
\]
\[
H_2O + SO_3^{2-} \rightarrow SO_4^{2-} + 2H^+ + 2e^-
\]

3) Equalize electrons:

\[
6e^- + 16H^+ + 2CrO_4^{2-} \rightarrow 2Cr^{3+} + 8H_2O
\]
\[
3H_2O + 3SO_3^{2-} \rightarrow 3SO_4^{2-} + 6H^+ + 6e^-
\]

4) Add:

\[
10H^+ + 2CrO_4^{2-} + 3SO_3^{2-} \rightarrow 2Cr^{3+} + 3SO_4^{2-} + 5H_2O
\]
5) Add 10 chlorides, four potassium ions and six sodium ions to the left-hand side:

\[ 10\text{HCl} + 2\text{K}_2\text{CrO}_4 + 3\text{Na}_2\text{SO}_3 \rightarrow 2\text{Cr}^{3+} + 3\text{SO}_4^{2-} + 5\text{H}_2\text{O} \]

6) On the right-hand side:

six chlorides go to the \(2\text{Cr}^{3+}\)
six sodium go to the \(3\text{SO}_4^{2-}\)
The remaining four \(K^+\) and four \(\text{Cl}^-\) for \(4\text{KCl}\)

\[ 10\text{HCl} + 2\text{K}_2\text{CrO}_4 + 3\text{Na}_2\text{SO}_3 \rightarrow 2\text{CrCl}_3 + 3\text{Na}_2\text{SO}_4 + 4\text{KCl} + 5\text{H}_2\text{O} \]

**Example**

\[ \text{Na}_2\text{S}_2\text{O}_3 + \text{KMnO}_4 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + \text{K}_2\text{SO}_4 + \text{MnO}_2 + \text{KOH} \]

**Solution:**

1) Half-reactions:

\[ \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} \]
\[ \text{MnO}_4^- \rightarrow \text{MnO}_2 \]

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

\[ 5\text{H}_2\text{O} + \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{SO}_4^{2-} + 10\text{H}^+ + 8e^- \]
\[ 3e^- + 4\text{H}^+ + \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2\text{H}_2\text{O} \]

3) Equalize electrons:

\[ 15\text{H}_2\text{O} + 3\text{S}_2\text{O}_3^{2-} \rightarrow 6\text{SO}_4^{2-} + 30\text{H}^+ + 24e^- \]
\[ 24e^- + 32\text{H}^+ + 8\text{MnO}_4^- \rightarrow 8\text{MnO}_2 + 16\text{H}_2\text{O} \]

4) Add, then change to basic:

\[ 2\text{H}^+ + 3\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + \text{H}_2\text{O} \]

Add two hydroxide to each side:

\[ \text{H}_2\text{O} + 3\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^- \]

One excess water was also eliminated.

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

\[ \text{H}_2\text{O} + 3\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 \rightarrow 8\text{MnO}_2 + 6\text{SO}_4^{2-} + 2\text{OH}^- \]

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

\[ \text{H}_2\text{O} + 3\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 \rightarrow 8\text{MnO}_2 + 3\text{Na}_2\text{SO}_4 + 3\text{K}_2\text{SO}_4 + 2\text{KOH} \]
Example

H₂SO₄ + KMnO₄ + H₂O₂ ----> MnSO₄ + O₂ + H₂O

Solution:

1) Half-reactions:

MnO₄⁻ ----> Mn²⁺
H₂O₂ ----> O₂

2) Balance:

5e⁻ + 8H⁺ + MnO₄⁻ ----> Mn²⁺ + 4H₂O
H₂O₂ ----> O₂ + 2H⁺ + 2e⁻

3) Equalize electrons:

10e⁻ + 16H⁺ + 2MnO₄⁻ ----> 2Mn²⁺ + 8H₂O
5H₂O₂ ----> 5O₂ + 10H⁺ + 10e⁻

4) Add:

6H⁺ + 2MnO₄⁻ + 5H₂O₂ ----> 2Mn²⁺ + 5O₂ + 8H₂O

5) Adding in spectator ions:

3H₂SO₄ + 2KMnO₄ + 5H₂O₂ ----> 2MnSO₄ + 5O₂ + 8H₂O + K₂SO₄

Three sulfates and two potassium ions were added back in.

Example

K₂S + KMnO₄ ----> S₈ + MnO₂ + KOH

Solution:

1) Half-reactions:

S²⁻ ----> S₈
MnO₄⁻ ----> MnO₂

2) Balance as if in acidic solution:

8S²⁻ ----> S₈ + 16e⁻
3e⁻ + 4H⁺ + MnO₄⁻ ----> MnO₂ + 2H₂O
3) Equalize electrons:

\[
24S^{2-} \rightarrow 3S_8 + 48e^- \\
48e^- + 64H^+ + 16MnO_4^- \rightarrow 16MnO_2 + 32H_2O
\]

4) Add:

\[
64H^+ + 24S^{2-} + 16MnO_4^- \rightarrow 3S_8 + 16MnO_2 + 32H_2O
\]

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

\[
64H_2O + 24S^{2-} + 16MnO_4^- \rightarrow 3S_8 + 16MnO_2 + 32H_2O + 64OH^- \\
\text{eliminate the water:} \\
32H_2O + 24S^{2-} + 16MnO_4^- \rightarrow 3S_8 + 16MnO_2 + 64OH^- \\
6) The only spectator ion is potassium:

\[
32H_2O + 24K_2S + 16KMnO_4 \rightarrow 3S_8 + 16MnO_2 + 64KOH
\]

Example

\[
HNO_3(aq) + H_2S(aq) \rightarrow NO(g) + S_8(s) + H_2O(l)
\]

Solution:

1) Half-reactions:

\[
NO_3^- \rightarrow NO \\
S^{2-} \rightarrow S_8
\]

2) Balance:

\[
3e^- + 4H^+ + NO_3^- \rightarrow NO + 2H_2O \\
8S^{2-} \rightarrow S_8 + 16e^-
\]

3) Equalize electrons:

\[
48e^- + 64H^+ + 16NO_3^- \rightarrow 16NO + 32H_2O \\
24S^{2-} \rightarrow 3S_8 + 48e^-
\]

4) Add:

\[
64H^+ + 16NO_3^- + 24S^{2-} \rightarrow 16NO + 3S_8 + 32H_2O
\]

5) Distribute the 64 hydrogen ions:

\[
16HNO_3 + 24H_2S \rightarrow 16NO + 3S_8 + 32H_2O
\]
Example

Na₂S₂O₃ + KMnO₄ + HNO₃ ----> MnSO₄ + Na₂SO₄ + NaNO₃ + KNO₃ + H₂O

Solution:

1) Half-reactions:
   \[ \text{S}_2\text{O}_3^{2-} \rightarrow \text{SO}_4^{2-} \]
   \[ \text{MnO}_4^- \rightarrow \text{Mn}^{2+} \]

2) Balance:
   \[ 5\text{H}_2\text{O} + \text{S}_2\text{O}_3^{2-} \rightarrow 2\text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \]
   \[ 5\text{e}^- + 8\text{H}^+ + \text{MnO}_4^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} \]

3) Equalize electrons:
   \[ 25\text{H}_2\text{O} + 5\text{S}_2\text{O}_3^{2-} \rightarrow 10\text{SO}_4^{2-} + 50\text{H}^+ + 40\text{e}^- \]
   \[ 40\text{e}^- + 64\text{H}^+ + 8\text{MnO}_4^- \rightarrow 8\text{Mn}^{2+} + 32\text{H}_2\text{O} \]

4) Add:
   \[ 14\text{H}^+ + 5\text{S}_2\text{O}_3^{2-} + 8\text{MnO}_4^- \rightarrow 8\text{Mn}^{2+} + 10\text{SO}_4^{2-} + 7\text{H}_2\text{O} \]

5) Add 14 nitrates, 10 sodium and 8 potassium to the left:
   \[ 14\text{HNO}_3 + 5\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 \rightarrow 8\text{MnSO}_4 + 2\text{SO}_4^{2-} + 7\text{H}_2\text{O} \]
   I also formed 8 MnSO₄ on the right side.

6) Four sodium with the two sulfates, the other six sodium with six nitrates and the eight potassium with the remaining 8 nitrates:
   \[ 14\text{HNO}_3 + 5\text{Na}_2\text{S}_2\text{O}_3 + 8\text{KMnO}_4 \rightarrow 8\text{MnSO}_4 + 2\text{Na}_2\text{SO}_4 + 6\text{NaNO}_3 + 8\text{KNO}_3 + 7\text{H}_2\text{O} \]

Example

FeC₂O₄(s) + H₂O₂(aq) + K₂C₂O₄(aq) ----> K₃[Fe(C₂O₄)₃](aq) + KOH(aq)

Solution:

1) Half-reactions:
   \[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} \]
   \[ \text{H}_2\text{O}_2 \rightarrow \text{OH}^- \]
2) Balance:

\[ \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \]

\[ 2e^- + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- \quad \text{no need to balance in acid, then shift to base} \]

3) Equalize electrons:

\[ 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{3+} + 2e^- \]

\[ 2e^- + \text{H}_2\text{O}_2 \rightarrow 2\text{OH}^- \]

4) Add:

\[ 2\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Fe}^{3+} + 2\text{OH}^- \]

5) Make molecular formulas on the right:

\[ 2\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow 2\text{K}_3[\text{Fe(C}_2\text{O}_4)_3] + 2\text{KOH} \]

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

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

\[ 2\text{FeC}_2\text{O}_4 + \text{H}_2\text{O}_2 + 4\text{K}_2\text{C}_2\text{O}_4 \rightarrow 2\text{K}_3[\text{Fe(C}_2\text{O}_4)_3] + 2\text{KOH} \]

Example

\[ \text{KIO}_3 + \text{KI} + \text{H}_2\text{SO}_4 \rightarrow \text{KIO}_3 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \]

Solution:

1) Half-reactions:

\[ \text{I}_2\text{O}_7^- \rightarrow \text{I}_3^- \]

\[ \text{I}^- \rightarrow \text{I}_3^- \]

2) Balance:

\[ 16\text{e}^- + 18\text{H}^+ + 3\text{I}_2\text{O}_7^- \rightarrow \text{I}_3^- + 9\text{H}_2\text{O} \]

\[ 3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^- \]

3) Equalize electrons:

\[ 16\text{e}^- + 18\text{H}^+ + 3\text{I}_2\text{O}_7^- \rightarrow 8\text{I}_3^- + 9\text{H}_2\text{O} \]

\[ 24\text{I}^- \rightarrow 8\text{I}_3^- + 16\text{e}^- \]
4) Add:

\[18H^+ + 3I_3^- + 24I^- \rightarrow 9I_3^- + 9H_2O\]  

I could take out a factor of three before making everything molecular. I missed that when I answered this question on Yahoo Answers, but I get rid of the factor of 3 at the end.

5) Make the left-hand side molecular:

\[9H_2SO_4 + 3KIO_3 + 24KI \rightarrow 9I_3^- + 9H_2O\]

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

6) Add 9 potassium ion to the right:

\[9H_2SO_4 + 3KIO_3 + 24KI \rightarrow 9KI_3 + 9H_2O\]

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

\[9H_2O SO_4 + 3KIO_3 + 24KI \rightarrow 9KI_3 + 9K_2SO_4 + 9H_2O\]

8) Remove a factor of 3:

\[3H_2SO_4 + KIO_3 + 8KI \rightarrow 3KI_3 + 3K_2SO_4 + 3H_2O\]

Example

\[C_2H_5OH + H_2CrO_4 + H_2SO_4 \rightarrow CH_3CHO + Cr_2(SO_4)_3 + H_2O\]

Solution:

1) Write the net-ionic equation:

\[C_2H_5OH + CrO_4^{2-} \rightarrow CH_3CHO + Cr^{3+}\]

2) Half-reactions:

\[C_2H_5OH \rightarrow CH_3CHO\]
\[CrO_4^{2-} \rightarrow Cr^{3+}\]

3) Balance in acidic solution:

\[C_2H_5OH \rightarrow CH_3CHO + 2H^+ + 2e^-\]
\[3e^- + 8H^+ + CrO_4^{2-} \rightarrow Cr^{3+} + 4H_2O\]

4) Equalize electrons:

\[3C_2H_5OH \rightarrow 3CH_3CHO + 6H^+ + 6e^-\]
\[6e^- + 16H^+ + 2CrO_4^{2-} \rightarrow 2Cr^{3+} + 8H_2O\]
5) Add:
3C₂H₅OH + 2CrO₄²⁻ + 10H⁺ --> 3CH₃CHO + 2Cr³⁺ + 8H₂O

6) Add in three sulfate ions:
3C₂H₅OH + 2H₂CrO₄ + 3H₂SO₄ --> 3CH₃CHO + Cr₂(SO₄)₃ + 8H₂O

**Example**

K₂Cr₂O₇ + HCl --> CrCl₃ + KCl + H₂O + Cl₂

**Solution:**

1) Write the net-ionic equation:
Cr₂O₇²⁻ + Cl⁻ --> Cr³⁺ + Cl₂

2) Half-reactions:

\[ \text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+} \]
\[ \text{Cl}^- \rightarrow \text{Cl}_2 \]

3) Balance half-reactions in acidic solution:

\[ 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
\[ 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \]

4) Equalize electrons:

\[ 6\text{e}^- + 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
\[ 6\text{Cl}^- \rightarrow 3\text{Cl}_2 + 6\text{e}^- \]

5) Add:

\[ 14\text{H}^+ + \text{Cr}_2\text{O}_7^{2-} + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 3\text{Cl}_2 + 7\text{H}_2\text{O} \]

6) Restore molecular equation:

\[ 14\text{H}^+ + \text{K}_2\text{Cr}_2\text{O}_7 + 6\text{Cl}^- \rightarrow 2\text{Cr}^{3+} + 3\text{Cl}_2 + 2\text{K}^+ + 7\text{H}_2\text{O} \] add two potassium ion
\[ 14\text{H}^+ + \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{Cl}^- \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2 + 2\text{KCl} + 7\text{H}_2\text{O} \] add eight chloride to each side
\[ \text{K}_2\text{Cr}_2\text{O}_7 + 14\text{HCl} \rightarrow 2\text{CrCl}_3 + 3\text{Cl}_2 + 2\text{KCl} + 7\text{H}_2\text{O} \] form 14HCl on the left-hand side
Example

As$_2$O$_3$ + HNO$_3$ -> H$_3$AsO$_4$ + NO$_2$ + H$_2$O

Solution:

1) Write the net-ionic equation:
As$_2$O$_3$ + NO$_3^-$ -> H$_3$AsO$_4$ + NO$_2$

2) Half-reactions:
As$_2$O$_3$ ---> H$_3$AsO$_4$
NO$_3^-$ ---> NO$_2$

3) Balance:
5H$_2$O + As$_2$O$_3$ ---> 2H$_3$AsO$_4$ + 4H$^+$ + 4e$^-$
e$^- + 2H$^+$ + NO$_3^-$ ---> NO$_2$ + H$_2$O

4) Equalize electrons:
5H$_2$O + As$_2$O$_3$ ---> 2H$_3$AsO$_4$ + 4H$^+$ + 4e$^-$
4e$^- + 8H$^+$ + 4NO$_3^-$ ---> 4NO$_2$ + 4H$_2$O

5) Add:
H$_2$O + As$_2$O$_3$ + 4HNO$_3$ ---> 2H$_3$AsO$_4$ + 4NO$_2$

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

Example

HNO$_3$ + I$_2$ ---> HIO$_3$ + NO$_2$ + H$_2$O

Solution:

1) Write the net-ionic equation:
NO$_3^-$ + I$_2$ ---> IO$_3^-$ + NO$_2$

2) Half-reactions:
NO$_3^-$ ---> NO$_2$
I$_2$ ---> IO$_3^-$
3) Balance:

$$e^- + 2H^+ + NO_3^- \longrightarrow NO_2 + H_2O$$
$$6H_2O + I_2 \longrightarrow 2IO_3^- + 12H^+ + 10e^-$$

4) Equalize electrons:

$$10e^- + 20H^+ + 10NO_3^- \longrightarrow 10NO_2 + 10H_2O$$
$$6H_2O + I_2 \longrightarrow 2IO_3^- + 12H^+ + 10e^-$$

5) Add:

$$8H^+ + 10NO_3^- + I_2 \longrightarrow 2IO_3^- + 10NO_2 + 4H_2O$$

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

$$10HNO_3 + I_2 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$
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 \( \text{C} - \text{C} \) 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 \( \pi \) electrons. Graphite has higher \( \text{C} - \text{C} \) bond order (due to \( \sigma \) and \( \pi \) bonds) than that of diamond (which has only \( \sigma \) 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 physiorption 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) I is physisorption and II is chemisorption  
(c) IV is chemisorption and II 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

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

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

The empirical formula of the compound is
(a) MX  
(b) MX_2  
(c) M_2X  
(d) M_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
The unit cell is
\[ 8 \left( \frac{1}{8} \right) + 6 \left( \frac{1}{2} \right) = 1 + 3 = 4 \]

There are four M atoms at the centre of edges and one M atom at the centre of the cube. Thus, the number of M atoms per unit cell is
\[ 4 \left( \frac{1}{4} \right) + 1(1) = 1 + 1 = 2 \]

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

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

Which of the following halides react(s) with AgNO3(aq) to give a precipitate that dissolves in Na2S2O3(aq)?
(a) HCl     (b) HF     (c) HBr     (d) HI

**Solution:**
The precipitates of AgCl, AgBr and AgI are soluble in Na2S2O3(aq) forming the complex Na3[Ag(S2O3)2]. For example,
\[ Na_2S_2O_3 + 2AgBr \rightarrow Ag_2S_2O_3 + 2NaBr \]
\[ Ag_2S_2O_3 + 3Na_2S_2O_3 \rightarrow 2Na_3[Ag(S_2O_3)_{2}] \]
AgF is soluble in water.
Therefore, the choices (a), (c) and (d) are correct.

Reversible expansion of an ideal gas

The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is(are) correct?
(a) \( T_1 = T_2 \)
(b) \( T_2 > T_1 \)
(c) \( w_{\text{isothermal}} < w_{\text{adiabatic}} \)
(d) \( \Delta U_{\text{isothermal}} < \Delta U_{\text{adiabatic}} \)

**Solution:**
We will have
\[ T_2 = T_2 \] 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

\[ a_0 = \frac{\hbar^2}{m_e k e^2} \]

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

\[ E_{\text{cell}} = E_{e_1} - \frac{RT}{nF} \ln Q = E_{e_2} - \frac{0.0592}{n} \log Q \]

Charles' Law

\[ \frac{V}{T} = k \]

Atomic Structure

<table>
<thead>
<tr>
<th>DESCRIPTION</th>
<th>EQUATION</th>
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<tbody>
<tr>
<td>Bohr Radius</td>
<td>[ a_0 = \frac{\hbar^2}{m_e k e^2} ]</td>
</tr>
<tr>
<td>De Broglie Wavelength</td>
<td>[ \lambda = \frac{\hbar}{mv} ]</td>
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<tr>
<td>Linear Momentum</td>
<td>[ p = mv ]</td>
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<tr>
<td>Planck's Quantized (Quantum) Energy Equation</td>
<td>[ \Delta E = h \nu ]</td>
</tr>
<tr>
<td>Radii of stable orbits in the Bohr model</td>
<td>[ r = n^2 \frac{\hbar^2}{m_e k Z e^2} = n^2 a_0 \frac{Z}{Z} ]</td>
</tr>
</tbody>
</table>
| Relationship between Energy and Principal Quantum Number | \[ E_n = -R_H \left( \frac{1}{n^2} \right) = -2.178 \times 10^{-18} \] 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**

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<tr>
<td>[ E_{cell} = E_{cell}^o - \frac{RT}{nF} \ln Q = E_{cell}^o - \frac{0.0592}{n} \log Q ]</td>
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<tr>
<td>Electric Current</td>
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<tr>
<td>[ I = \frac{q}{t} ]</td>
<td></td>
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<tr>
<td>Reaction Quotient</td>
<td></td>
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<tr>
<td>[ Q = \frac{[C]^d[D]^d}{[A]^a[B]^b} ] where [ aA + bB \rightarrow cC + dD ]</td>
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<tr>
<td>Relationship between Equilibrium Constant and Cell Voltage</td>
<td></td>
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<tr>
<td>[ \log K = \frac{nE^o}{0.0592} ]</td>
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**Equilibrium**

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<td>Base Ionization Constant</td>
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<tr>
<td>[ K_b = \frac{[OH^-] [HB^+]}{[B]} ]</td>
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</tr>
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<td>Buffer Design Equation</td>
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</tr>
<tr>
<td>[ pH \approx pK_a - \log \frac{[HA]}{[A^-]} ]</td>
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<td>Gas Pressure and Concentration Relationship</td>
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<tr>
<td>[ K_p = K_c (RT)^{Δn} ]</td>
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<td>Ion Product Constant for Water</td>
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<tr>
<td>[ K_w = [OH^-] [H^+] = K_a \times K_b ]</td>
<td></td>
</tr>
<tr>
<td>[ = 1.0 \times 10^{-14} \text{ at } 25°C ]</td>
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<tr>
<td>pH and pOH Relationship</td>
<td></td>
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<tr>
<td>[ pH = pK_a = - \log [H^+] ]</td>
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<tr>
<td>pH Defined</td>
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<tr>
<td>[ pH = - \log [H^+] ]</td>
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<tr>
<td>pK_a Definition</td>
<td></td>
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<tr>
<td>[ pK_a = - \log K_a ]</td>
<td></td>
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</tbody>
</table>
pK_b Definition

\[ pK_b = -\log K_b \]

pOH and Base Ionization Equilibrium Constant

\[ pOH = pK_b + \log \frac{[HB^+]}{[B]} \]

Gases, Liquids, and Solutions

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<tr>
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<td>( PV = k )</td>
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<tr>
<td>Boiling Point Elevation</td>
<td>( \Delta T_b = iK_b \times \text{molality} )</td>
</tr>
<tr>
<td>Charles’ Law</td>
<td>( \frac{V}{t} = k )</td>
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<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>
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<tr>
<td>Freezing Point Depression</td>
<td>( \Delta T_f = iK_f \times \text{molality} )</td>
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<tr>
<td>Graham’s Law of Effusion</td>
<td>( \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} )</td>
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<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>
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Thermochemistry

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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 \( \left( p + \frac{a}{V^2} \right)V = RT \) i.e. \( pV = RT - \frac{a}{V} \)
The plot of $pV$ versus $1/V$ will be a straight line with slope equal to $-\alpha$. Hence

Slope of the given straight line is

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

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

Therefore, the choice (c) is correct.

Dilute solution containing 2.5 gm of nonvolatile

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

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

Solution:

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

$$m = \frac{\Delta T_b}{K_b} = \frac{2}{0.76 \text{ K kg mol}^{-1}} = 2.63 \text{ mol kg}^{-1}$$

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

$$n_2 = m m_1 = \left(\frac{2}{0.76} \text{ mol kg}^{-1}\right) (0.1 \text{ kg}) = \frac{2}{7.6} \text{ mol}$$

From the expression $-\Delta p = x_2 p_1^2$ of the relative lowering of vapour pressure of solvent (whose vapour pressure is 1 atm as the solute is non-volatile), we find that

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

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

$$p = p_1^2 - \Delta p = 760 \text{ mmHg} - 36 \text{ mmHg} = 724 \text{ mmHg}$$

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 dsp^3 hybridization leading to the trigonal bipyramidal arrangement of five pairs of electrons. The structure of XeO_2F_2 is

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

Various increasing and Decreasing properties

Decreasing order of reactivity towards S_n2 displacement:
- n-Butyl bromide, isobutyl bromide, sec-butyl bromide, tert-butyl bromide

Increasing order of reactivity towards S_n1 displacement:
- 1-bromopentane, 2-bromopentane, 2-bromo-2-methylbutane

Increasing reactivity sequence of S_n1 displacement of halogen:
- CH_3X, 1° X, 2° X, 3° X

Increasing reactivity sequence of S_n2 displacement of halogen:
- CH_3X, 1° X, 2° X, 3° X

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

Increasing order or reactivity towards E2 dehydrohalogenation of the bromides:
- ethyl bromide, n-proyl bromide, isobutyl bromide, neopentyl bromide

Increasing stability of alkenes:
- R_2C═CR_2, R_2C═CHR, R_2C═CH_2, RCH═CH_2, CH_2═CH_2

Increasing dehydration of alcohol in the presence of H_2SO_4:
- ethyl alcohol, isopropyl alcohol, tert-butyl alcohol

Decreasing order of reactivity towards E2 dehydrohalogenation:
- 2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane

Increasing order of dehydrohalogenation:
- 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane
Calculate multiple bond energy of a C triple bond

Using the data provided, calculate the multiple bond energy of a C≡C bond in C₂H₂:

\[ 2C(s) + H₂(g) \rightarrow C₂H₂(g) \quad \Delta H₁ = 225 \text{ kJ mol}^{-1} \]
\[ 2C(s) \rightarrow 2C(g) \quad \Delta H₂ = 1410 \text{ kJ mol}^{-1} \]
\[ H₂(g) \rightarrow 2H(g) \quad \Delta H₃ = 330 \text{ kJ mol}^{-1} \]

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

\textbf{Solution:}

Consider the following transformations:

\[ \begin{align*}
2C(s) + H₂(g) & \xrightarrow{\Delta H₁} \quad \text{H} \quad \text{C} \equiv \text{C} \quad \text{H} \\
\Delta H₂ & \quad 2C(g) \quad 2H(g) \\
\Delta H₃ & \quad \text{C} \equiv \text{C} \quad \text{H} \quad \text{H} \\
2C(g) + 2H(g) & \xrightarrow{\Delta H₃} \quad \text{C} \equiv \text{C} \quad \text{H} \quad \text{C} \equiv \text{C} \quad \text{H}
\end{align*} \]

According to Hess’s law

\[ \Delta H₁ = \Delta H₂ + \Delta H₃ - 2\epsilon_{\text{C—H}} - \epsilon_{\text{C≡C}} \]

This gives

\[ \epsilon_{\text{C≡C}} = \Delta H₂ + \Delta H₃ - \Delta H₁ - 2\epsilon_{\text{C—H}} = (1410 + 330 - 225 - 2 \times 350) \text{ kJ mol}^{-1} = 815 \text{ kJ mol}^{-1} \]

Therefore, the choice (d) is correct.

\textbf{Some facts student must know}

\textbf{Largest Anion} - At⁻

\textbf{Metals having highest b.pt and m.pt.} = mercury and tungsten

\textbf{Most reactive solid element} - Li

\textbf{Most reactive liquid element} - Cs

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

\textbf{TOTAL NO. OF LIQUID elements} - 6 (Ga, Br, Cs, Hg, Fr, Eka)

\textbf{Liquid radioactive element} - Francium

\textbf{N.metal wid highest M.Pt} - Carbon

\textbf{Metal wid highest valency} = Plutonium

\textbf{highest tensile strength} - Boron

\textbf{Most ionic compound} = CsF
Strongest base = Cs (OH)

Strongest basic oxide = Cs₂O

Most conducting metal = Ag

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

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 Ag₂O 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):
\[ \text{Pb}(s) + \text{HSO}_4(aq) \rightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- \]

Cathode (reduction):
\[ \text{PbO}_2(s) + 3\text{H}^+(aq) + \text{HSO}_4(aq) + 2e^- \rightarrow \text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \]

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

Overall (cell) reaction (recharge):
\[ 2\text{PbSO}_4(s) + 2\text{H}_2\text{O}(l) \rightarrow 	ext{PbO}_2(s) + \text{Pb}(s) + \text{H}_2\text{SO}_4(aq) \]
Nickel Metal Hydride Battery

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

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

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

Laptops, Cell-phones most commonly use Lithium ion Batteries

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

Cathode (reduction):
\[ \text{Li}_x\cdot\text{Mn}_2\text{O}_4(s) + x\text{Li}^+ + x\text{e}^- \rightarrow \text{LiMn}_2\text{O}_4(s) \]

Overall (cell) reaction:
\[ \text{Li}_x\text{C}_6(s) + \text{Li}_x\cdot\text{Mn}_2\text{O}_4(s) \rightarrow \text{LiMn}_2\text{O}_4(s) \quad E_{\text{cell}} = 3.7 \text{ V} \]

Hydrogen Fuel Cell

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

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

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

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

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

Anode: \[ \text{Ag(s)} \rightarrow \text{Ag}^+ + \text{e}^- \quad E^+_{\text{ox}} = -0.80 \text{ V} \]

Cathode: \[ \text{AgCl} + \text{e}^- \rightarrow \text{Ag(s)} + \text{Cl}^- \quad E^-_{\text{red}} = 0.22 \text{ V} \]

Overall (\( ^\circ K_{sp} \) reaction):
\[ \text{AgCl} \leftarrow \text{Ag}^+ + \text{Cl}^- \quad E^+_{\text{cell}} = -0.58 \text{ V (not very spontaneous)} \]

\[ \ln K = \frac{nFE^+_{\text{cell}}}{RT} = \frac{1 \times 96485 \times (-0.58) \text{V}}{8.3145 \times 298.15K} = 22.5 \text{ mol} \]

\[ K = 6.3 \times 10^{-9} \]
Ion Concentrations can also be calculated...

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

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

The Nernst equation is

\[
E = E^\circ - \frac{0.0257 \text{ V}}{2} \ln \left( \frac{a(H^+)^2}{a(Cu^{2+}) \times a(H_2)} \right)
\]

Since

\[
\frac{8.31451 \frac{J}{\text{mol K}} \times 298.15 \text{ K}}{2 \text{ mol} \times 96485 \frac{\text{C}}{\text{mol}}} = 0.0258 \text{ V}
\]

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

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

(Note: \( \ln Y = 2.303 \times \log Y \) and \(-0.257 \times 2.303 = 0.05917\)

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

\[
E = E^\circ + 0.05917 \text{ V } \times \text{pH}
\]

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

The electrochemical cell shown below is a concentration cell.

\[ M | M^{2+} (\text{saturated solution of a sparingly soluble salt, MX}_2) | M^{2+} (0.001 \text{ mol dm}^{-3}) | M \]

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

- The solubility product (\( K_{sp} \)) of \( MX_2 \) at 298 K based on the information available for the given concentration cell (take \( 2.303 \frac{RT}{F} = 0.059 \text{ V at 298 K} \)) is:
  - (a) \( 1 \times 10^{-13} \text{ mol dm}^{-3} \)
  - (b) \( 4 \times 10^{-15} \text{ mol dm}^{-3} \)
  - (c) \( 1 \times 10^{-12} \text{ mol dm}^{-3} \)
  - (d) \( 4 \times 10^{-12} \text{ mol dm}^{-3} \)

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

**Solutions:**

The cell reaction may be obtained as follows:
- LHC: Oxidation \( \text{M(s)} \rightarrow \text{(M}^{2+})_\text{L} + 2\text{e}^- \)
- RHC: Reduction \( \text{(M}^{2+})_\text{R} + 2\text{e}^- \rightarrow \text{M(s)} \)

The cell potential is:

\[ E = \frac{RT}{2F} \log \left( \frac{[\text{M}^{2+}]_\text{L}}{[\text{M}^{2+}]_\text{R}} \right) \text{ mol dm}^{-3} \]

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

From the reaction

\[ \text{MX}_2(\text{s}) \rightleftharpoons \text{M}^{2+}(\text{aq}) + 2\text{X}^- (\text{aq}); \]

\[ K_{sp} = [\text{M}^{2+}] [\text{X}^-] = (\sigma)(2\sigma) = 4 \times 4 = 16 \times 10^{-5} \text{ mol dm}^{-3} \]

The \( \Delta G \) 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 the first question.
- The choice (d) is correct in the second question.

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

Adding of Oxygen, or Halogens (F, Cl, Br, I) or other p-Block elements which accept electrons, is oxidation. So if Potassium (K) gets Oxygen (attaches to O) to form K₂O or KO₂ (Superoxide), K is getting oxidized. If Cs attaches with F then Cs is getting oxidized, while F is being reduced. Cs is a reducing agent as it is loosing electrons. F is an oxidizing agent as it is gaining electrons.

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

As my experience of teaching more than 25 years, almost every student understands these. Knowing this is essential but does not ensure success in chemistry. There are many kinds of details of oxidizing agent or Reducing agent that vary from reactions / situations.
A simple binary ionic compounds contains only two elements - a metal and a non-metal. When the ionic compound is in the molten state, the locked ions within the ionic structure will be free to move about (conduct electricity).

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

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

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

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

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

Case Study: Electrolysis of molten sodium chloride, NaCl

Electrodes: Carbon rods (Graphite)

Electrolytes: Molten sodium chloride

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

Reaction at the CATHODE:

- $Na^+$ ions are attracted to the cathode.
  - Each $Na^+$ ion gains one electron from the cathode to form one sodium atom.
  - Molten sodium is formed at the anode.
  - equation: $Na^+(l) + e^- \rightarrow Na(s)$ (Reduction)

Reaction at the ANODE:

- $Cl^-$ ions are attracted to the anode.
Each Cl\(^-\) ion loses one electron to the anode to form one chlorine atom.

Chlorine gas is liberated at the anode.

**equation:** \(2Cl^- (l) \rightarrow Cl_2(g) + 2e^-\) (Oxidation)

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

**Case Study: Electrolysis of molten magnesium oxide, MgO**

**Electrodes:** Carbon rods (Graphite)

**Electrolyte:** Molten magnesium oxide

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

**Reaction at the CATHODE:**
- Each Mg\(^2+\) ion gains two electrons from the cathode to form one magnesium atom.
- \(Mg^2+ (l) + 2e^- \rightarrow Mg(s)\)

**Reaction at the ANODE:**
- Each O\(^2-\) ion loses two electrons to the anode to form one oxygen atom.
- \(2O^2- (l) \rightarrow O_2(g) + 4e^-\)

**Overall reaction:**
- Every two moles of magnesium oxide produce two moles of magnesium metal and one mole of oxygen gas.
- \(2MgO(l) \rightarrow 2Mg(s) + O_2(g)\)
Gyan Question:

Determine the standard potential of the \( \text{Cu}^{2+}/\text{Cu}^+ \) cell from two other standard cell potentials.

\( E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.340 \text{V} \) and \( E^\circ(\text{Cu}^+/\text{Cu}) = +0.522 \text{V} \).

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

The two reactions that will occur are:

(a) \( \text{Cu}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2 \text{e}^- \quad \Delta G = -2(-0.340 \text{V}) \quad \Delta G = 0.680 \text{kJ/mol} \)

(b) \( \text{Cu}^+(aq) + \text{e}^- \rightleftharpoons \text{Cu}(s) \quad \Delta G = +0.522 \text{V} \quad \Delta G = +0.522 \text{kJ/mol} \)

(c) \( \text{Cu}^{2+}(aq) + \text{e}^- \rightleftharpoons \text{Cu}^+(aq) \quad \Delta G = +0.158 \text{V} \quad \Delta G = 0.158 \text{kJ/mol} \)

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

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

If the final reaction is a complete cell reaction, with no electrons remaining, then we can skip to just adding the cell potentials because the factor \( v \) would be the same in all equations and hence, cancel out.
(1): \[ \text{Cu}^+ \text{(aq)} + e^- \rightarrow \text{Cu} \text{(s)} \quad E^\circ = 0.521 \text{ V} \]
(2): \[ \text{Cu}^{2+} \text{(aq)} + e^- \rightarrow \text{Cu}^+ \text{(aq)} \quad E^\circ = 0.153 \text{V} \]

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

\[ 2 \text{Cu}^+ \text{(aq)} \rightarrow \text{Cu}^{2+} \text{(aq)} + \text{Cu} \text{(s)} \quad E^\circ_{\text{cell}} = 0.521 - 0.153 = 0.368 \text{ V} (> 0) \]

Which means \( E^\circ_{m_n} > 0 \) and \( \Delta G^\circ_{m_n} < 0 \), spontaneous. Yes, it disproportionates.

\[
\begin{align*}
\text{Cu}^+(\text{aq}) + e^- &= \text{Cu(s)} \\
\text{Cu}^+(\text{aq}) &= \text{Cu}^{2+} (\text{aq}) + e^- \\
2\text{Cu}^+(\text{aq}) &= \text{Cu}^{2+} (\text{aq}) + \text{Cu(s)}
\end{align*}
\]

\[
E^\circ = 0.521 \text{V} \quad E^\circ = -0.153 \text{V} \quad E^\circ = 0.368 \text{V}
\]

We have the value of \( K \)

\[
\ln K = \frac{nFE^\circ}{RT}
\]

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

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

The large \( K \) indicates that the point of equilibrium in the reaction is far toward products, and disproportionation will occur until \( a_{\text{Cu}^+} \) becomes very small.
Discuss Disproportion of Iron

Decide whether Fe$^{2+}$ (aq) in its standard state at 25°C is stable wrt disproportionation.

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

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

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

( a ) 10x \hspace{1cm} ( b ) 100x \hspace{1cm} ( c ) \( 10^5 / x \) \hspace{1cm} ( d ) \( 10^5 \times x \)

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

\[
V = \frac{1}{0.01} = 100 \text{ litres/eq}
\]

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

\[
kV = \frac{1}{\text{Specific resistance}} = \frac{1}{x} \text{ ohm}^{-1} \text{ cm}^{-1}
\]

**Equivalent conductance**

\[
\lambda V = kV \times V
\]

\[
= \frac{1}{x} \times 100 \times 1000
\]

\[
= \frac{10^5}{x} \text{ ohm}^{-1} \text{ cm}^2
\]
Recall again

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

For example, if same quantity of electricity is passed through three voltameters or coulometers containing a dilute solution of H₂SO₄, a solution of CuSO₄ and a solution of AgNO₃, it has been found that one coulomb of electricity liberates \(1.036 \times 10^{-3}\) g. of hydrogen, \(3.292 \times 10^{-4}\) g. of copper and \(1.118 \times 10^{-3}\) g. of silver. The weight of element obtained in each case is proportional to the equivalent weight. Thus,

\[
\frac{\text{Weight of } H_2}{\text{Weight of } Cu} = \frac{\text{Eq. Wt. of } H_2}{\text{Eq. Wt. of } Cu} = \frac{1.008}{31.78} = 0.0318
\]

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

- **Hydrogen:** \([1.008/1.036 \times 10^{-3}] = 96515\) Coulombs
- **Copper:** \([31.78/3.292 \times 10^{-4}] = 96567\) Coulombs
- **Silver:** \([107.88/1.118 \times 10^{-3}] = 96494\) Coulombs

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

\[Ag^+ + e^- \rightarrow Ag\]

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

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

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

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

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

Hence Faraday (F) is the quantity of current in Coulombs required to deposit one gm equivalent of any substance. Passage of one Faraday of electricity means flow of \(6.023 \times 10^{23}\) electrons.

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

\[Na^+ + e^- \rightarrow Na\]  
*(One electron is taken up)*
If one Faraday of electricity is passed through CuCl₂ solution, one gm. equivalent weight of copper ions is discharged at the cathode. This is only 1/2 mole of copper, since copper is bivalent.

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \quad \text{(Two electrons are taken up)} \]

If one Faraday of electricity is passed through AlCl₃ solution, one gm. equivalent of Al³⁺ ions is discharged at the cathode. This is only 1/3 mole of Al³⁺ ions, because Al is trivalent.

\[ \text{Al}^{3+} + 3e^- \rightarrow \text{Al} \quad \text{(Three electrons are taken up)} \]

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

\[ M = e \times Z \times F \]

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

\[ \frac{W}{M} = \frac{e \times Q}{e \times Z \times F} = \frac{Q}{Z \times F} = \frac{\varepsilon \times t}{Z \times F} \]

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

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

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

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

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

\[ E = \frac{1 \text{Gm Mole}}{Z} = \frac{M}{Z} \]

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

Applications of electrolysis – There are various industrial applications of electrolysis. For example, (a) Electrometallurgy – The metals like Na, K, Mg, Al etc. are obtained by the electrolysis of fused electrolytes. (b) Electrefining of metals – A large number of metals, such as Cu, Ag, Au, Al, Sn etc. are purified by electrolysis. (c) Manufacture of compounds – Electrolysis has also been used in the large scale production of various compounds such as NaOH, KOH, KCl, Na₂CO₃, H₂O₂ etc. (d) Manufacture of non-metals – Electrolysis has been employed also in the manufacture of H₂, Cl₂, F₂ etc. (e) Electroplating – Deposition of precious metals like Ag, Au, Pt etc. on less expensive metals like Cu is known as electroplating. This is also carried out by electrolysis. (f) Preparation of alloys and electrotyping – Electrolysis is very useful in the preparation of alloys and also in electrotyping.
Electrical conductivity – Electrical conductivity is the conductivity in mhos of a solution containing one gm equivalent of solute when placed between two sufficiently large electrodes which are one cm apart. It is denoted by $\lambda_v$. The equivalent conductivity is related to the specific conductivity by the expression

$$\lambda_v = \frac{K_v \times V}{V} \quad \text{...(9)}$$

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

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

$$\lambda_m = \lambda_v \times V \quad \text{...(10)}$$

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

$$R = \frac{p \times l}{a} = \frac{x}{a} = \text{cell constant}$$

Thus $x = \frac{R}{p}$ = observed conductivity

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

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

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

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

The important conditions for the cell to be reversible are:

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

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

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

(d) A cell which does not fulfil the above conditions is said to be irreversible.
Effect of dilution on conductivity – (a) The conductivity of the solution increases with dilution, because it depends upon the number of ions present in the solution. On dilution, the degree of ionisation of electrolyte increases and more ions are produced in the solution. The greater the number of ions, the greater is the conductivity.

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

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

It should be noted that increase in equivalent conductivity in the case of strong electrolytes like KCl, NaCl, HCl etc is not so large (because these are already highly ionised) as in case of weak electrolytes such as CH₃COOH, NH₄OH etc (because they are slightly ionised and their ionisation increases with dilution).

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

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

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

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

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

\[
\begin{align*}
\text{Fall Round Anode} & = \text{Speed of Cation} \\
\text{Fall Round Cathode} & = \text{Speed of Anion}
\end{align*}
\]

This relation is valid on the assumption that the discharged ions do not react with the atoms or material of the electrodes. But in many cases, they do combine with the electrode and in such cases, the concentration around such an electrode shows an increase, rather than a decrease. Electrolysis of AgNO₃ solution using silver electrodes is an example of such a case. On electrolysis, it has been observed that instead of fall, the concentration of AgNO₃ around the anode increases, because every NO₃ ion that reaches at the anode dissolves from it one Ag⁺ ion to form AgNO₃.

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

\[
\begin{align*}
n_a & = \frac{\text{Current Carried by Anion}}{\text{Total Current Carried}} \\
n_c & = \frac{\text{Current Carried by Cation}}{\text{Total Current Carried}}
\end{align*}
\]

and $n_a + n_c = 1$

Concentration has marked effect on the transport number, especially in the case of some partially dissociated electrolytes such as ZnI₂, CdI₂ etc. For example, concentration has a marked effect on the transport number of cadmium ion in CdI₂. The value decreases from 0.49 at low concentration to almost zero at higher concentrations and the values become negative at still higher concentrations. The transport numbers of cadmium ions in 0.01N, 0.05N, 0.02N and 0.05N CdI₂ at 25°C are 0.449, 0.402, 0.131, and 0.005 respectively. This abnormal behaviour can be explained by assuming:

(a) That in very dilute solution, CdI₂ ionises to $\text{Cd}^{2+}$ ions and I⁻ ions and thus $\text{Cd}^{2+}$ shows the usual transport number. $\text{CdI}_2 \rightarrow \text{Cd}^{2+} + 2\text{I}^-$.

(b) That with increase in concentration, $\text{CdI}_2$ takes on $\text{I}^-$ ions and forms complex, $\text{CdI}_2 + 2\text{I}^- \rightarrow [\text{CdI}_4]^{2-}$.
Thus the concentrated solution contains both very charged \( \text{Cd}^{2+} \) ions and negatively charged \([\text{CdI}_4]^{2-}\) ions. Hence some of the cadmium forms a part of the anion and migrates towards the anode. Therefore, fall off of concentration round the anode is not as much as it should be. Since relative amounts of two ions depend upon the concentration of electrolyte \( \text{CdI}_2 \), higher the concentration of \( \text{CdI}_2 \) greater would be the proportion of the complex \([\text{CdI}_4]^{2-}\) ion. Thus, if anion \([\text{CdI}_4]^{2-}\) moves faster than the cation \( \text{Cd}^{2+} \), there will be an increase in the concentration round the anode, instead of decrease and thus explains the negative value for the transport number of \( \text{Cd}^{2+} \) ion at much higher concentration.

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

(A) Consider the reaction, \((\text{Hg}^{2+} + \text{Ag} \rightarrow \text{Ag}^+ + \text{Hg})\)

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

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

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

Given: \(E_{\text{Ag}^+/\text{Ag}}^0 = 0.80 \text{ V}, E_{\text{Hg}^{2+}/\text{Hg}}^0 = 0.79 \text{ V}\).

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

What will be the values of

(i) Entropy change \(\Delta S\)

(ii) Free energy change \(\Delta G\)?

Sol. (A) \(E_{\text{cell}}^0 = E_{\text{c}}^0 - E_{\text{a}}^0 = 0.79 - 0.80 = -0.01 \text{ V}\)

The net cell reaction is

\(\text{Hg}^{2+} + 2\text{Ag} \rightarrow 2\text{Ag}^+ + \text{Hg}\)

Anode : \(\text{2Ag} \rightarrow 2\text{Ag}^+ + 2e^-\)

Cathode : \(\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}\)

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

So Reaction not feasible as \(E(\text{cell})\) is negative
Case-II: $E_{\text{cell}} = -0.01 + \frac{0.059}{2} \log \frac{10^{-2}}{10^{-4}} = +0.049 \text{ V}$

Feasible because $E_{\text{cell}}$ is $+ve$.

(B) The given process is

$\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(s)$

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

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

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

$$\lambda_e = \lambda_a + \lambda_c$$

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

$$\frac{\lambda_a}{\lambda_c} = \frac{n_a}{n_c} = \frac{n_a}{1 - n_a}$$

(Since $n_a + n_c = 1$)

The absolute velocity of an ion may be defined as the velocity of an ion in cm per sec. when it moves under an electric field due to two electrodes placed one cm. apart and having a potential difference

of one volt between them (i.e., under unit potential gradient).

Hence unit of absolute velocity is cm per sec. (volts per cm), i.e., cm$^2$ per sec. per volt. The absolute velocity is numerically equal to the ionic mobility divided by one Faraday (96500 Coulombs).

Thus,

$$\text{V} = \frac{\lambda_a}{96500} = \frac{\lambda_c}{96500}$$

From equation(13) We have

$$\frac{\lambda_a}{\lambda_c} = \frac{n_a}{1 - n_a}$$

or

$$\lambda_a - n_a \lambda_c = n_a \lambda_c$$

$$\lambda_a = n_a (\lambda_a + \lambda_c) = n_a \times \lambda_e$$

(Since $\lambda_a + \lambda_c = \lambda_e$)

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

$$\lambda_c = n_c \times \lambda_e$$

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

Q: What is carborundum? Does it conduct electricity?

Ans:

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

Grains of silicon carbide can be bonded together by sintering to form very hard ceramics that are widely used in applications requiring high endurance, such as car brakes, car clutches and ceramic plates in bulletproof vests. Electronic applications of silicon carbide as light-emitting diodes (LEDs) and detectors in early radios were first demonstrated around 1907, and today SiC is widely used in high-temperature/high-voltage semiconductor electronics.
Relative tendencies of electrodes to liberate electrons – When two electrodes are connected to a cell, a competition sets in between the two electrodes to liberate electrons. For example, if the cell consists of zinc and copper electrodes, as in Daniell cell, the electrons flow from negative zinc electrode to positive copper electrode, because zinc has a greater tendency to liberate electrons than copper. If the cell is constituted with copper and zinc electrodes, then copper has a greater tendency to liberate electrons than silver. This indicates that copper is negative electrode and silver is positive electrode and electrons flow from copper to silver electrode. If a cell is set up with Zn and H₂(g) electrodes, then zinc has a greater tendency to liberate electrons than the H₂(g) electrode. This indicates that electrons will flow from negative zinc electrode to positive H₂(g) electrode. If the cell is constituted with copper and H₂(g) electrodes, then H₂(g) electrode has a greater tendency to liberate electrons than the copper electrode. This indicates that electrons will flow from negative H₂(g) electrode to positive copper electrode. Thus in the above cases, the tendency of the electrodes to release electrons decreases in the order Zn > H₂(g) > Cu > Ag.

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

\[ \text{Cu} \mid \text{Cu}^{2+} \rightleftharpoons \text{Ag}^{+} \rightleftharpoons \text{Ag} \mid \text{Zn} \mid \text{Zn}^{2+} \rightleftharpoons \text{H}^{+} \rightleftharpoons \text{H}_2 \text{(g)} \]

AgNO₃ solution turns blue when a piece of copper is added to it, because copper metal can be oxidised by Ag⁺ ions. Ag can not be oxidised by Cu²⁺ ions.

Also remember that the metal which goes into the solution in the form of its salt is undergoing oxidation and thus will act as negative electrode (anode), while the other metal acts as positive electrode (cathode). For example, in the reaction Zn + H₂SO₄ → ZnSO₄ + H₂, the Zn is oxidised to ZnSO₄, hence zinc will be negative electrode or anode and the cell will be constructed as:

\[ \text{Zn} \mid \text{ZnSO}_4 \rightleftharpoons \text{H}_2\text{SO}_4 \rightleftharpoons \text{H}_2 \rightleftharpoons \text{Pt} \]

Role of salt bridge – Most often salt bridges, which are U-shaped tubes are made with agar-agar gel containing KCl or KNO₃. Sometimes NH₄NO₃ is also used. The reason of using these salts is that the ions of these salts, e.g., KCl (K⁺ ion and Cl⁻) have almost the same speed as well as almost same transport numbers. If a salt bridge is not used, say, in the Daniell cell, the electrons released by the zinc electrode (Zn → Zn²⁺ + 2e⁻) can flow to the copper electrode through the external circuit. These electrons neutralise or reduce some Cu²⁺ ions of the CuSO₄ solution (Cu²⁺ + 2e⁻ → Cu). As a result, copper sulphate solution acquires a negative charge for a short while, due to discharge of positively charged Cu²⁺ ions. In the mean time zinc sulphate solution becomes positively charged because of the formation of Zn²⁺ ions from the zinc electrode. Hence there will be accumulation of charges near the two electrodes, which prevents further flow of current. Hence the electrochemical change stops and current drops to zero.

The salt bridge provides a passage for the flow of charges in the internal circuit and thus prevents the accumulation of charges. In the presence of salt bridge, the charges present flow towards the oppositely charged electrodes. The –ve ions move from the copper electrode end through the CuSO₄ solution, salt bridge and zinc sulphate solution to the zinc rod. The positive ions move in the reverse direction, i.e., zinc rod to copper rod. Hence flow of electricity is maintained when the salt bridge is used in the Galvanic cell.

To calculate the \(E_{\text{CELL}}\) of Daniell Cell:

\[ \text{Zn} \mid \text{Zn}^{2+} \rightleftharpoons \text{Cu}^{2+} \rightleftharpoons \text{Cu} \]

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

Reaction at LHE

\[ \text{Zn} \rightleftharpoons \text{Zn}^{2+} + 2e^- \] (Oxidation)

Reaction at RHE

\[ \text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu} \] (Reduction)

Now \(E_{\text{LHE}}^* = E_{\text{Zn}^{2+},\text{Zn}}^* = -0.76\text{V}\) and \(E_{\text{RHE}}^* = E_{\text{Cu}^{2+},\text{Cu}}^* = +0.34\text{V}\). Thus

\[ E_{\text{CELL}}^* = E_{\text{RHE}}^* - E_{\text{LHE}}^* = E_{\text{Cu}^{2+},\text{Cu}}^* - E_{\text{Zn}^{2+},\text{Zn}}^* = +0.34\text{V} - (-0.76\text{V}) = 1.10\text{Volts}. \]

Since \(E_{\text{CELL}}^*\) is positive, the cell reaction is spontaneous.
To calculate the $E^\circ_{\text{CELL}}$ of the cell \( \text{Zn} \parallel \text{Zn}^{2+} \parallel \text{Pb}^{2+} \parallel \text{Pb} \)

Reaction at LHE: \( \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \) \hspace{1cm} (Oxidation)

Reaction at RHE: \( \text{Pb}^{2+} + 2e^- \rightarrow \text{Pb} \) \hspace{1cm} (Reduction)

Cell Reaction: \( \text{Zn} + \text{Pb}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Pb} \)

\[ E^\circ_{\text{CELL}} = E^\circ_{\text{LHE}} - E^\circ_{\text{RHE}} = E^\circ_{\text{Zn}^{2+},\text{Zn}} - E^\circ_{\text{Pb}^{2+},\text{Pb}} = -0.130 - (-0.76) = -0.130 + 0.76 = +0.640 \text{ V}. \]

As the $E^\circ_{\text{CELL}}$ is positive, the above reaction is spontaneous and thus cell is a source of electricity.

To calculate $E^\circ_{\text{CELL}}$ of the cell \( \text{Cu} \parallel \text{Cu}^{2+} \parallel \text{Zn}^{2+} \parallel \text{Zn} \)

Reaction at LHE: \( \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \) \hspace{1cm} (Oxidation)

Reaction at RHE: \( \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn} \) \hspace{1cm} (Reduction)

Cell Reaction: \( \text{Cu} + \text{Zn}^{2+} \rightleftharpoons \text{Cu}^{2+} + \text{Zn} \)

\[ E^\circ_{\text{CELL}} = E^\circ_{\text{RHE}} - E^\circ_{\text{LHE}} = E^\circ_{\text{Cu}^{2+},\text{Cu}} - E^\circ_{\text{Zn}^{2+},\text{Zn}} = -0.130 - (-0.76) = -0.130 + 0.76 = -1.10 \text{ Volts}. \]

Since the $E^\circ_{\text{CELL}}$ is negative, the reaction \( \text{Cu} + \text{Zn}^{2+} \rightleftharpoons \text{Cu}^{2+} + \text{Zn} \) is non-spontaneous.

To calculate $E^\circ_{\text{CELL}}$ of the cell \( \text{Cu} \parallel \text{Cu}^{2+} \parallel \text{Ag}^{+} \parallel \text{Ag} \)

Reaction at RHE: \( 2\text{Ag}^{+} + 2e^- \rightarrow 2\text{Ag} \) \hspace{1cm} (Reduction)

Reaction at LHE: \( \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \) \hspace{1cm} (Oxidation)

Cell Reaction: \( \text{Cu} + 2\text{Ag}^{+} \rightleftharpoons \text{Cu}^{2+} + 2\text{Ag} \)

\[ E^\circ_{\text{CELL}} = E^\circ_{\text{RHE}} - E^\circ_{\text{LHE}} = E^\circ_{\text{Ag}^{+},\text{Ag}} - E^\circ_{\text{Cu}^{2+},\text{Cu}} = 0.8 - (-0.34) = 0.46 \text{ V}. \]

Since the $E^\circ_{\text{CELL}}$ is positive, the cell reaction is spontaneous.

To calculate $E^\circ_{\text{CELL}}$ of the cell \( \text{Ag} \parallel \text{Ag}^{+} \parallel \text{Cu}^{2+} \parallel \text{Cu} \)

\[ E^\circ_{\text{CELL}} = E^\circ_{\text{RHE}} - E^\circ_{\text{LHE}} = (0.34 - 0.80) = -0.46 \text{ V}. \]

Reaction at LHE: \( 2\text{Ag} \rightarrow 2\text{Ag}^{+} + 2e^- \) \hspace{1cm} (Oxidation)

Reaction at RHE: \( \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \) \hspace{1cm} (Reduction)

Cell Reaction: \( 2\text{Ag} + \text{Cu}^{2+} \rightleftharpoons 2\text{Ag}^{+} + \text{Cu} \)

Since $E^\circ_{\text{CELL}}$ is negative, the above reaction is non-spontaneous.

Displacement of metals — The reduction potentials of electrodes given in table 1 are very useful in predicting whether a metal can displace another from its salt solution. When a metal $M_1$ displaces another metal $M_2$ from its salt solution, $M_1$ gets oxidised as $M_1 \rightarrow M_1^{2+} + 2e^-$ and $M_2$ is reduced as $M_2^{2+} + 2e^- \rightarrow M_2$. If $M_1$ has the higher oxidation potential than that of $M_2$, then $M_1$ has a greater tendency to get oxidised and hence $M_1$ can displace $M_2$ from its salt solution. For example, zinc displaces silver from AgNO₃ solution, because standard oxidation potential of zinc (+0.76 V) is greater than that of silver (-0.80 V). Similarly aluminium can displace nickel from nickel salt solution because oxidation potential of Al (Al³⁺ (+1.66 V) is greater than Ni (Ni²⁺ (0.25 V). Copper can not displace zinc from copper sulphate solution when zinc piece is added to copper sulphate solution, because standard oxidation potential of copper (-0.34 V) is less than the standard oxidation potential (+0.76 V) of zinc. This also indicates that more electropositive metals displace less electropositive metals from their salt solutions. Copper is thus less electropositive than zinc.
the strongest reducing agent and the one at the bottom is the weakest reducing agent. Hence lower the reduction potential stronger the reducing agent. The decreasing order of the reducing property of some of the metals is Na > Mg > Zn > Fe > Cu > Ag (More the reduction potential lesser is the reducing power).

Note that this is also the arrangement of metals (as given in the electrochemical series) when arranged in the order of their electrode potentials. The arrangement of metals in the order of decreasing tendency of their atoms to give electrons (i.e. undergoing oxidation) is also known as electrochemical series.

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

Zn + H₂SO₄ → ZnSO₄ + H₂

This reaction is a combination of two half cells.

Zn(s) → Zn²⁺ + 2e⁻  (Oxidation) or 2H⁺ + 2e⁻ → H₂(g)  (Reduction)

In a Galvanic cell oxidation occurs at the left hand electrode and reduction at the right hand electrode. Thus the cell can be represented as, Zn, Zn²⁺ || H⁺, H₂(g), Pt

Thus \( E_{\text{CELL}} = E_{\text{RH}} - E_{\text{LH}} = E_{\text{Zn}^{2+}, \text{Zn}(s)} - E_{\text{H}^+, \text{H}_2(g)} = 0 - (-0.76V) = +0.76 \text{ V} \)

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

2Ag + H₂SO₄ → Ag₂SO₄ + H₂

The cell may be represented as Ag, Ag⁺ || H⁺, H₂(g), Pt

Thus \( E_{\text{CELL}} = E_{\text{Ag}^{2+}, \text{Ag}(s)} - E_{\text{H}^+, \text{H}_2(g)} = 0 - (-0.80V) = +0.80 \text{ V} \)

Since \( E_{\text{CELL}} \) is negative, the reaction of silver with dilute H₂SO₄ is non-spontaneous or not feasible.

In general, any metal lying above hydrogen electrode will reduce H⁺ ions to give H₂ gas, while any metal lying below hydrogen electrode will not reduce H⁺ ions to give H₂ gas. Thus metals like Zn, Cd, Fe etc., lying above hydrogen are capable of reacting with dilute acids such as H₂SO₄, HCl etc. while metals like Ag, Cu etc., which lie below hydrogen electrode, can not evolve hydrogen with dilute acids.

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

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

**The Leclanché or dry cell** — This is a primary cell used in torches, radio, transistors, hearing aids etc. and consists of a negative zinc electrode, a carbon electrode acting as positive electrode, surrounded by a paste of MnO₂ and ZnCl₂ as an electrolyte. The zinc plate usually forms the outer covering of the cell. The oxidation taking place at the negative zinc electrode (anode) is

\[ \text{Zn} + 2\text{MnO}_2 + \text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{Mn}_2\text{O}_3 + 2\text{OH}^- \]

The reduction taking place at positive electrode (cathode) is

\[ 2\text{MnO}_2 + \text{H}_2\text{O} + 2e^- \rightarrow 2\text{Mn}_2\text{O}_3 + 2\text{OH}^- \]

The net cell reaction is:

\[ \text{Zn} + 2\text{MnO}_2(s) + \text{H}_2\text{O} \rightarrow \text{Zn}^{2+} + 2\text{Mn}_2\text{O}_3 + 2\text{OH}^- \]
During the electrolysis of fused NaCl, chloride ions are oxidised at anode. If current is passed into the solution of an electrolyte, anions move towards anode and cations move towards cathode. In the electrolysis of dilute H₂SO₄ using platinum electrodes H₂ is evolved at cathode and O₂ is evolved at anode. Electrolytes when dissolved in water dissociate into ions because the forces of electrostatic attraction are broken down by water. Magnesium can liberate H₂ gas from hydrochloric acid.

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

By convention, if the oxidation potential of an electrode is positive, the natural tendency of the electrode reaction is oxidation. If it is negative, the natural tendency of the electrode reaction is reduction. Similar is the case with reduction potential. If the reduction potential is positive the natural tendency for the electrode reaction is reduction. If it is negative, the tendency for the electrode reaction is oxidation. The reduction potential is positive for strong oxidising agents, which have great tendency to accept electrons and be reduced. The oxidising power of some species follows the order F₂(g) > MnO₂ > Br₂ (aq) > Ag⁺ > Cu²⁺ > H⁺ > Pb²⁺ > Zn²⁺ > Na⁺.

Fluorine gas (F₂) is the strongest oxidising agent and oxidises almost every other element of the periodic table and is reduced to fluoride ion, F⁻. The more negative the reduction potential, the stronger is the reducing agent. The reducing powers of some species decreases in the order Na > Zn > Pb > H₂ > Cu > Ag > Br⁻ > Mn²⁺ > F⁻. Thus sodium metal is the strongest reducing agent and F⁻ is the weakest reducing agent: of all the oxidising agents given above, the sodium ion, Na⁺ is the weakest oxidising agent. Stronger the reducing agent, the weaker is its corresponding oxidising agent. Thus fluorine gas is a strong oxidising agent and F⁻ is a weak reduction agent. We know that weaker an acid, the stronger is its conjugate base. Similarly, the weaker an oxidising agent, the stronger is its corresponding reducing agent.

\[
\text{F}_2(g) + 2e^- \rightarrow 2\text{F}^- \\
\text{Na}^+ + e^- \rightarrow \text{Na}
\]

A reducing agent will react spontaneously with any oxidising agent stronger than the oxidising agent with which it is coupled (that is, any oxidising agent above its corresponding oxidising agent in the
table of standard reduction potentials). Hence Pb will reduce H\(^{+}\)(aq), Cu\(^{2+}\), Ag\(^{+}\), Br\(_2\) etc but not react with Zn\(^{2+}\) or Na\(^{+}\). An oxidising agent will react with any reducing agent stronger than the reducing agent with which it is coupled (that is, any reducing agent below its corresponding reducing agent in the table of standard reduction potentials). Hence Br\(_2\) will oxidise Ag, Cu, H\(_2\), Pb, Zn and Na, but it will not react with Mn\(^{2+}\) or F\(^{-}\) ions. For example Cu will reduce Ag\(^{+}\) ions because Ag\(^{+}\) is stronger oxidising agent than Cu\(^{2+}\) because Ag\(^{+}\) is above Cu\(^{2+}\) in the table). Similarly Cu will not reduce Pb\(^{2+}\) ions, because Pb\(^{2+}\) is below Cu\(^{2+}\) in the table.

In general, a strong oxidising agent is a species which is readily reduced and hence has a large positive standard reduction potential. Such species are F\(_2\) > Cl\(^{2-}\) > Br\(_2\) > I\(_2\). Strong reducing agents are those which are easily oxidised. They have large positive standard oxidation potentials. They include Li > K > Na > ; Ba > Ca > Mg ; Al and some of the transition metals, Zn > Fe > Cd. Hydrogen gas, (SOP) = 0 is moderately good reducing agent. Species below H\(_2\) (which all have negative standard oxidation potentials) are relatively weak reducing agents.

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

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

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

The metal having lesser value of standard reduction potential can displace the other from its aqueous salt solution. Thus Sn can displace lead from lead bromide solution because standard reduction potential of Sn is less than that of Pb. When Zn piece is kept in CuSO\(_4\) solution, copper gets precipitated because standard reduction potential of zinc is less than copper.

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

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

One coulomb = 6.28 x 10\(^{28}\) electrons. One electric charge = 1.6 x 10\(^{19}\) coulombs. In galvanic cell electrical energy is generated at the expense of chemical energy. In an electrolytic cell the chemical energy is generated at the expense of electrical energy. In an electrolytic cell current flows from anode to cathode inside the cell. The electrode which pushes the electrons into the external circuit is called anode. The electrodes which do not participate in the chemical changes are called inert electrodes. The electrode at which electrons flow into an electrolyte is called cathode. Cathode is negatively charged electrode while anode is positively charged. Unless oxidising and reducing agents are kept separate, electric current will not be produced.
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; \( CH_3CHO \)) reacts with ethanol (\( C_2H_5OH \)) as follows: \( CH_3CHO + C_2H_5OH \leftrightarrow CH(OH)(CH_3)(C_2H_5O) \) The hemiacetal has a central carbon atom (from the aldehyde) attached to a hydrogen, a hydroxyl group, a hydrocarbon group (methyl - \( CH_3 \)), and an alkoxy group (\( C_2H_5O \)). If a ketone is used rather than an aldehyde, the resulting hemiacetal contains two hydrocarbon groups. For example, reaction of the ketone \( R1COR2 \) with the alcohol \( R3OH \) is:

\[
R1COR2 + R3OH \leftrightarrow CR1R2(OH)(OR3)
\]
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:

\[
\text{CH(OH)(CH₃)(OC₃H₇)} + \text{C₃H₇OH} \rightarrow \text{CH(CH₃)(OC₃H₇)} \]

The overall reaction of an aldehyde or ketone with an alcohol to give an acetal can be written: R₁COR₂ + R₃OH \rightarrow 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 ketal. 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**

\[ \text{H}_3\text{C}-\text{CH}_3 \rightarrow \cdot\text{CH}_3 + \cdot\text{CH}_3 \]

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**

\[ \text{H}_3\text{C}-\text{OH} \rightarrow \overset{+}{\text{CH}_3} + \cdot\text{OH} \]

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 \textit{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).

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

![Two different geometries of free radicals. The single electrons are shown as black dots.](Image)

So to summarize free radicals:

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

**Carbocations**

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

The precipitating out of the silver salt forces the equilibrium to shift towards the forwards reaction.

A Similar reaction is **Finkelstein reaction** is particularly useful for preparing iodoalkanes. The iodoalkanes are obtained by heating chloro or bromoalkanes with a concentrated solution of sodium iodide in dry acetone.

In Acetone after Reflux (Heating in enclosed container) for a long time [Refluxing is a process of heating a liquid in a flask provided with a condenser. The vapours of the liquid which rise up get condensed back into the flask.]

\[ RX + NaI \rightarrow RI + NaX \] 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 \( NaI \cdot 3(CH_3)\_2CO \) can be formed, in which each Na\(^+\) is coordinated by 6 acetone ligands via oxygen lone pairs, and the I\(^-\) ions fill in the gaps between these octahedral units, being surrounded by the methyl groups of the acetones. I\(^-\) has a larger ionic radius compared to Cl\(^-\) and Br\(^-\) and thus fills the gap completely, thereby minimizing empty space in the lattice and its distance to Na\(^+\), which is, however, still larger than in solvent-free sodium iodide. This larger distance between the ions decreases the lattice energy, which in turn makes the compound readily soluble in acetone. Cl\(^-\) and Br\(^-\) are too small to fit in these gaps, and as the cation-anion distance becomes too large, the only way to minimize the lattice energy is the formation of a solvent-free structure NaX (X = Cl, Br).
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 in 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.

![Diagram of 2-methylbutane, 3-methylpentane, and 2,2-dimethylbutane](image)

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

13 \( \text{CH}_3 \) \(-[\text{CH}_3]_2\) \(-\text{CH}_2\) \(-\text{CH}_2\) \(-\text{CH}_2\) \(-\text{CH}_2\) \(-\text{CH}_3\)

12-\(\text{CH}_3\) \(-\text{CH}\) \(-\text{CH}\) \(-\text{CH}_2\) \(-\text{CH}_2\) \(-\text{CH}_2\) \(-\text{CH}_2\)

1\(\text{CH}_2\) \(-\text{CH}_3\)

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

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
- Alicyclic compounds
- Aromatic compounds

Heterocyclic 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 (Chloroform)
- Nitrobenzene
- Bromobenzene

How Isomers are made?

(a) Normal to branched chain in alkane

\[
\text{n-Alkane} \rightarrow \text{AlCl}_3 (570 \text{ K}) \rightarrow \text{AlCl}_3 + \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_3
\]

(b) Shift of double bond

In the presence of catalyst like \( \text{Al}_2(\text{SO}_4)_3 \), alkene undergo isomerization at high temperature (770 – 970 K).

\[
\text{CH}_2\text{CH} = \text{CH} \rightarrow \text{CH}_3\text{CH} = \text{CH}_2 + \text{H}_2\text{O}
\]

(c) Shift of triple bond

\[
\text{CH}_3\text{C} \equiv \text{C} \rightarrow \text{CH}_3\text{C} = \text{C} \rightarrow \text{CH}_3\text{C} = \text{C} - \text{H}_2\text{O}
\]

CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams
Heating with ethanoic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodium 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) $\text{CH}_2\text{CH} = \text{CHCHO} \xrightarrow{\text{H}_2, \text{Ni}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
(b) $\text{CH}_3\text{CH} = \text{CHCHO} \xrightarrow{\text{9-BBN}} \text{HOCH}_3\text{CH}_2\text{NH}_2$  
(c) $\text{CH}_3\text{CH} = \text{CHCHO} \xrightarrow{\text{Zn + Conc. HCl}} \text{CH}_3\text{CH} = \text{CHCH}_2\text{OH}; \text{9-BBN is 9-Borabicyclo[3.3.1]nonane}$
(d) $\text{CH}_3\text{COCH}_3 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CHCH}_3$
(e) $\text{RCOOH} \xrightarrow{1.\text{LiAlH}_4, 2.\text{H}_2\text{O}} \text{RCH}_2\text{OH}$
(f) $\text{NO}_2 \xrightarrow{\text{H}_2\text{Pt}, \text{or So}_2, \text{HCl heat or Fe, HCl}} \text{NH}_2$
(g) $\text{CN} \xrightarrow{\text{H}_2, \text{Ni}, 140^\circ \text{C}} \text{CH}_3\text{CH}_2\text{NH}_2$
(h) $\text{NO}_2 \xrightarrow{(\text{NH}_3)_2\text{S}} \text{NH}_2$
(i) $\text{RCI} \xrightarrow{\text{Mg}} \text{RMgCl} \xrightarrow{\text{H}_2\text{O}} \text{RH} + \text{Mg(OH)}$
(j) *Rosenmund’s reduction*

Various methods of Oxidation

**Oxidation**

(a) $\text{RCH}_2\text{OH} \xrightarrow{\text{Pyridinium chlorochromate}} \text{RCHO}$
(b) $\text{R’CH}_2\text{OH} \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{R’C=O}$
(c) $\text{RCH}_2\text{OH} \xrightarrow{\text{KMnO}_4} \text{RCOOH}$
(d) $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{CrO}_3, \text{Ac}_2\text{O}} \text{CHO}$
(e) $\text{CH}_3\text{COOH}$
(f) $\text{RCH} = \text{CHCHO} \xrightarrow{\text{Tollens reagent}} \text{RCH} = \text{CHCOOH}$
Synthesis of p-bromonitrobenzene in 2 steps

\[
\begin{align*}
\text{C}_{6}H_{5} & \xrightarrow{\text{Br}_2/\text{Fe}} \text{C}_6\text{H}_4\text{Br} \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} \text{C}_6\text{H}_4\text{BrNO}_2 + \text{C}_6\text{H}_4\text{NO}_2 \\
\quad & \text{ortho (38\%)} \quad \text{para (62\%)}
\end{align*}
\]

Fractional crystallization of the para-isomer crystallizes out first.

**Secondary alcohol to tertiary alcohol**

\[
\begin{align*}
\text{CH}_3\text{CHCH}_3 & \xrightarrow{\text{K}_2\text{Cr}_2\text{O}_7} \text{CH}_3\text{C}\text{CCH}_3 \\
\text{CH}_3\text{C}\text{CCH}_3 & \xrightarrow{1. \text{CH}_3\text{MgBr}, 2. \text{H}^+} \text{CH}_3\text{C} \text{C} \text{CH}_3
\end{align*}
\]

Prepare m-bromoiodobenzene from benzene

Prepare p-bromoiodobenzene from benzene (in not more than 5-7 steps)?

Alternatively, we may proceed as follows:

\[
\begin{align*}
\text{NH}_2 & \text{NO}_2 \\
\text{NO}_2 & \text{NH}_2 \text{NO}_2
\end{align*}
\]
Secondary alcohol to Primary alcohol

\[
\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow{\text{conc. H}_2\text{SO}_4} \text{CH}_3\text{CH}==\text{CH}_2 \xrightarrow{\text{HBr/peroxide}} \text{CH}_3\text{CH}==\text{CHBr} \xrightarrow{\text{aq. KOH}} \text{CH}_3\text{CH}==\text{CH}_2\text{OH}
\]

To convert Ethylebenzene to Benzene and Ethylebenzene to phenylpropionic acid

Show the steps to carry out the following transformations.
(i) Ethylebenzene → benzene

\[
\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{[\text{O}]} \text{CH}_3==\text{CH}_2\text{COOH} \xrightarrow{\text{soda lime}} \text{CH}_3\text{CH}==\text{CH}_2
\]

(ii) Ethylebenzene → 2-phenylpropionic acid.

\[
\text{CH}_3\text{CH}_2\text{CH}_3 \xrightarrow{\text{Br}_2/\text{hv}} \text{CH}_3\text{CH}==\text{CHBr} \xrightarrow{\text{Mg, KCN}} \text{CH}_3\text{CH}==\text{CHCH}_3 \xrightarrow{\text{H}^+} \text{CH}_3\text{CH}==\text{CHCH}_2\text{COOH}
\]

Alcohol to alcohol with one carbon more

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

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

\[
\text{CH}_3==\text{CHCH}==\text{CH}_3 \xrightarrow{\text{[O]}} \text{CH}_3\text{C}==\text{CCH}_3 \\
\text{CH}_3\text{CH}_2\text{C}==\text{CH} + \text{Na}^+\text{NH}_3^- \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{C}==\text{C}^-\text{Na}^+ \\
\text{CH}_3\text{CH}_2\text{C}==\text{C}^-\text{Na}^+ \xrightarrow{\text{H}_2\text{O}^+, \text{Hg}^{2+}} \text{CH}_3\text{CH}_2\text{C}==\text{C}==\text{CH}_3
\]

Alcohol to alcohol with one carbon less

\[
\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{[\text{O}_3]} \text{CH}_3\text{COOH} \xrightarrow{\text{soda lime}} \text{CH}_4 \xrightarrow{\text{Cl}_2/\text{hv}} \text{CH}_3\text{Cl} \xrightarrow{\text{aq. KOH}} \text{CH}_3\text{OH}
\]
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

\[
\text{RCH}_2\text{NH}_2 + \text{HNO}_2 \xrightarrow{0 \degree C} \text{RCH}_2\text{OH} + \text{HNO}_3 + \text{H}_2\text{O} \\
\text{RCH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{RCH}_2\text{Br} + \text{PBr}_3 \\
\text{RCH}_2\text{Br} + \text{NaCN} \xrightarrow{} \text{RCH}_2\text{CN} + \text{NaBr} \\
\text{RCH}_2\text{CN} \xrightarrow{\text{H}_2/\text{Ni}} \text{RCH}_2\text{CH}_2\text{NH}_2
\]

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.

\[
\begin{array}{c}
\text{Br} \xrightarrow{\text{HNO}_2/\text{H}_2\text{SO}_4} \text{Br} \xrightarrow{\text{OCH}_3} \text{NO}_2 \xrightarrow{160 \degree C} \text{NO}_2 \\
\text{OCH}_3 \xrightarrow{\text{H}_2/\text{Pt}} \text{OCH}_3 \\
\text{OH} \xrightarrow{\text{H}^+} \text{OH} \xrightarrow{\text{NaNO}_2/\text{HCl}} \text{N}=\text{N}^+=\text{Cl}^- \\
\text{Nu}_1 \xrightarrow{\text{Br}} \text{Nu}_1 \xrightarrow{\text{Br}} \text{Nu}_1 \xrightarrow{\text{Br}} \text{Nu}_1 \xrightarrow{\text{Br}} \text{Nu}_1
\end{array}
\]

The introduction of \(-\text{NO}_2\) group at \textit{para} position in bromobenzene facilitates the nucleophilic replacement of \(-\text{Br}\) by \(-\text{OCH}_3\).

The negative charge is strongly stabilised by resonance involving \textit{para}-nitro group.

\[\text{Write chemical tests to distinguish}\]

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

\[\text{both an aldehyde } \left( \begin{array}{c} \text{H} \\ \text{C=O} \end{array} \right) \text{ as well as carboxyl}\]
Convert Benzoic acid to meta fluorobenzoic acid (2-fluorobenzoic acid)

**Group** \(\left(\begin{array}{c}
\text{C} \\
\text{O} \\
\text{OH}
\end{array}\right)\) but acetic acid contain only a carboxyl group. Formic acid behaves as reducing agent whereas acetic acid does not.

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

\[
\text{HCOOH} + 2[\text{Ag(NH}_3\text{)}_2]^+ + 2\text{(OH)}^- \\
\text{Tollen's reagent} \\
\rightarrow 2\text{Ag} \downarrow + \text{CO}_2 \uparrow + 2\text{H}_2\text{O} + 4\text{NH}_3 \\
\text{silver mirror}
\]

No silver mirror is formed with acetic acid.

(b) Formic acid reduced Fehling solution to red ppt. of Cu\(_2\)O but acetic acid does not.

\[
\text{HCOOH} + 2\text{Cu}^{2+} + 4\text{(OH)}^- \rightarrow \text{Cu}_2\text{O} \downarrow + \text{CO}_2 \uparrow + 3\text{H}_2\text{O} \\
\text{Fehling solution} \quad \text{red ppt. (cuprous oxide)}
\]

Anine to amine containing one carbon less:

\[
\text{RCH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2, 0^\circ\text{C}} \text{RCH}_2\text{OH} \xrightarrow{[\text{O}] \text{KmO}_4} \text{RCOOH} \xrightarrow{\text{SO}_2\text{Cl}_2} \text{RCOCl} \xrightarrow{\text{NH}_3} \text{RCONH}_2 \xrightarrow{\text{OBr}^-} \text{RNH}_2
\]

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

**Convert**

\[
\begin{align*}
\text{COOH} & \rightarrow \quad \text{COOH} \\
\text{metafluoro benzoic acid} & \quad \text{(not more than 3 steps)}
\end{align*}
\]
Convert Nitrobenzene to meta hydroxynitrobenzene (or 4-nitrophenol)

Conditions and intermediates in the above conversion.
The given conversion can be carried out as follows.
Nitrobenzene resonance structure

4 nitrophenol or metahydroxynitrobenzene
Many conversions or preparations

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

(i) Ethylbenzene from benzene \([C_6H_5CH_2CH_3, \text{anhydrous AlCl}_3]\)
(ii) Propanoic anhydride from propanol \([\text{AgNO}_3/\text{NH}_4\text{OH}, \text{P}_2\text{O}_5]\)
(iii) Acetoxime from acetaldehyde \([\text{K}_2\text{Cr}_2\text{O}_7/H^+, \text{Ca(OH)}_2\text{ and NH}_2\text{OH.HCl}]\)

(i) \(C_2H_5OH + \text{PCl}_3 \rightarrow C_2H_5Cl + \text{POCl}_3 + \text{HCl}\)
(ii) \(C_2H_6 + C_2H_5Cl \rightarrow C_6H_5C_2H_3 + \text{HCl}\)
(iii) \(C_2H_2 + C_2H_5Cl \rightarrow C_6H_5C_2H_3 + \text{HCl}\)

\[\text{C}_2\text{H}_4\text{O}_2\text{H} + \text{AgNO}_3/\text{NH}_4\text{OH} \rightarrow \text{C}_2\text{H}_5\text{COOH};\]

\[2\text{C}_2\text{H}_5\text{COOH} \rightarrow \text{C}_2\text{H}_5\text{CO} \cdot \text{CO}_2\text{H};\]

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

\[\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOCH}_3;\]

\[\text{CH}_3\text{COOH} + \text{Ca(OH)}_2 \rightarrow (\text{CH}_3\text{COO})_2\text{Ca};\]

Benzene to p-toluic acid

\[\text{Benzene to p-toluic acid}\]

\[\text{Benzene to m-chlorobenzoic acid}\]

\[\text{Benzene to m-chlorobenzoic acid}\]
Benzene to p-chlorobenzoic acid

\[
\text{Benzene to } p\text{-chlorobenzoic acid}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5\text{CH}_3 & \xrightarrow{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_{3}\text{Cl} \\
\text{C}_6\text{H}_5\text{CH}_{3}\text{Cl} & \xrightarrow{\text{Fe}} \text{C}_6\text{H}_5\text{Cl} \\
\text{C}_6\text{H}_5\text{Cl} & \xrightarrow{\text{KMnO}_4} \text{C}_6\text{H}_5\text{COOH}
\end{align*}
\]

Acetic acid to Malonic acid

\[
\text{Acetic acid to malonic acid}
\]

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

Ethylene to propanoic acid

\[
\text{Ethylene to propanoic acid}
\]

\[
\begin{align*}
\text{HC}≡\text{CH} & \xrightarrow{\text{Lindlar catalyst}} \text{H}_2\text{C}≡\text{CH}_2 \\
\text{H}_2\text{C}≡\text{CH}_2 & \xrightarrow{\text{HCl}} \text{CH}_3\text{CH}_2\text{Cl} \\
\text{CH}_3\text{CH}_2\text{Cl} & \xrightarrow{\text{KCN}} \text{C}_3\text{H}_5\text{CN} \\
\text{C}_3\text{H}_5\text{CN} & \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{C}_3\text{H}_5\text{COOH}
\end{align*}
\]

Isopropyl alcohol to β-hydroxybutyric acid

\[
\text{Isopropyl alcohol to } \beta\text{-hydroxybutyric acid}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{AlCl}_3, 250°C} \text{CH}_3\text{CH}≡\text{CH}_2 \\
\text{CH}_3\text{CH}≡\text{CH}_2 & \xrightarrow{\text{HOCl}} \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{Cl} \\
\text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{Cl} & \xrightarrow{\text{KCN}} \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{CN} \\
\text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{CN} & \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{CH}_3\text{C}(\text{OH})\text{CH}_2\text{COOH}
\end{align*}
\]

Acetic acid to Propanoic acid

\[
\text{Acetic acid to propanoic acid}
\]

\[
\begin{align*}
\text{CH}_3\text{COOH} & \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \\
\text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{PCl}_3} \text{CH}_3\text{CH}_2\text{Cl} \\
\text{CH}_3\text{CH}_2\text{Cl} & \xrightarrow{\text{KCN}} \text{CH}_3\text{CH}_2\text{CN} \\
\text{CH}_3\text{CH}_2\text{CN} & \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{CH}_3\text{CH}_2\text{COOH}
\end{align*}
\]
Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

Alternatively, we may proceed as follows.

Propanoic acid to acetic acid
Aniline to 1, 2, 3-tribromobenzene

Benzene to m-bromophenol

Ethyl alcohol to Vinyl alcohol

Methylamine to ethylamine
Benzene to m-bromotoluene

Benzaldehyde to cyanobenzene

Aniline to Chlorobenzene

Ethylamine to Methylamine
Benzene to m-dibromobenzene

\[
\text{Benzene} \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NO}_2 \xrightarrow{\text{Br}_2, \text{Fe}} \text{NO}_2 \xrightarrow{\text{Sn}, \text{HCl}} \text{NH}_2 \xrightarrow{\text{NaNO}_2, \text{HCl}} \text{N}_2\text{Cl}^- \xrightarrow{\text{CuBr}} \text{Br}
\]

Aniline to p-nitroaniline

\[
\text{NH}_2 \xrightarrow{\text{CH}_3\text{COCl} - \text{HCl}} \text{NHCOCH}_3 \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{NO}_2
\]

Toluene to m-nitrotoluene

\[
\text{CH}_3 \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NO}_2 \xrightarrow{(\text{CH}_3\text{CO})_2\text{O}} \text{NO}_2 \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NHCOCH}_3 \xrightarrow{\text{H}_2\text{O}} \text{H}^+
\]
Convert Benzene + Alcohol to α-methylphenylacetic acid

Benzene + alcohol to α-methylphenylacetic acid

\[
C_2H_5OH + C_6H_5NH^+CrO_4Cl^- \rightarrow CH_3CHO
\]

\[
\text{Br}_2 \xrightarrow{\text{Fe}} \text{MgBr} \rightarrow \text{Br}_2 \rightarrow \text{Mg} \rightarrow \text{MgBr}
\]

\[
\text{MgBr} + CH_3CHO \rightarrow \text{CH}_3\text{CH} - \text{OH} \rightarrow \text{HCl} \rightarrow \text{Mg}
\]

\[
\text{CH}_3\text{CHOH} \xrightarrow{\text{CO}_2} \text{CHMgCl} \rightarrow \text{Mg}
\]

\[
\text{R}^1\text{C} = \text{O} \xrightarrow{\text{H}^+} \left[\text{R}^1\text{C} \xrightarrow{\text{OR}^3} \text{R}^2\text{OH} \xrightarrow{\text{OR}^3} \text{H}_2\text{O} \right]
\]

ketone

hemiketal

ketal

Toluene to 3,5 dibromotoluene

Toluene to 3, 5-dibromotoluene

\[
\text{CH}_3\text{Cl} \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{CH}_3\text{NO}_2 \xrightarrow{\text{Fe}, \text{H}^+} \text{CH}_3\text{NH}_2 \xrightarrow{2\text{Br}_2} \text{CH}_3\text{Br}_2\text{Br}
\]

\[
\text{Br}_2 \xrightarrow{\text{H}_3\text{PO}_2} \text{Br} \rightarrow \text{Br} \rightarrow \text{Br} \rightarrow \text{HNO}_2
\]
Benzene to $p$-chloronitrobenzene

Benzene to $p$-chloronitrobenzene

$$\text{Cl}_2 \xrightarrow{\text{Fe}} \text{Cl} \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{Cl} \xrightarrow{\text{NO}_2}$$

Toluene to 2,6-dibromotoluene

Toluene to 2,6-dibromotoluene

$$\text{CH}_3 \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{NO}_2 \xrightarrow{2\text{Br}_2, \text{Fe}} \text{Br} \xrightarrow{\text{Fe}, \text{H}^+} \text{Br} \xrightarrow{\text{Br}_2, \text{Fe}} \text{Br} \xrightarrow{\text{H}_3\text{PO}_2, \text{Fe}} \text{Br} \xrightarrow{\text{HNO}_2}$$

Benzene to 3,4-dibromonitrobenzene

Benzene to 3,4-dibromonitrobenzene

$$\text{Br}_2 \xrightarrow{\text{Fe}} \text{Br} \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{Br} \xrightarrow{\text{Br}_2, \text{Fe}} \text{Br} \xrightarrow{\text{Br}_2, \text{Fe}} \text{Br}$$
Benzene to m-chloronitrobenzene

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{Nitrobenzene} \\
& \xrightarrow{\text{Cl}_2, \text{Fe}} \text{m-Chloronitrobenzene}
\end{align*}
\]

Nitrobenzene to benzamide

\[
\begin{align*}
\text{Nitrobenzene} & \xrightarrow{\text{Sn/HCl}} \text{Benzyl chloride} \\
& \xrightarrow{\text{NaNNO}_2, \text{HCl}} \text{Nitrilbenzene} \\
& \xrightarrow{\text{KCN}} \text{Cyanobenzene} \\
& \xrightarrow{\text{H}^+} \text{Carboxybenzene} \\
& \xrightarrow{\text{heat}} \text{Benzamide}
\end{align*}
\]

Benzene to 4-nitrobenzaldehyde

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{CH}_3\text{Cl}, \text{AlCl}_3} \text{Benzyl chloride} \\
& \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{Nitrobenzene} \\
& \xrightarrow{\text{Cr}_2\text{O}_7^{2-}, \text{CICH}_2\text{CO}_2\text{H}} \text{Nitrobenzaldehyde}
\end{align*}
\]

Benzene to 4-amino-2-bromotoluene

\[
\begin{align*}
\text{Benzene} & \xrightarrow{\text{CH}_3\text{Cl}, \text{AlCl}_3} \text{Benzyl chloride} \\
& \xrightarrow{\text{HNO}_3, \text{H}_2\text{SO}_4} \text{Nitrobenzene} \\
& \xrightarrow{\text{Br}_2, \text{Fe}} \text{Bromonitrobenzene} \\
& \xrightarrow{\text{Fe, H}^+} \text{Aminobromotoluene}
\end{align*}
\]

2,4-Dinitrophenol (DNP)
Convert a mixture of cis-2-pentene and trans-2-pentene into cis-2-pentene or trans-2-pentene.

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

Benzene to p-chlorobenzylalcohol

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

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

4-chloropentane-2-one

3-Bromo-4-methylpentanoic acid

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

\[\text{Hex-2-ene-4-ynoicacid}\]

\[\text{Heptan-2-one}\]
Benzene to Mandelic Acid

\[
\text{Benzene to Mandelic acid (CH\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}COOH)}
\]

4-Bromo-2-methylhexane

\[
\text{H}_3\text{C} \quad \text{Br} \quad \text{CH}_3 \quad \text{CH}_3
\]

Heptanal

\[
\text{H}_3\text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_3 \quad \text{O}
\]

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

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

4-phenylprop-3-ene-2-one

\[
\text{H}_3\text{C} \quad \text{O}
\]

\[
\text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CH}_2
\]
3-phenylprop-2-ene-1-al

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

cyclopentancarbaldehyde

Benzophenone also diphenylmethanone
Tollen’s Reagent

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

Free silver

An aldehyde

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

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
Identify the compounds

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

\[
\begin{align*}
ROR & \quad \overset{\text{HI}}{\longrightarrow} \quad 2RI \\
(X) & \quad \overset{\text{H}_2\text{O}}{\longrightarrow} \quad 2ROH \\
(Y) & \quad \overset{\text{I}_2/P}{\longrightarrow} \quad 2R'COOH \\
(Z)
\end{align*}
\]

Now the equivalent weight of R'COOH is 60. From this, it follows that R' is \( -\text{CH}_3 \) group and hence R is \( -\text{CH}_2\text{CH}_3 \) group. Thus, the compounds X, Y and Z are

\[
\begin{align*}
X & : \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3; \\
Y & : \text{CH}_3\text{CH}_2\text{I}; \\
Z & : \text{CH}_3\text{CH}_2\text{OH}
\end{align*}
\]

Steric Effects and the Relative Reactivity of Carboxylic Acid Derivatives
Identify the compound
A hydrocarbon reacts with Bromine to give dibromo compound

One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound C\textsubscript{6}H\textsubscript{10}Br\textsubscript{2}. Substance A on treatment with cold, dilute alkaline potassium permanganate solution forms a compound C\textsubscript{6}H\textsubscript{12}O\textsubscript{2}. On ozonolysis, A gives equimolar quantities of propanone and ethanol. Deduce the structural formula of A.

\textit{Solution} From the products of ozonolysis, we conclude that

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} + \text{O}=\text{C} & \xrightarrow{\text{cold}} \text{CH}_3\text{C}=\text{C} \xrightarrow{\text{dil alkaline KMnO}_4} \text{CH}_3\text{C}=\text{C}-\text{CH}_3 \text{ (A) }
\end{align*}
\]

propanone ethanol 2-methylbut-2-one

The compound A contains a double bond. This is also confirmed from the fact that the compound A reacts with one mole of bromine. Thus, the given reactions are

\[
\begin{align*}
\text{OH} & \text{ OH} \\
\text{CH}_3\text{C} & \text{ CH}_3 \xrightarrow{\text{dil alkaline KMnO}_4} \text{Br}_2 \xrightarrow{\text{cold}} \text{CH}_3\text{C} & \text{ CH}_3 \xrightarrow{\text{Br}_2} \text{CH}_3\text{C} & \text{ CH}_3
\end{align*}
\]

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

An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with bromine in presence of phosphorus, it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

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

\[
\begin{align*}
\text{CH}_3\text{C}=\text{O} \xrightarrow{\text{HCN}} \text{CH}_3\text{C}=\text{CN} \xrightarrow{\text{H}^+} \text{CH}_3\text{C}=\text{COOH} \text{ (D)}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3\text{C}=\text{H} & \xrightarrow{\text{Br}_2\text{P}} \text{CH}_3\text{C}=\text{Br} \\
\text{CH}_3\text{COOH} & \xrightarrow{\text{HO}_2} \text{CH}_3\text{C}=\text{COOH}\text{ (C)}
\end{align*}
\]

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

\[
\begin{align*}
\text{CH}_3\text{C}=\text{H} & \text{ (B)}
\end{align*}
\]

Now, the ozonolysis of the compound A gives acetone and 2-methyl-propanal, i.e.
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 = \(\frac{1}{2} \left(\frac{1}{400}\right)\) 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 CxH2yOy was burnt with twice the amount of oxygen needed for complete combustion to CO2 and H2O. The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound.

Solution: The combustion reaction is CxH2yOy + xO2 → xCO2 + yH2O

To start with, the amount of O2 taken is 2x. Hence, after the combustion reaction, we will be left with the following amounts.

Amount of oxygen left unreacted = x; Amount of carbon dioxide = x; Amount of water = y

When this mixture is cooled to 0 °C and 1 atm, we will be left with oxygen and carbon dioxide. Hence, the amount 2x occupies the given volume of 2.24 L at STP. Hence,

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

Now, Mass of water collected = 0.9 g

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

Thus, the empirical formula of the compound is C_{0.05}H_{x/0.05}O_{y/0.05}, i.e., CH3O. Now, according to Raoult’s law

\frac{\Delta P}{\Delta T} = x_2, \text{ i.e.,} \frac{0.104 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{(50 \text{ g/M})}{(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 CH$_2$O in the molecular formula = $\frac{150.5}{12 + 2 + 16} = 5$

Hence, Molecular formula of the compound is C$_3$H$_{10}$O$_5$.

Identify the Compound

Alcohol when heated with concentrated H$_2$SO$_4$

An alcohol A, when heated with concentrated H$_2$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 H$_2$SO$_4$ in presence of HgSO$_4$. D can also be obtained either by oxidizing A with KMnO$_4$ or from acetic acid through its calcium salt. Identify A, B, C and D.

Solution

The given reactions are as follows:

$$
\xrightarrow{\text{conc. } \text{H}_2\text{SO}_4 {/ \text{alcohol}}} \quad \xrightarrow{\text{alkene}} \quad \xrightarrow{1 \text{ Br}_2, 2 \text{ HBr}} \quad \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \quad \xrightarrow{\text{CH}_3\text{COO}^-} \quad \xrightarrow{\text{Ca}}
$$

The reaction of obtaining D from calcium acetate is

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

Hence, D is acetone. Since the latter is also obtained from the oxidation of alcohol A, compound A will be CH$_3$CH(CH$_3$)$_2$.

Hence, the reactions depicted above are as follows.

$$
\text{CH}_3\text{CHCH}_3 \xrightarrow{\text{Conc. } \text{H}_2\text{SO}_4 {/ \text{2-propanol}}} \text{CH}_3\text{CH}==\text{CH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3\text{CH}==\text{CH}_2
$$

$$
\text{2-propanol} \quad \text{propene} \quad \text{(B)}
$$

$$
\text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C}==\text{CH}_2
$$

$$
\text{propyne} \quad \text{(C)}
$$

$$
\text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{H}_2\text{O}} \text{HgSO}_4/\text{H}_2\text{SO}_4
$$

$$
\text{propyne} \quad \text{(C)}
$$

$$
\text{CH}_3\text{C}==\text{CH} \xrightarrow{\text{H}_2\text{O}} \text{HgSO}_4/\text{H}_2\text{SO}_4
$$

$$
\text{propyne} \quad \text{(C)}
$$
Identify the compound

Certain hydrocarbon was found to contain 85.7% carbon

A certain hydrocarbon $A$ was found to contain 85.7% carbon and 14.3% hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon $B$. 1.0 g of hydrocarbon $A$ just decolourized 38.05 g of a 5% per cent solution (by mass) of $Br_2$ in CCl$_4$. Compound $A$, on oxidation with concentrated KMnO$_4$, gave compound $C$ (molecular formula C$_6$H$_{12}$O$_2$) 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 $\frac{85.7}{12} : \frac{14.3}{1} : 7.14 : 14.3 : 1 : 2$. Thus, Empirical formula of $A$ is CH$_2$.

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

- Mass of bromine absorbed by 1.0 g of hydrocarbon $= \frac{5}{100} \times 38.05$ g
- Mass of hydrocarbon absorbing 160 g (= 1 mol) of $Br_2$ = $\frac{1.0}{(5 \times 38.05/100)} \times 160$ g = 84.1 g.

Hence, Molar mass of $A$ is 84.1 g mol$^{-1}$.

The number of repeating CH$_2$ group in one molecule of $A$ will be 6 (= 84.1/14). Hence, Molecular formula of $A$ is C$_6$H$_{12}$. Now, it is given that

$$C_6H_{12} \xrightarrow{\text{conc. KMnO}_4} C_4H_6O + CH_2COOH$$

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

$$\text{CH}_3\text{C}=\text{CCH}_3 + \text{H}_2\text{O} \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \text{CH}_3\text{C} \equiv \text{CCH}_3 \xrightarrow{\text{OH}} \text{CH}_3\text{CCH}_2\text{CH}_3$$

Identify the compound

A liquid $X$ having a molecular formula C$_6$H$_{12}$O$_2$ is hydrolyzed with water

A liquid $X$, having a molecular formula C$_6$H$_{12}$O$_2$ is hydrolysed with water in the presence of an acid to give a carboxylic acid, $Y$, and an alcohol $Z$. Oxidation of $Z$ with chromic acid gives $Y$. What are the structures of $X$, $Y$ and $Z$?

**Solution**

Since the hydrolysis of $X$ gives a carboxylic acid ($Y$) and an alcohol ($Z$), the compound $X$ must be an ester. Let it be RCOOR’. The compounds $Y$ and $Z$ will be RCOOH and R’OH, respectively. Since the oxidation of $Z$ gives $Y$, we will have

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

Hence, the given compound $X$ may be written as RCOOCH$_2$R. From this it follows that

$$2\text{R’}=\text{C}_6\text{H}_5\text{O}_2-\text{C}_2\text{H}_5\text{O}=\text{C}_6\text{H}_{10} \quad \text{or} \quad \text{R’}=\text{C}_2\text{H}_5$$

$X$ : CH$_3$CH$_2$COCH$_2$CH$_3$ Propylpropanate $Y$ : CH$_3$CH$_2$COOH Propanoic acid $Z$ : CH$_3$CH$_2$OH Propanol
Identify the compound

An unknown compound of carbon, hydrogen, and oxygen contains 69.77% carbon and 11.63% hydrogen and has a molar mass of 86 g mol⁻¹. It does not reduce Fehling's solution, but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures?

**Solution**  The given compound is a ketone as it does not reduce Fehling's solution, but forms a bisulphite addition compound. It will also contain CH₃CO group as it shows positive iodoform test.

The ratios of atoms in the compound are  

\[
\begin{align*}
\text{C} : \text{O} : \text{H} & : \frac{69.77}{12} : \frac{18.60}{16} : \frac{11.63}{1} : 5.81 : 1.16 : 11.63 : 5 : 1 : 10
\end{align*}
\]

Hence, Empirical formula is C₂H₅O₂.  Molar empirical mass = 86 g mol⁻¹; same as the given molar mass

Thus, Molecular formula is C₅H₈O₄.

The structure of the compound will be

- CH₃C(CH₂)₂CH₃ or 2-pentanone
- CH₃C(\begin{align*}
\text{CH₃} \\
\text{O}
\end{align*}) \text{CH₃} or 3-methylbutan-2-one

Identify the compound

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

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

**Solution**  The given reactions are

\[
\begin{align*}
\text{A} + \text{CH₃COOH} & \xrightarrow{\text{H₂SO₄}} \text{ester}; \\
\text{A} & \xrightarrow{\text{mild oxidation}} \text{C} \xrightarrow{50\% \text{ KOH}} \xrightarrow{-\text{H₂O}} \text{A} + \text{D} \\
\text{D} & \xrightarrow{-\text{PCl₅}} \xrightarrow{-\text{NH₃}} \xrightarrow{-\text{H₂O}} \text{E} \\
\text{D} & \xrightarrow{-50\% \text{ KOH}} \xrightarrow{+\text{NH₃}} \xrightarrow{+\text{H₂O}} \text{HCN}
\end{align*}
\]

The reaction \( \text{C} \xrightarrow{-50\% \text{ KOH}} \xrightarrow{+\text{NH₃}} \xrightarrow{+\text{H₂O}} \text{HCN} \) is a Cannizzaro reaction and thus the compound C is an aldehyde with no \( \alpha \)-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.

\[
\begin{align*}
\text{CH₃OH} + \text{CH₃COOH} & \rightarrow \text{CH₃COOCH₃} \quad \text{(methyl acetate)} \\
\text{CH₃OH} & \rightarrow \text{HCHO} \xrightarrow{-50\% \text{ KOH}} \text{CH₃OH} + \text{HCOOH} \\
\text{HCOOH} & \rightarrow \text{HCOCl} \xrightarrow{-\text{H₂O}} \text{HCN}
\end{align*}
\]

Hence

\[
\begin{align*}
\text{A} & : \text{CH₃OH} \quad \text{methanol} \\
\text{B} & : \text{CH₃COOCH₃} \quad \text{methyl ethanoate} \\
\text{C} & : \text{HCHO} \quad \text{methanal} \\
\text{D} & : \text{HCOOH} \quad \text{methanoic acid} \\
\text{E} & : \text{HCONH₂} \quad \text{methanamide}
\end{align*}
\]
Iodoform Test

\[
\text{RCH}_3\text{O} + 3\text{I}_2 + 4\text{NaOH} \rightarrow \text{RCO}^-\text{Na}^+ + 3\text{NaI} + 3\text{H}_2\text{O} + \text{CH}_3\text{I}\text{(aq)}
\]

\[
\text{RCH}_2\text{CHO} \xrightarrow{\text{H}_2\text{O}} \text{RCH} = \text{O} \rightarrow \text{RCO}^-\text{Na}^+ + \text{CH}_3\text{I}
\]

\[
\text{RCH}_2\text{CH}_3 \xrightarrow{\text{I}_2, \text{NaOH}} \text{RCH} = \text{O}^-\text{Na}^+ + \text{CH}_3\text{I}
\]

This bond is broken.
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 sodium hydroxide solution gives a dihydroxy compound, while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z.

Solution  Mass percent of chlorine in the organic compound X

\[
\text{Mass percent of chlorine} = \frac{M_{\text{Cl}} \times m_{\text{AgCl}}}{M_{\text{compound}} \times m_{\text{compound}}} \times 100 = \frac{35.5 \times 2.90}{143.5 \times 1.0} \times 100 = 71.21
\]

The ratios of atoms in the molecule of X are

\[
C : H : Cl : \frac{24.24}{12} : \frac{4.04}{1} : \frac{71.72}{35.5} = 2 : 4 : 2 : 1 : 2 : 1
\]

Empirical formula of X is \(\text{C}_2\text{H}_5\text{Cl}_2\).

Since the isomer Y of the compound gives a dihydroxy compound on treating with aqueous KOH, it follows that the compound must contain two Cl atoms. Hence,

Molecular formula of X is \(\text{C}_2\text{H}_4\text{Cl}_2\).

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

The reaction are

\[
\text{(Z)} \quad \text{CH}_3\text{CHCl}_2 \xrightarrow{\text{aq. KOH}} [\text{CH}_3\text{CH(OH)}_2] \rightarrow \text{CH}_3\text{CHO}
\]

\[
\text{ClCH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{aq. KOH}} \text{HOCH}_2\text{CH}_2\text{OH}
\]

Ethanal

ethylene glycol

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

(a) Cyclopropane, chlorine and light
(b) Propanone and sodium bisulphite
(c) Ethanal and Methanal
(d) Benzene, nitric acid and sulphuric acid
(e) Propene, hydrogen bromide and a peroxide catalyst

(p) Electrophilic substitution
(q) Homologous pair
(r) Homolytic addition
(s) Free radical substitution
(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 (+ anhydrous AlCl₃)
(c) CH₂COOC₂H₅ + NaOH
(d) Preparation of alkanes
(e) Phenol + CHCl₃ (NaOH)
(f) C₂H₅Br + alk KOH

(p) Elimination reaction
(q) Saponification
(r) Wurtz reaction
(s) Friedel-craft reaction
(t) Reimer-Tiemann reaction
(u) Cracking

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

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 with 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 C₆H₄O₂. Identify the compounds A, B, C, D, and E and write their structures.

Solution We have

Mixtures of A and B

<table>
<thead>
<tr>
<th>CHCl₃ + KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>organic layer (A)</td>
</tr>
<tr>
<td>alc KOH</td>
</tr>
<tr>
<td>C₂H₅N</td>
</tr>
<tr>
<td>unpleasant odour</td>
</tr>
<tr>
<td>aqueous layer (B)</td>
</tr>
<tr>
<td>CHCl₃</td>
</tr>
<tr>
<td>H⁺</td>
</tr>
<tr>
<td>C₆H₄O₂</td>
</tr>
<tr>
<td>C₆H₄O₂</td>
</tr>
</tbody>
</table>

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

N == C

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

\[ \text{OH} \quad \xrightarrow{1. \text{CHCl₃}} \quad \text{OH} \quad \xrightarrow{2. \text{H}⁺} \quad \text{CHO} \]
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.

\[
\begin{align*}
\text{Cl} & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{Br} & \quad \text{Cl}_2 \\
\text{CH}_3\text{CHBrCH}_3 & \quad \text{CH}_3\text{CHBrCH}_2\text{-rearr.} \quad \text{CH}_3\text{CHCH}_2\text{Br}
\end{align*}
\]

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

\[
\begin{align*}
\text{Cl} & \quad \text{(CH}_3\text{)}_2\text{CCHBr} & \quad \text{Cl} \\
\text{(CH}_3\text{)}_2\text{CBr} & \quad \text{(CH}_3\text{)}_2\text{CCHBr} & \quad \text{Br}
\end{align*}
\]

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 CO₂ and 0.072 g of H₂O. A is insoluble NaOH and NaHCO₃ while B is soluble in NaOH. A reacts with concentrated H₂SO₄ to give compounds C and D. C can be separated from D by the ethanolic AgNO₃ solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula, C₃H₅OBr₃. Identify A, B, C, D and E with justification and give their structures.

**Solution**

We have

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

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

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

The ratios of atoms in the compound are

\[
C : H : O :: 77.78 : 7.41 : 14.81 \quad :: \quad 6.48 : 7.41 : 0.926 :: 7 : 8 : 1
\]

Hence, Empirical formula of the compound is C₇H₈O₇.

Since the isomer B on reacting with bromine water gives compound E (C₃H₅OBr₃), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and NaHCO₃ and compound B is soluble in NaOH, it may be concluded that B is a phenolic compound and A is an ether. Hence, the structures of A and B are

- A: \[ \text{OCH}_3 \] \quad \text{(A) anisol} \\
- B: \[ \text{OH} \quad \text{OH} \] \quad \text{(B) -cresol}

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, odourless gas whose volume corresponded to 112 mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule.

Solution: Since the compound gives a foul smelling gas on treating with CHCl₃ and alcoholic KOH, the compound must be a primary amine.

\[
RNH₂ + CHCl₃ + 3KOH → RNC + 3KCl + 3H₂O
\]

(1) 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.

\[
RNH₂ + HNO₂ → ROH + N₂ + H₂O
\]

(2)

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 \((59 - 16) \text{ g mol}^{-1}\), i.e., \(43 \text{ g mol}^{-1}\). Hence, \( R \) must be \( C_3H_7 \).

From Eq. (2), it is obvious that the liquid obtained after distillation is ROH. Since this gives yellow precipitate with alkali and iodine (iodoform test), it must contain \( \text{CH}_3 - \text{C} - \text{CH}_3 \) group. Hence, it is concluded that ROH is

\[ \text{CH}_3 - \text{CH} - \text{CH}_3, \text{ thus, the original compound is } \text{CH}_3 - \text{CH} - \text{CH}_3 \]

Thus, the original compound is \( \text{CH}_3 - \text{CH} - \text{CH}_3 \) 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, \( C_6H_{12} \), 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

\[ \text{A} \overset{\text{H}_2\text{SO}_4}{\rightarrow} \text{B} \overset{\text{AlCl}_3}{\rightarrow} \text{C}_6\text{H}_{12} + \text{acid chloride} \]

\[ \text{C}_6\text{H}_{12} + \text{I}_2/KOH \rightarrow \text{C} + \text{D} \]

The reaction of B with I₂ in KOH is iodoform reaction. The compound D is iodoform, \( \text{CH}_3\text{I} \). The compound B must contain \( \text{–COCH}_3 \) group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone (\( \text{C}_6\text{H}_5\text{COCH}_3 \)). The compound C must be an acid.

The compound A may be represented as \( \text{C}_6\text{H}_5\text{C}_2\text{H} \). Since it gives \( \text{C}_6\text{H}_5\text{COCH}_3 \) on treating with dilute \( \text{H}_2\text{SO}_4 \) and \( \text{H}_2\text{SO}_4 \), 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 \((C_2H_4)\) on hydrogenation gives compound F \((C_3H_8)\). 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

\[
C_3H_8 + 4H \longrightarrow C_3H_{12} \quad \text{(E)}
\]

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

\[
C_3H_8 + O_3 \rightarrow HCHO + CH_3-C=CHO \quad \text{(E) Formaldehyde 2-ketopropanal}
\]

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

\[
H_2C=O + O=CH-C=CH_{3} + O_3 \rightarrow CH_2=CH-C=CH_3 \quad \text{(E)}
\]

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

\[
\begin{align*}
\text{Friedel-Crafts Reaction} & \quad \text{CH}_3 \\
\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} & \xrightarrow{\text{AlCl}_3} -18^\circ \text{C to } 80^\circ \text{C} \quad \text{C}_6\text{H}_5\text{CH}_{\text{CH}_2}\text{CH}_3 + \text{C}_6\text{H}_5\text{CHCH}_3 \\
\text{C}_6\text{H}_6 + \text{CH}_3\text{CHCH}_2\text{Cl} & \xrightarrow{\text{AlCl}_3} -18^\circ \text{C to } 80^\circ \text{C} \quad \text{C}_6\text{H}_5 + \text{C} - \text{CH}_3 \\
& \quad \text{CH}_3 \\
\text{C}_6\text{H}_6 + \text{CH}_3\text{CH}_2\text{OH} & \xrightarrow{\text{BF}_3} 60^\circ \text{C} \quad \text{C}_6\text{H}_5\text{CH}_2\text{CH}_3 + \text{CH}_3 \\
& \quad \text{CH}_3 \\
\end{align*}
\]

Identify the compound

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

An organic compound A has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with FeCl₃ solution. The compound A when treated with CO₂ and NaOH at 140 °C under pressure gives B which on being acidified gives C. The compound C reacts with acetyl chloride to give D which is a well known pain killer. Identify A, B, C and D and explain the reactions involved.

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

\[\text{C : H : O} = \frac{76.6}{12} : \frac{6.38}{2} : \frac{17.02}{16} = 6.38 : 6.38 : 1.064 \approx 6 : 6 : 1\]

Hence, empirical formula of A is C₆H₆O. Molar empirical formula mass of A = 94 g mol⁻¹.

This tallies with the given molar mass (≈ 147 g mol⁻¹). Thus, molecular formula of A is C₆H₅O₂.

Since, the compound A gives characteristic colour with FeCl₃, it must be a phenol.

The given reactions are

\[
\begin{align*}
\text{(A)} + \text{CO}_2 & \xrightarrow{\text{NaOH}, \text{high pressure}} \text{(B)} \\
\text{(B)} & \xrightarrow{\text{H}^+} \text{(C)} \\
& \xrightarrow{\text{Aspirin (pain killer)}} \text{(D)}
\end{align*}
\]
Identify the compound

An organic compound A of molar mass 140.5 gm per mole has 68.32% Hydrogen

An organic compound A of molar mass 140.5 g mol\(^{-1}\) has 68.32\% C, 6.4\% H and 25.26\% Cl. Hydrolysis of A with dilute acid gives compound B, \(\text{C}_8\text{H}_8\text{O}\). Compound B can be oxidized under mild conditions to compound C, \(\text{C}_8\text{H}_8\text{O}_2\). Compound C forms a phenylhydrazine D with Ph\(\text{NHNH}_2\) and gives a positive iodoform test. Deduce the structures of compounds A to D with proper reasoning.

**Solution** The ratios of atoms in a molecule of A are

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

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

This tallies with the given molar mass. Thus, molecular formula of A is \(\text{C}_8\text{H}_{12}\text{Cl}\).

The high content of carbon indicates the presence of aromatic (or benzene) ring in the molecule.

Since Cl atom in the compound A is easily replaced during hydrolysis of A with dilute acid, the Cl atom must be attached to the aliphatic portion of the molecule.

Since the compound C gives a positive iodoform test, it must contain —CO\(\text{CH}_3\) group.

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

Bleaching powder and bleach solution are produced on a large scale and used in several household products. The effectiveness of bleach solution is often measured by iodometry. 25 mL of household bleach solution was mixed with 30 mL of 0.50 M KI and 10 mL of 4 N acetic acid. In the titration of the liberated iodine, 48 mL of 0.25 N Na$_2$S$_2$O$_3$ was used to reach the end point. The molarity of the household bleach solution is

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

Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

(a) Cl$_2$O  
(b) Cl$_2$O$_7$  
(c) ClO$_2$  
(d) Cl$_2$O$_6$

**Solutions:**

For Q.11, we may write

Household bleach + 2 KI → I$_2$ + products

$I_2$ + 2Na$_2$S$_2$O$_3$ → Na$_2$S$_4$O$_6$ + 2NaI

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

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

Assuming 1 mol of household bleach produces 1 mol I$_2$, we will have

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

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 $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HOC}_2\text{H}_2\text{O}_2$

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) C$_2$H$_4$CHO</td>
<td>(p) gives precipitate with 2,4-dinitrophenylhydrazine</td>
</tr>
<tr>
<td>(b) CH$_3$C=CH</td>
<td>(q) gives precipitate with AgNO$_3$</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) $\text{HNO}_3$, NO, $\text{NH}_4\text{Cl}$, $\text{N}_2$  
(b) $\text{HNO}_3$, NO, $\text{N}_2$, $\text{NH}_4\text{Cl}$  
(c) $\text{HNO}_3$, $\text{NH}_4\text{Cl}$, NO, $\text{N}_2$  
(d) NO, $\text{HNO}_3$, $\text{NH}_4\text{Cl}$, $\text{N}_2$

**Solution:**

The oxidation states of nitrogen in the given compounds are as follows.

$\text{HNO}_3 : +1 + x + 3 (-2) = 0 \Rightarrow x = +5$  
$\text{NO} : x + (-2) = 0 \Rightarrow x = +2$  
$\text{NH}_4\text{Cl} : x + 4 (+1) + (-1) = 0 \Rightarrow x = -3$  
$\text{N}_2 : 2x = 0 \Rightarrow x = 0$

Thus, the decreasing oxidation numbers of nitrogen is $\text{HNO}_3$, NO, $\text{N}_2$ and $\text{NH}_4\text{Cl}$. Therefore, the choice (b) is correct.

**Gyan Question**

The Kinetic energy of an electron in the second Bohr orbit

The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom ($a_0$ is Bohr radius) is

(a) $\frac{\hbar^2}{16\pi^2ma_0^2}$  
(b) $\frac{\hbar^2}{16\pi^2ma_0^2}$  
(c) $\frac{\hbar^2}{32\pi^2ma_0^2}$  
(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.  
* Quantization of angular momentum, i.e. $mvr = n\left(\frac{\hbar}{2\pi}\right)$

Eliminating $v$ in these two expressions, we get

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

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

$$KE = \frac{1}{2}mv^2 = \frac{1}{2} \left[ \frac{n^2 a_0}{Z} \right]^2 = \frac{1}{2} m \left[ \frac{n}{m(Za_0/2\pi)} \right]^2 = \frac{Z^2}{n^2} \left(\frac{\hbar^2}{8\pi^2ma_0^2}\right)$$

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

$$KE = \frac{1}{32} \left(\frac{\hbar^2}{\pi^2ma_0^2}\right)$$

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

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

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

is

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

**Solution:**

The given reaction may be formulated as follows.

- **First aldol condensation**
  \[
  \text{HCHO} \xrightarrow{\text{OH}^-} \text{CH},\text{CHO} \rightarrow \text{H} \quad \text{C-} \quad \text{CH}_2\text{CHO}
  \]

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

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

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

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

**Solution:**

For first-order decomposition of \(A\), the rate law is \(\ln ([A]/[A]_0) = -kt\)
Hence \(\ln(1/8) = -k t_{1/8}\) and \(\ln(1/10) = -k t_{1/10}\)
Thus \(\frac{\ln(1/8)}{\ln(1/10)} = \frac{t_{1/8}}{t_{1/10}}\) or \(\frac{\log 8}{\log 10} = \frac{t_{1/8}}{t_{1/10}}\)
Hence \((t_{1/8} / t_{1/10}) = 1.3^2 = 3 \times 0.3 = 0.9\) or \(10(t_{1/8} / t_{1/10}) = 10 \times 0.9 = 9\)
Therefore, the answer is 9.
Allene has sp hybridization

In allene ($C_3H_4$), the type(s) of hybridization of the carbon atom is (are)
(a) $sp$ and $sp^3$  
(b) $sp$ and $sp^2$  
(c) $sp^3$ only  
(d) $sp^2$ and $sp^3$

**Solution:**

The structure of allene is $\text{H}_2\text{C} = \text{C} = \text{C} = \text{H}_2$.

In this molecule, carbon atoms 1 and 3 are $sp^2$ hybridized while the carbon atom 2 is $sp$ hybridized.
Therefore, the choice (b) is correct.

Number of chiral carbon and optically active products

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

$$\text{CH}_3 - \text{CH} = \text{CH} - \text{C} - \text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{CH}_3$$

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

**Solution:**

$$\text{CH}_3 - \text{CH} = \text{CH} - \text{C} - \text{C} - \text{CH} = \text{CH} = \text{CH} - \text{CH}_3 \rightarrow \text{CH}_3\text{CHO + OCH} - \text{C} - \text{CHO} + \text{OCH} - \text{CH}_3 + \text{OCH} - \text{CH}_3$$

Ozonolysis

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

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

_Solution:
_The structures of the given compounds are as follows.

Picric acid

Barbituric acid

Ascorbic acid

Aspirin

Therefore, the _choice (d) _is correct.

Identify the compound

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

\[
\begin{align*}
I & \quad \text{(CH}_3\text{CO})_2O \quad J \quad \text{Pd/C} \quad K \\
\text{CH}_3\text{COONa} & \quad \text{H}_2\text{Pd/C} \quad \text{NaHCO}_3 \quad \text{Baeyer’s test}
\end{align*}
\]

_1_ - The compound _K_ is

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

_2_ - The compound _I_ is

(a) (b) (c) (d)
Perkin Condensation

_Solutions:_

The compound J must contain a —COOH group as it gives effervescence with NaHCO₃. Also, it is an unsaturated compound as it gives positive Baeyer’s test (decolourization of pink colour of alkaline KMnO₄). Since the compound J is obtained by treating the compound I with (CH₃CO)₂O and CH₃COONa, and more over the compound J seems to be aromatic (high carbon content), the compound J amongst the choices given in Q.14 seems to be benzaldehyde as it shows Perkin condensation shown in the following:

![Chemical reaction diagram]

The conversion J to K is as follows.

![Chemical reaction diagram]

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

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

**Solution:**

In D-configuration, the hydroxyl group at the asymmetric carbon placed at the bottom of Fischer projection lies to the right of the straight skeleton. Thus, we will have
There are four chiral carbon atoms in the pyranose form of the given aldohexose. Thus, there will be $16 \ (= 2^4)$ stereoisomers, out of which 8 are of D-configurations (CH$_2$OH group above the ring) and 8 are of L-configurations (CH$_2$OH group below the ring).

Therefore, the correct answer is 8.

**Peptides**

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

![Peptide Structure]

<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$_2$)$_2$NH$_2$</td>
</tr>
<tr>
<td>V</td>
<td>CH$_2$CONH$_2$</td>
<td>CH$_2$CONH$_2$</td>
</tr>
<tr>
<td>VI</td>
<td>(CH$_2$)$_2$NH$_2$</td>
<td>(CH$_2$)$_2$NH$_2$</td>
</tr>
<tr>
<td>VII</td>
<td>CH$_3$COOH</td>
<td>CH$_2$CONH$_2$</td>
</tr>
<tr>
<td>VIII</td>
<td>CH$_3$OH</td>
<td>(CH$_2$)$_2$NH$_2$</td>
</tr>
<tr>
<td>IX</td>
<td>(CH$_2$)$_2$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:

- Acidic side chain < neutral chain < basic side chain
- (pH = 3) < (pH = 5.5–6.0) < (pH = 9–10)

This pH is known as isoelectric point.

At pH = 7, the acidic side chain (for which isoelectric point < 7) exists as a negatively–charged species (e.g., $-$COO$^-$) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g., $-$NH$_3^+$). Since peptides IV, VI, VIII and IX contain $-$NH$_2$ group in $R_1$ and/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 < isobutyl alcohol < sec-butyl alcohol < tert-butyl alcohol. Polarity of O—H bond increases in the same order.

(CH₃)₂CCOOH < (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

adipic acid < sucinic 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:
   CICH₂COOH, CH₃CH₂COOH, CICH₂CH₂COOH, (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

\[
\text{CH₃-CH₂-CO-CH₃} + \text{HCN} \xrightarrow{95\% \text{ H}_2\text{SO}_4, \text{Heat}} \text{H}
\]

is

(a) CH₃-CH=C=COOH
(b) CH₃-CH=C=CN
(c) CH₃-CH₂-C=COOH
(d) CH₃-CH=C=CO-NH₂

Solution:
The first reaction is nucleophilic addition reaction across the −C=O bond.

In the second reaction, −CN is hydrolysed to −COOH. The resultant molecule undergoes dehydration on heating.

Therefore, the choice (a) is correct.
Decreasing order of acidity of substituted benzoic acids:
- p-chlorobenzoic acid, 2, 4-dichlorobenzoic acid, 2,4,6-trichlorobenzoic acid.

Decreasing order of acidity of carboxylic acids:
- α-chlorophenylacetic acid, p-chlorophenylacetic acid, phenylacetic acid, α-phenylpropionic acid

Decreasing order of acidity of carboxylic acids:
- p-nitrobenzoic acid, p-nitrophenylacetic acid, β-(p-nitrophenyl) propionic acid

Increasing order of basicity: ammonia, aniline, cyclohexylamine

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

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

Decreasing 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 nitrations: benzene, chlorobenzene, nitrobenzene, toluene

Increasing order of reactivity towards alcoholic silver nitrate:
- 1-bromo-1-butene, 3-bromo-1-butene, 4-bromo-1-butene

Explain these by solving in right order:

Increasing reactivity towards S_N1 solvolysis:
- benzyl chloride, p-chlorobenzyl chloride, p-methoxybenzyl chloride, p-methylbenzyl chloride

Increasing order of reactivity towards elimination by alcoholic KOH:
- 1-phenyl-2-bromopropane, 1-phenyl-2-bromopropane

Decreasing order of reactivity towards aqueous HBr: Isomeric pentyl alcohols

Increasing order of reactivity towards aqueous HBr:
- 1-phenyl-1-propanol, 3-phenyl-1-propanol, 1-phenyl-2-propanol

Decreasing order of reactivity towards aqueous HBr:
- benzyl alcohol, p-cyanobenzyl alcohol, p-hydroxybenzyl alcohol

Increasing order of reactivity towards aqueous HBr:
- benzyl alcohol, diphenylmethanol, methanol and triphenylmethanol

Decreasing order of reactivity towards bromination:
- anisole, benzene, toluene, chlorobenzene, nitrobenzene, phenol

Increasing order of reactivity towards bromination:
- hydroquinone, p-methoxyphenol, p-methylphenol, p-chlorophenol, p-nitrophenol, sym-trihydroxybenzene

Decreasing order of acidity of carboxylic acids:
- butanoic acid, 2-bromobutanoic acid, 3-bromobutanoic acid, 4-bromobutanoic acid

Decreasing reactivity towards S_N1 substitution: 1-chloropropene 3-chloropropene, n-propylchloride

Decreasing acidity: H_2O, H=CH, NH_3, RH, ROH

Decreasing basicity: R^-, H=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: \( ^\cdot \text{CH}_3, 1^\circ, 2^\circ, 3^\circ, \) allyl, vinyl
Increasing stability of carbocation: \( \text{CH}_3^+, 1^\circ, 2^\circ, 3^\circ \)

Increasing enthalpy of reaction:
\[
\begin{align*}
\text{CH}_3\text{Br} & \rightarrow \text{CH}_3^+ + \text{Br}^- & \Delta H_1 \\
\text{CH}_3\text{CH}_2\text{Br} & \rightarrow \text{CH}_3\text{CH}_2^+ + \text{Br}^- & \Delta H_2 \\
\text{CH}_3\text{CHCH}_3 & \rightarrow \text{CH}_3\text{CHCH}_3 + \text{Br}^- & \Delta H_3 \\
\text{CH}_3 & \rightarrow \text{CH}_3 + \text{Br}^- & \Delta H_4 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \rightarrow \text{CH}_3-\text{CH}-\text{CH}_3 + \text{Br}^- & \Delta H_5
\end{align*}
\]

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

\( \text{COOH} \)
\[
\begin{align*}
\text{(a)} & \quad \text{CH}_2\text{COOH} & \quad \text{COOH} \\
\text{(b)} & \quad \text{COOH} & \quad \text{COOH} \\
\text{(c)} & \quad \text{COOH} & \quad \text{COOH} \\
\text{(d)} & \quad \text{CH}_2\text{COOH}
\end{align*}
\]

**Solution:**

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

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

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
\( \text{(a) } \text{C}_4\text{H}_6\text{C} = \text{CH} \quad \text{(b) } \text{C}_4\text{H}_6\text{C} = \text{CH} \quad \text{(c) } \text{C}_4\text{H}_6\text{C} = \text{CH} \quad \text{(d) } \text{C}_4\text{H}_6\text{C} = \text{CH} \)

**Ans:**
More the number of electron withdrawing group stronger is the acid

\[ \text{Cl}_2\text{C}O\text{OH} > \text{Cl}_2\text{CH}C\text{OOH} > \text{ClICH}_2\text{COOH} > \text{CH}_3\text{COOH} \]

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

Try to figure out what sequence is depicted

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

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

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

\[ \text{HO} - \text{COOH} < \text{H}_3\text{C} - \text{CH}_2\text{COOH} < \text{H}_3\text{C} - \text{COOH} < \text{Br} - \text{C} - \text{COOH} < \text{Cl} - \text{C} - \text{COOH} < \text{O}_2\text{N} - \text{C} - \text{COOH} \]

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

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

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

\[ (\text{CH}_3)_2\text{N} < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}. \quad (\text{CH}_3)_2\text{N} \text{ is the weakest because of steric factors.} \]

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 NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67\%Ag. The compound A is

(a) \text{CH}_3\text{CONH}_2 \quad (b) \text{C}_2\text{H}_5\text{CONH}_2 \quad (c) \text{C}_3\text{H}_7\text{CONH}_2 \quad (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 NaOH gives nitrogen free carboxylic acid whose silver salt contains 59.67\%Ag. The compound A is

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

Hence \( \frac{108}{M_R + 44 + 108} = 0.5967 \). This gives \( M = 29 \) i.e. \( \text{R} = \text{C}_2\text{H}_5 \).

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

\[
\begin{align*}
\text{CHO} &< \text{COCH}_3 < \text{CH}_3\text{COCH}_2\text{CHO} < \text{CH}_3\text{COCH}_2\text{COCH}_3 \\
\text{NO}_2 &> \text{F} > \text{Cl} > \text{OCH}_3 > \text{C}_6\text{H}_4 > \text{H}_2 > \text{C}_2\text{H}_3 > (\text{CH}_3)_2\text{CH} > (\text{CH}_2)_3\text{C}.
\end{align*}
\]

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

\[
\text{CH}_3 = \text{CH}_2 < \text{CH}_2 = \text{CH}-\text{CH}_3 < (\text{CH}_3)_2\text{C} = \text{CH}_2
\]

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

\[
\text{CH}_2 = \text{CHCH}_2\text{H}_4 < \text{CH}-\text{CH} = \text{CHCH}_3 < \text{CH}_2 = \text{CH} = \text{CH} = \text{CH}_2 < \text{CH}_2 = \text{CH} = \text{CH} = \text{CH} = \text{CH}_2
\]

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

\[
\text{C}_6\text{H}_5\text{CH}_3 < \text{C}_6\text{H}_5\text{CH}_2\text{Cl} < \text{C}_6\text{H}_5\text{CHCl}_2 < \text{C}_6\text{H}_5\text{CCl}_3
\]

 tert-butanol < sec-butanol < n-butanol < CH}_3\text{OH}. Alkyl group makes an alcohol less acidic. Bigger the alkyl group, the less acidic the alcohol. Methanol is the strongest and tertiary alcohols are the weakest.

\[
(\text{CH}_3)_2\text{CHC} = \text{O} < \text{C}_2\text{H}_5\text{COOH} < \text{CH}_3\text{COOH} < \text{C}_6\text{H}_5\text{C} = \text{O} < \text{HCOOH} < \text{CICH}_2\text{COOH}
\]

An aromatic compound contains 69.4% C and 5.8% H

An aromatic compound contains 69.4% C and 5.8% H. A sample of 0.3 g of this compound give ammonia which neutralizes 25 mL of 0.05 M H\text{SO}_4. The empirical formula of the compound is

\[
\begin{align*}
\text{CH}_3\text{N}_2\text{O} & \quad (\text{a}) \\
\text{C}_6\text{H}_5\text{NO} & \quad (\text{b}) \\
\text{C}_6\text{H}_5\text{NO}_2 & \quad (\text{c}) \\
\text{C}_6\text{H}_6\text{NO}_3 & \quad (\text{d})
\end{align*}
\]

Ans :

\[
\begin{align*}
\text{Amount of H}_2\text{SO}_4 \text{ neutralized} &= (25 \times 10^{-3} \text{L})(0.05 \text{ M}) = 1.25 \times 10^{-3} \text{ mol} \\
\text{The neutralization reaction is} \quad 2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4. \\
\text{Amount of NH}_3 \text{ evolved} &= 2 \times 1.25 \times 10^{-3} \text{ mol} = 2.5 \times 10^{-3} \text{ mol} \\
\text{Mass of N in the compound} &= (2.5 \times 10^{-3} \text{ mol})(14 \text{ g} \text{ mol}^{-1}) = 0.035 \text{ g} \\
\text{Per cent of N in the compound} &= \frac{0.035}{0.3} \times 100 = 11.67 \\
\text{Per cent of O in the compound} &= 100 - (69.4 + 5.8 + 11.67) = 13.13 \\
\text{Ratio of atoms in the compound is} \quad \text{C} : \text{H} : \text{N} : \text{O} :: \frac{69.4}{12} : \frac{5.8}{1} : \frac{11.67}{14} : \frac{13.13}{16} :: 5.78 : 5.8 : 0.83 : 0.82 :: 7 : 7 : 1 : 1 \\
\text{Hence, empirical formula:} \quad \text{C}_6\text{H}_5\text{NO}
\end{align*}
\]

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 Carbon monoxide.

**IMPORTANT ORDER AND FACTS OF ORGANIC CHEMISTRY**

1. $\text{RCOCl} > \text{RCOOCOR} > \text{RCOOR} > \text{RCONH}_2$ Nucleophilic substitution reaction.
2. $\text{HI} > \text{HBr} > \text{HCl} > \text{RCOOH} > \text{C}_6\text{H}_5\text{OH} > \text{H}_2\text{O} > \text{CH}_3\text{CH} > \text{NH}_3$ (Acidic nature).

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3. $\text{CCl}_3\text{CHO} > \text{HCHO} > \text{CH}_2\text{CHO} > \text{CH}_3\text{COCH}_3$ Nucleophilic addition reaction.

4. $\text{CH}_2 = \text{CH}_2 > \text{CH} = \text{CH}_2 > \text{C}_2\text{H}_4$ Electrophilic addition reaction.

5. $\text{NH}_2 > \text{OH} > \text{OR} > \text{H}_2\text{O}$ Substitution Reaction

6. $\text{CH}_2\text{Cl} > \text{Cl} - \text{CH}_2\text{CH}_2\text{Cl} > \text{CH}_2\text{H}_2\text{Cl} > \text{CH}_2 = \text{Cl}$ Nucleophilic Substitution Reaction

7. $\text{(C}_2\text{H}_4\text{Cl)} > \text{Cl} - \text{CH}_2\text{CH}_2\text{Cl} > \text{CH}_2\text{H}_2\text{Cl}$ Nucleophilic Substitution Reaction

8. $\text{(C}_2\text{H}_4\text{Cl)} > \text{C}_6\text{H}_5\text{CH}_2 > \text{CH}_2\text{CH}_2\text{Cl} > \text{Cl}$ Carbocation stability

9. $\text{CH}_2\text{Cl} > \text{CH}_2\text{CH} = \text{CH}_2 > \text{CH}_2\text{H} > 1^\circ > 2^\circ > 3^\circ$ Carbanion stability

10. $\text{(CH}_3\text{)}_2\text{CH} = \text{C} = \text{C} - \text{CH}_2\text{CH}_2 > \text{CH}_2\text{CH} = \text{CH}_2 > \text{CH}_2\text{CH}_2\text{CH}_3 > \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (Stability)

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

12. $\text{NH}_3 > \text{OH} > \text{H}_2\text{O}$ (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 diehl’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 occurs in HgSO$_4$ and dil H$_2$SO$_4$. 
24. Cis-2-butene reacts with Br₂ to forms dl(±) pair of enantiomers of 2,3-dibromobutane while in case of trans-2-butene forms meso-2,3-dibromo butane due to anti addition always.


26. Chloral reacts with chloro butane in the presence of 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 carbarylamine 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

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

36. Ether’s reacts with HI to form alcohol and halide where fission of lower ether by S² mechanism while higher ethers like tert. 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 tollen’s reagent.

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

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

43. Aldehydes with hydrogogen atom in the presence of dil base undergo enolization and form \(\text{CH}_3\text{CHO} + \text{H}_2\text{O}\).
44. If there is two-CHO group with hydrogen atom to form cyclic intra aldol product.

45. Aldehydes without hydrogen atom in the presence of con. alkali to form each molecule of acid and alcohol by hydride active species.

46. Glyoxal reacts with con. KOH to form glycolate ion by Intra Cannizaro’s.

47. Pinacol pinacolone type reactions involve protonation, deprotonation and alkyl shift.

48. Aldol, Perkin, reformatsky and knovengel’s reactions are classified as carbanian active reaction.

49. In Beckmann’s rearrangement migration of group which is anti to-OH group takes place.

50. Beckmann’s rearrangent is a reaction of oximes in the presence of H$_2$SO$_4$ or PCl$_5$ to produce N-alkyl amide derivatives.

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

52. Cyclohexanone oxime on beckmann’s reaction gives caprolectum which on reaction with $\text{H}_2$ to give polymer nylon-6.

53. 2-methyl propanal even contains hydrogen atom but does not give aldol reaction.

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

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

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

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

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

59. HCOOH respond to oxidising agent due to presence of -CHO group.

60. HI > H$_2$SO$_4$ > HNO$_3$ > RCOOH > H$_2$CO$_3$ > C$_6$H$_5$OH > H$_2$O > CH$_3$CH > NH$_3$ > CH$_3$ - C$_2$H$_5$ > CH$_2$ = CH$_2$ > H$_2$ this is decreasing acidic nature.

61. Acids with hydrogen atom when reacts with halogen in the presence of P to form -haloacid (HVZ).

62. Carboxylic acid on reaction with PCl$_5$, CH$_2$N$_2$ and H$_2$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 PCl$_5$ to form alkane nitrile.

65. Anhydride on reaction with carbonyl compound in the presence of base (carbanian) forms $\sigma$, $\beta$-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 -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 closen’s ester condensation of four types

(a) Simple closen’s ester condensation.
(b) CROSS closen’s ester condensation.
(c) Intra CEC (Dieckmann’s condensation).
(d) mixed closen 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>1. B.P. of CH₃CH₂OH, CH₃OCH₃, CH₃CH₂, CH₃I</td>
<td>I &gt; II &gt; III</td>
<td>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.</td>
</tr>
<tr>
<td>2. B.P. of o, m, p-nitro phenol</td>
<td>o &lt; m &lt; p</td>
<td></td>
</tr>
</tbody>
</table>

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3. Reactivity of $\ldots$ with Tollen’s reagent

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO,</td>
<td>CH$_3$CHO,</td>
<td>CH$_2$COCH$_3$,</td>
<td>C$_3$H$_5$CHO</td>
</tr>
</tbody>
</table>

$\text{--CHO group is easily oxidised compared to keto group due to reducing hydrogen.}$

4. Reactivity of $\ldots$ with Fehling’s solution

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV (above)</th>
</tr>
</thead>
</table>

$\text{Aldehydes are more hydrated than ketones. Halide makes C of carbonyl group more electropositive.}$

5. Extent of hydration of

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
</table>

$\text{Aldehydes are more hydrated than ketones. Halide makes C of carbonyl group more electropositive.}$

6. Electrophilic nature of $\ldots$ for nucleophilic attack

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
</table>

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

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

$3° < 2° < 1°$ due to stability of intermediate carbocation

8. Dehydration of

<table>
<thead>
<tr>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
</table>

$\text{Alcohol leading to increase in conjugation due to dehydration is more easily dehydrated. IV is vinylic, hence least.}$

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

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

10. **Stability of**

   - (I)
   - (II)
   - (III)

   **II** is more substituted than **III** (More hyperconjugation more stability)

11. **Stability of**

   - (I)
   - (II)
   - (III)
   - (IV)

   **IV** is vinylic while in conjugative, **II** allylic.

12. **Stability of**

   - (I)
   - (II)
   - (III)
   - (IV)

   **III** is 3° allylic and **II** is 1° allylic

13. **Dehydration of**

   - 1°, 2°, 3° isomeric butyl alcohol

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

14. **Boiling points of**

   - \( n \)-butyl amine, \( n \)-butyl alcohol, \( n \)-pentane

   \( \text{I} > \text{II} > \text{III} \)

   I, II have H-bonding but electronegativity of O > N hence H-bonding in II > I greater the stability, easier the formation of particular species.

15. **Formation of**

   - \( \text{R}_3 \text{C} \cdot \text{CH}_2 \cdot \text{R}_2 \text{CH} \cdot \text{RCH}_2 \)

   \( \text{I} > \text{II} > \text{III} > \text{IV} \) (easiest I)

17. Leaving nature (tendency) of ... in $S_N$ reaction.

- $\text{H}^+$, $\text{R}^+$, $\text{MeO}^-$, $\text{OH}^-$, $\text{CN}^-$, $\text{CH}_2\text{COO}^-$,
- $\text{I} < \text{II} < \text{III} < \text{IV} < \text{V} < \text{VI} < \text{VII} < \text{VIII}$

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

18. Rate of esterification of the following acids with MeOH

- $\text{MeCH}_2\text{COOH}$, $\text{Me}_2\text{CHCOOH}$, $\text{Me}_3\text{COOH}$,
- $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V}$

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 ... with electrophile in $S_E$ reaction

- $\text{CH}_3$, $\text{CH}_3$, $\text{CH}_3$, $\text{OH}$,
- $\text{I} > \text{II} > \text{IV} > \text{III} > \text{V}$

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

20. Relative reactivity of these compounds with electrophile in $S_E$ reaction

- $\text{I} > \text{II} > \text{III} > \text{IV}$

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

21. Relative reactivity of ... with electrophile in $S_E$ reaction

- $\text{II} > \text{I} > \text{IV} > \text{I}$

As the number of $\text{sp}^3$ hybridized $\text{C}$
22. Activating effects of the following o, p-directors.

\[
\begin{align*}
\text{OH} & \quad \text{O}^\ominus \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

Relative reactivity of ... towards $S_N1$ reaction

-benzyl chloride, $p$-methoxy benzyl chloride

and $p$-nitro benzyl chloride

23. Relative reactivity of ... towards $S_N1$ and $S_N2$ reaction

$S_N1$:

\[
\begin{align*}
\text{PhCH}_2\text{Cl} & \quad \text{PhCHClMe} \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

$S_N2$:

\[
\begin{align*}
\text{PhCClMe}_2 & \\
\text{I} & \quad \text{II} & \quad \text{III}
\end{align*}
\]

(Ph stands for phenyl, $C_6H_5$)

24. Relative reactivity of ... with $E^\ominus$ (electrophile) in $S_E$ reaction.

\[
\begin{align*}
\text{S}_E^1 : & \quad 1^\ominus < 2^\ominus < 3^\ominus \\
\text{alkyl halide} & \\
\text{S}_E^2 : & \quad 3^\ominus < 2^\ominus < 1^\ominus \\
\text{alkyl halide} & \\
\text{NO}_2 & \quad \text{deactivates}
\end{align*}
\]

atoms separating the ring from the positively charged substituent increases, deactivating effect decreases due to less electronegativity.

$O^\ominus$ is best able to donate electrons there by giving a very stable uncharged intermediate. In cross conjugation diminished its ability to donate electrons to an arenium ion. Intermediates are benzylic cations. So $\text{CH}_3\text{O}$ (electron repelling) gives greater stability through delocalisation while $\text{NO}_2$ (electron attracting) decreases stability.

25. Relative reactivity of ... with $E^\ominus$ (electrophile) in $S_E$ reaction.

\[
\begin{align*}
\text{S}_E : & \quad I > II > III
\end{align*}
\]

$\text{NO}_2$ deactivates benzene ring for $S_E$
26. Order of $S_N2$ reactivity of alkoxide nucleophiles

$S_N2$ reactivity is susceptible to steric hindrance by the nucleophile as well as by the size of alkyl group.

Basic power - Chemistry Fact Sheet - 2

**Basic power** | **Order** | **Why?**
---|---|---

1. (I) | (II) | (III)

$I > III > II$

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 (hyper conjugation and induction) II (induction) IV (ortho effect), ortho effect normally decreases basic nature.
4. II > I > III
In II there is sp³ hybridised C, In I, sp². NO₂ is electron withdrawing.

5. III > I > II
lone pair on N is used in delocalisation of π electrons in aromatic amines while cyclohexyl is electron repelling (III); in II, lone pair on N is used by two benzene ring. NO₂ is electron-withdrawing, thus nitroanilines are less basic than aniline. IV is less basic than III because —NO₂ is closer and exerts a stronger inductive effect.

6. I > II > III > IV
phenyl and —COCH₃ are electron withdrawing and —C₆H₅ < COCH₃

7. III > I > II
Electron donating nature of C₂H₅ > CH₃ So more basic strength.

8. I < II < III
9. I < II < III  ortho effect in I.

10. 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>III &lt; II &lt; I</td>
<td>Farther the (-I) group (Cl), lesser the acidic strength</td>
</tr>
<tr>
<td>2. 1-, 2-, 3- methyl pentanoic acid</td>
<td>I &lt; II &lt; III</td>
<td>Farther the (+I) group, greater the acidic power</td>
</tr>
<tr>
<td>3.</td>
<td>II &lt; I &lt; III</td>
<td>−CH₃ is electron donating and −NO₂ is electron attracting</td>
</tr>
<tr>
<td>4.</td>
<td>II &lt; I &lt; III</td>
<td>−CH₃ is electron repelling; decreases acidic strength of phenol</td>
</tr>
<tr>
<td>5.</td>
<td>III &lt; I &lt; II</td>
<td>−OCH₃ group contains +M effect and decreases acidic power.</td>
</tr>
</tbody>
</table>
6. I < II < III

- NO₂ is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative. sp² hybridised carbon of I, II are more electronegative hence acid strength is increased.

7. I > II > III

- Oxalic acid, succinic acid, malonic acid, adipic acid (all dibasic)

8. I > II > III > IV

- NO₂ is electron attracting (-I effect)
- OH shows electron withdrawing nature at o- and m- and electron repelling at p-
- o- isomer due to intramolecular bonding in salicylate ion is stronger than m- isomer

9. II < III < I

- NO₂ is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative.

10. III < II < I

- NO₂ is electron attracting; III is more resonance stabilised than I and also than II. In I, only inductive effect is operative.
11. o- m- p- methoxy benzoic acid III < II < I —do—

12. o- m- p- amino benzoic acid I < III < II —NH₂ is electron donating.

---

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

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**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 (X) and (Y)?**

**Ans:** X is Sodium Borate and 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 $\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6$ (Hydrofluosilicic acid).

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

The brown ring test for $\text{NO}_3^-$ 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.

Hypersulfuric acid is the name given to $\text{H}_2\text{S}_2\text{O}_8$. It has peroxide linkages.

Hypersulfuric acid is a strong oxidizing agent.
KNO₂  Potassium Nitrite  BaSO₃  Barium Sulfite
Mg(NO₃)₂  Magnesium Nitrate  Na₂SO₄  Sodium Sulfate
LiClO₄  Lithium Perchlorate  Ca(BrO)₂  Calcium Hypobromite
NaClO₃  Sodium Chlorate  Al(IO₂)₃  Aluminum Iodite
RbClO₂  Rubidium Chlorite  KBrO₃  Potassium Bromate
CsClO  Cesium Hypochlorite  LiIO₄  Lithium Periodate
Calcium Nitrate  Ca(NO₃)₂  Ammonium Sulfite  (NH₄)₂SO₃
Strontium Sulfate  SrSO₄  Lithium Nitrite  LiNO₂
Potassium Hypochlorite  KClO  Lithium Perbromate  LiBrO₄
Rubidium Chlorate  RbClO₃  Calcium Iodite  Ca(IO₂)₂
Ammonium Chlorite  NH₄ClO₂  Boron Bromate  B(BrO₃)₃
Sodium Perchlorate  NaClO₄  Magnesium Hypoiodite  Mg(IO)₂
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 \( \text{A} + \text{CO}_2 + \text{H}_2\text{O} \) and compound A on reduction with Carbon gives \( \text{CO} + \text{B} \)

Identify A and B

Solution: \( \text{CuCO}_3.\text{Cu(OH)}_2 \rightarrow 2\text{CuO (A)} + \text{CO}_2 + \text{H}_2\text{O} \)

\( \text{CuO} + \text{C} \rightarrow \text{Cu (B)} + \text{CO} \)

Some examples of Complex Anions

\[ \text{K}_2\text{PtCl}_6 <\rightarrow 2\text{K}^+ + [\text{PtCl}_6]^{2-} \]

\[ \text{Na}_3\text{AlF}_6 <\rightarrow 3\text{Na}^+ + \text{AlF}_6^{3-} \]

\[ \text{K}_2\text{SiF}_6 <\rightarrow 2\text{K}^+ + \text{SiF}_6^{2-} \]
The ionization potential of Pb is higher than Sn due to poor shielding by 14f electrons present in Pb.

Selenous acid $\text{H}_2\text{SeO}_3$ (Oxidation Number of Se is $+4$)

Telluric acid $\text{H}_6\text{TeO}_6$ (Oxidation Number of Te is $+6$)
Electronegativity Values (in Pauling Scale)

Microscopic Salt is Na(NH$_4$)$_2$HPO$_4$ Sodium ammonium hydrogen phosphate

Which of the following electrolyte will be most effective in coagulation of gold sol?

(1) NaNO$_3$  (2) K$_4$Fe(CN)$_6$  (3) Na$_3$PO$_4$  (4) MgCl$_2$

Gold sol is a negatively charged coagulation which is carried out by positively charged ion furnished by electrolyte.

Coagulating power depends on the valency of cation of electrolyte. (Schulze Hardy Law) Mg$^{2+}$ ion has highest valency so MgCl$_2$ is most effective.

Organometallic compounds are Metal atoms directly linked with Carbon. So Ti(OC$_3$H$_7$)$_4$ is not an organometallic compound.
IUPAC name of Diamminetetraaquacobalt(III) chloride

As per IUPAC nomenclature, the name of the complex $\text{[Co(H}_2\text{O})_4\text{(NH}_3)\text{]Cl}_3$ is
(a) Tetraaquadiaminocobalt(III) chloride  
(b) Tetraaquadiaminocobalt(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 CuSO₄

The colour of light absorbed by an aqueous solution of CuSO₄ is
(a) orange-red     (b) blue-green     (c) yellow      (d) violet

Solution:
An aqueous solution of CuSO₄ 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.
**BaCl$_2$·5H$_2$O**  
Ba$^{2+}$ is the cation Barium, Cl$^-$ is the Chloride anion. There are five water molecules therefore the name is: **Barium Chloride Pentahydrate**

**Magnesium Perchlorate**  
Magnesium is the Mg$^{2+}$ cation, and perchlorate is the ClO$_4^-$ anion, therefore we need two perchlorate anions for each Mg cation therefore the formula is: **Mg(ClO$_4$)$_2$**

**(NH$_4$)$_2$SO$_3$**  
NH$_4^+$ is the ammonium ion, and SO$_3^{2-}$ is the sulfite anion, therefore the name is: **Ammonium Sulfite**

**Calcium Nitrate**  
Calcium is the Ca$^{2+}$ cation, and nitrate is the NO$_3^-$ anion, therefore the formula is: **Ca(NO$_3$)$_2$**
Group 1 Elements—Alkali Metals

Group 1 contains lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs) and francium (Fr).

All alkali metals contain one electron in their outermost orbitals. Due to contribution of one electron per atom towards the metallic bonding, all the elements are soft and low melting. Because of low ionization energies, the metals are strong reducing agents. The alkali metals dissolve in liquid ammonia and form a deep blue solution when dilute. The blue colour is due to the solvated electrons. The conducting ability of their ions in aqueous solution follows the order: Li⁺ < Na⁺ < K⁺ < Rb⁺ < Cs⁺.

The alkali metals are very reactive and tarnish in air to form oxide. They burn in air, Li forms Li₂O, Na forms Na₂O₂ and higher alkali metals form superoxide (MO₂⁻). The oxides of alkali metals are basic in nature. The peroxides are diamagnetic and are oxidizing agents. The superoxides are paramagnetic and are stronger oxidising agents than peroxides.

The melting points of alkali metal halides decrease in the order: MF > MCl > MBr > MI. Lithium halides have melting points less than those of sodium halides due to the more covalent character possessed by lithium salts.

The solubilities of carbonates and bicarbonates increase on descending the group.

Lother Meyer Plot of Atomic Volume vs Atomic mass

In Lother Meyer plot of atomic volume versus atomic mass, the peaks are occupied by

(a) alkali metals  (b) alkaline earth metals (c) halogens  (d) noble gases

Ans: (a)
KOBr Potassium hypobromite Structure

\[
\begin{array}{c}
\text{K}^+ \\
\text{O} \\
\text{Br}
\end{array}
\]

**Group 2 Elements—Alkaline Earth Metals**

Group 2 contains beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).

All alkaline earth metals contain two electrons in their outermost orbitals. These are soft. But compared to alkali metals, they are harder and have higher cohesive energy. Their melting points are higher than those of Group 1 elements and vary irregularly because of different structures. The atomic and ionic radii are smaller than those of the elements of Group 1. The alkaline earth metals dissolve in liquid ammonia giving bright blue colour due to the solvated electrons.

Alkaline earth metals are typically divalent and form colourless ionic compounds. When burnt in air, Be, Mg and Ca form monoxide while Sr, Ba and Ra form peroxides. When burnt in oxygen, they all form oxides which are basic in nature. The base strength of hydroxides increases on descending the group. Their solubility also increases on descending the group.

The solubilities of carbonates and sulphates decrease on descending the group. In deciding the solubilities of hydroxides, lattice energy predominates over hydration energy whereas in carbonates and sulphates, hydration energy predominates over lattice energy.
Temperature dependent Magnetic behaviour

NiCl₂[P(C₂H₅)₃]₂(C₂H₅OH)₂ exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of Ni²⁺ 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 Ni²⁺ ion, whereas no such electrons (i.e. all the 3d electrons will be paired) are present in the diamagnetic state.

The electronic configuration of ⁷⁷Ni²⁺ is

\[
\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\downarrow \\
\downarrow \\
\downarrow \\
\end{array}
\]

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.
Chlorine dioxide can be made by carefully adding sulfuric acid to potassium chlorate, $\text{KClO}_3$. It would be expected that this mixture would react to produce chloric acid, $\text{HClO}_3$, and then, because of the dehydrating power of sulfuric acid, to produce the anhydride of chloric acid, $\text{Cl}_2\text{O}_5$:

\[
\begin{align*}
\text{KClO}_3 + \text{H}_2\text{SO}_4 &\rightarrow \text{KHSO}_4 + \text{HClO}_3 \\
2\text{HClO}_4 &\rightarrow \text{H}_2\text{O} + \text{Cl}_2\text{O}_5
\end{align*}
\]

Dichlorine pentoxide, $\text{Cl}_2\text{O}_5$, however, is very unstable—its existence has never been verified. If it is formed at all, it decomposes at once to give chlorine dioxide and oxygen:

\[2\text{Cl}_2\text{O}_5 \rightarrow 4\text{ClO}_2 + \text{O}_2\]

The molecule has a triangular structure, with $\text{O}—\text{Cl}—\text{O}$ angle $118^\circ$ and bond lengths $1.49\ \text{Å}$. We assign it the structure $\overset{\cdot\cdot}{\text{Cl}}—\overset{\cdot}{\text{O}}$, with interchange of the two kinds of bonds (resonance).

![Rare Earth Elements](image)

Atomic radii of fluorine and neon in Angstrom units are respectively given by

(a) $0.72, 1.60$  
(b) $1.60, 1.60$  
(c) $0.72, 0.72$  
(d) none of these values

**Ans : ( a )**

**Atomic radius of Neon will be larger than Fluorine**
Reaction of white phosphorus with aqueous NaOH

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

(a) redox reaction, -3 and -5
(b) redox reaction, 3 and +1
(c) disproportionation reaction, -3 and +5
(d) disproportionation reaction, -3 and +3

**Solution:**

The reaction is:

\[
P_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \rightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2
\]

The salt NaH_2PO_2 undergoes the following changes on heating:

\[
+1 \quad +5 \quad -3
\]

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

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 II A 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^{12+}, 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
Bromine forms only two stable oxygen acids—hypobromous acid and bromic acid—and their salts:

HBrO, hypobromous acid
HBrO₃, bromic acid

KBrO, potassium hypobromite
KBrO₃, potassium bromate

Their preparation and properties are similar to those of the corresponding compounds of chlorine. They are somewhat weaker oxidizing agents than their chlorine analogues.

Group 13 Elements—Boron Family

Group 13 contains boron (B), aluminium (Al), gallium (Ga), indium (In), and thallium (Tl). These elements have outer electronic configuration \(\text{(ns)}^2 \text{(np)}^1\), where \(n\) varies from 2 to 6. Boron is nonmetal while others are metals. The atomic litter of Ga, In and Tl are smaller than the expected values due to d-block contraction. The atomic radius of Tl is a little larger than in due to lanthanide contraction. On descending the group, +1 oxidation state becomes more stable than +3 state due to the inert pair effect.

The very high melting point of boron is due to its icosahedral structure. In boron family, gallium has the lowest melting point. The ionization energies do not follow the expected trend of decreasing values on descending the group.

All elements burn in oxygen at high temperatures forming \(\text{M}_2\text{O}_3\). The reaction of aluminium with oxygen (known as thermite reaction) is strongly exothermic. Aluminium is amphoteric. It dissolves in dilute mineral acids and in aqueous sodium hydroxide.

The acidic character of hydroxides decreases on descending the group.

Boric acid is a very weak monobasic acid. It does not liberate hydrogen ion but accepts a hydroxyl ion. In the presence of 1,2-ethanol (glycerol, mannitol or sugars), boric acid behaves as a strong acid and can be titrated with \(\text{NaOH}\) in the presence of phenolphthalein indicator.
BF₃ is hydrolysed as follows:

\[ 4\text{BF}_3 + 12\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{BO}_3 + 12\text{HF} \]
\[ 12\text{HF} + 3\text{H}_2\text{BO}_3 \rightarrow 3\text{H}^+ + 3[\text{BF}_4]^- + 9\text{H}_2\text{O} \]

\[ 4\text{BF}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{H}_3\text{BO}_3 + 3\text{H}^+ + 3[\text{BF}_4]^- \]

Hydrolysis of BC1₃ or Bi₃ produces boric acid.

BCl₃ + 3H₂O → H₃BO₃ + 3HCl

The fluorides of Al, Ga, In and Tl are ionic while the other halides are generally covalent and exist as dimer.

The trihalides of boron are electron-deficient compounds. Due to back bonding, the electron density on boron is increased. The tendency to form π-π bond is maximum in BF₃ and falls rapidly on passing to BCl₃ to BBF₃. The increasing order of acid strength follows the order BF₃ < BCl₃ < BBF₃.

### Results of the Flame Test for Various Cations

<table>
<thead>
<tr>
<th>1 H</th>
<th>2 He</th>
<th>3 Li</th>
<th>4 Be</th>
<th>5 B</th>
<th>6 C</th>
<th>7 N</th>
<th>8 O</th>
<th>9 F</th>
<th>10 Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>11 Na</td>
<td>12 Mg (MgO)</td>
<td>13 Al</td>
<td>14 Si</td>
<td>15 P</td>
<td>16 S</td>
<td>17 Cl</td>
<td>18 Ar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19 K</td>
<td>20 Ca</td>
<td>21 Sc</td>
<td>22 Ti</td>
<td>23 V</td>
<td>24 Cr</td>
<td>25 Mn</td>
<td>26 Fe</td>
<td>27 Co</td>
<td>28 Ni</td>
</tr>
<tr>
<td>37 Rb</td>
<td>38 Sr</td>
<td>39 Y</td>
<td>40 Zr</td>
<td>41 Nb</td>
<td>42 Mo</td>
<td>43 Tc</td>
<td>44 Ru</td>
<td>45 Rh</td>
<td>46 Pd</td>
</tr>
<tr>
<td>55 Cs</td>
<td>56 Ba</td>
<td>57 La</td>
<td>58 Hf</td>
<td>59 Ta</td>
<td>60 W</td>
<td>61 Re</td>
<td>62 Os</td>
<td>63 Ir</td>
<td>64 Pt</td>
</tr>
<tr>
<td>73 Fr</td>
<td>74 Ra</td>
<td>75 Ac</td>
<td>76 Th</td>
<td>77 Pa</td>
<td>78 U</td>
<td>79 Np</td>
<td>80 Pu</td>
<td>81 Am</td>
<td>82 Cm</td>
</tr>
</tbody>
</table>
The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation number from $-1$ to $+7$, as shown in the accompanying chart.

<table>
<thead>
<tr>
<th>Oxidation Number</th>
<th>Compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>$+7$</td>
<td>$\text{HClO}_4$, $\text{Cl}_2\text{O}_7$</td>
</tr>
<tr>
<td>$+6$</td>
<td>$\text{Cl}_2\text{O}_6$</td>
</tr>
<tr>
<td>$+5$</td>
<td>$\text{HClO}_3$</td>
</tr>
<tr>
<td>$+4$</td>
<td>$\text{HBrO}_3$</td>
</tr>
<tr>
<td>$+3$</td>
<td>$\text{ClO}_2$</td>
</tr>
<tr>
<td>$+2$</td>
<td>$\text{Br}_2\text{O}$</td>
</tr>
<tr>
<td>$+1$</td>
<td>$\text{HClO}$, $\text{Cl}_2\text{O}$</td>
</tr>
<tr>
<td>$0$</td>
<td>$\text{Cl}_2$, $\text{HCl}$, $\text{Cl}^-$</td>
</tr>
<tr>
<td>$-1$</td>
<td>$\text{HF}$, $\text{F}^-$</td>
</tr>
</tbody>
</table>

Other combinations include $\text{HIO}$, $\text{HBrO}$, $\text{Br}_2\text{O}$.
The 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) O₂ and CO, respectively
(b) O₂ 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. \[ \text{Ag}_2\text{S} + 4\text{NaCN} \rightarrow 2\text{Na}[\text{Ag(CN)}_2] + \text{Na}_2\text{S} \]
The air blown removes Na₂S as Na₂S₂O₃ and Na₂SO₃ 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 O₂ (from air) and the reducing agent is Zn.
Therefore, the choice (b) is correct.
Magnitude of electron affinity (kJ/mol), s-, p-, and d-block elements

- **s block**
- **p block**
- **d block**
- **f block**

<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>
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</table>
alcohol, wood  methyl alcohol
alum  aluminum potassium sulfate
alumina  aluminum oxide
antichlor  sodium thiosulfate
antimony black  antimony trisulfide
antimony bloom  antimony trioxide
antimony glance  antimony trisulfide
antimony red (vermillion)  antimony oxysulfide
aqua ammonia  aqueous solution of ammonium hydroxide
aqua fortis  nitric acid
aqua regia  nitrohydrochloric acid
aromatic spirit of ammonia  ammonia in alcohol
arsenic glass  arsenic trioxide
azurite  mineral form of basic copper carbonate
asbestos  magnesium silicate
aspirin  acetylsalicylic acid
baking soda  sodium bicarbonate
banana oil (artificial)  isoamyl acetate
barium white  barium sulfate
benzol  benzene
bicarbonate of soda  sodium hydrogen carbonate or sodium bicarbonate
bichloride of mercury  mercuric chloride
bichrome  potassium dichromate
bitter salt  magnesium sulfate
black ash  crude form of sodium carbonate
black copper oxide  cupric oxide
black lead  graphite (carbon)
blanc-fixe  barium sulfate
bleaching powder  chlorinated lime; calcium hypochlorite
blue copperas  copper sulfate (crystals)
blue lead  lead sulfate
blue salts  nickel sulfate
blue stone  copper sulfate (crystals)
blue vitriol     copper sulfate
bluestone       copper sulfate
bone ash        crude calcium phosphate
bone black      crude animal charcoal
boracic acid    boric acid
borax           sodium borate; sodium tetraborate
bremen blue     basic copper carbonate
brimstone       sulfur
burnt alum      anhydrous potassium aluminum sulfate
burnt lime      calcium oxide
burnt ochre     ferric oxide
burnt ore       ferric oxide
brine           aqueous sodium chloride solution
butter of antimony antimony trichloride
butter of tin   anhydrous stannic chloride
butter of zinc  zinc chloride
calomel         mercury chloride; mercurous chloride
carbolic acid   phenol
carbonic acid   carbon dioxide
carbonic acid gas carbon dioxide
caustic lime    calcium hydroxide
caustic potash  potassium hydroxide
caustic soda    sodium hydroxide
chalk           calcium carbonate
Chile saltpeter sodium nitrate
Chile nitre     sodium nitrate
Chinese red     basic lead chromate
Chinese white   zinc oxide
chloride of soda sodium hypochlorite
chloride of lime calcium hypochlorite
chrome alum     chromic potassium sulfate
chrome green    chromium oxide
chrome yellow   lead (VI) chromate
chromic acid    chromium trioxide
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Formula or Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>copperas</td>
<td>ferrous sulfate</td>
</tr>
<tr>
<td>corrosive sublimate</td>
<td>mercury (II) chloride</td>
</tr>
<tr>
<td>corundum (ruby, sapphire)</td>
<td>chiefly aluminum oxide</td>
</tr>
<tr>
<td>cream of tartar</td>
<td>potassium bitartrate</td>
</tr>
<tr>
<td>crocus powder</td>
<td>ferric oxide</td>
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<tr>
<td>crystal carbonate</td>
<td>sodium carbonate</td>
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<td>dechlor</td>
<td>sodium thiophosphate</td>
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<tr>
<td>diamond</td>
<td>carbon crystal</td>
</tr>
<tr>
<td>emery powder</td>
<td>impure aluminum oxide</td>
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<tr>
<td>epsom salts</td>
<td>magnesium sulfate</td>
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<td>ethanol</td>
<td>ethyl alcohol</td>
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<td>farina</td>
<td>starch</td>
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<td>ferro prussiate</td>
<td>potassium ferricyanide</td>
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<tr>
<td>ferrum</td>
<td>iron</td>
</tr>
<tr>
<td>flores martis</td>
<td>anhydride iron (III) chloride</td>
</tr>
<tr>
<td>fluorspar</td>
<td>natural calcium fluoride</td>
</tr>
<tr>
<td>fixed white</td>
<td>barium sulfate</td>
</tr>
<tr>
<td>flowers of sulfur</td>
<td>sulfur</td>
</tr>
<tr>
<td>'flowers of' any metal</td>
<td>oxide of the metal</td>
</tr>
<tr>
<td>formalin</td>
<td>aqueous formaldehyde solution</td>
</tr>
<tr>
<td>French chalk</td>
<td>natural magnesium silicate</td>
</tr>
<tr>
<td>French vergidris</td>
<td>basic copper acetate</td>
</tr>
<tr>
<td>galena</td>
<td>natural lead sulfide</td>
</tr>
<tr>
<td>Glauber's salt</td>
<td>sodium sulfate</td>
</tr>
<tr>
<td>green verditer</td>
<td>basic copper carbonate</td>
</tr>
<tr>
<td>green vitriol</td>
<td>ferrous sulfate crystals</td>
</tr>
<tr>
<td>gypsum</td>
<td>natural calcium sulfate</td>
</tr>
<tr>
<td>hard oil</td>
<td>boiled linseed oil</td>
</tr>
<tr>
<td>heavy spar</td>
<td>barium sulfate</td>
</tr>
<tr>
<td>hydrocyanic acid</td>
<td>hydrogen cyanide</td>
</tr>
<tr>
<td>hypo (photography)</td>
<td>sodium thiosulfate solution</td>
</tr>
<tr>
<td>Indian red</td>
<td>ferric oxide</td>
</tr>
<tr>
<td>Isinglass</td>
<td>agar-agar gelatin</td>
</tr>
</tbody>
</table>
jeweler's rouge  ferric oxide
killed spirits  zinc chloride
lampblack  crude form of carbon; charcoal
laughing gas  nitrous oxide
lead peroxide  lead dioxide
lead protoxide  lead oxide
lime  calcium oxide
lime, slaked  calcium hydroxide
limewater  aqueous solution of calcium hydroxide
liquor ammonia  ammonium hydroxide solution
litharge  lead monoxide
lunar caustic  silver nitrate
liver of sulfur  sufurated potash
lye or soda lye  sodium hydroxide
magnesia  magnesium oxide
manganese black  manganese dioxide
marble  mainly calcium carbonate
mercury oxide, black  mercurous oxide
methanol  methyl alcohol
methylated spirits  methyl alcohol
milk of lime  calcium hydroxide
milk of magnesium  magnesium hydroxide
milk of sulfur  precipitated sulfur
"muriate" of a metal  chloride of the metal
muriatic acid  hydrochloric acid
natron  sodium carbonate
nitre  potassium nitrate
nordhausen acid  fuming sulfuric acid
oil of mars  deliquescent anhydrous iron (III) chloride
oil of vitriol  sulfuric acid
oil of wintergreen (artificial)  methyl salicylate
orthophosphoric acid  phosphoric acid
Paris blue  ferric ferrocyanide
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Elemental Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paris green</td>
<td>copper acetoarsenite</td>
</tr>
<tr>
<td>Paris white</td>
<td>powdered calcium carbonate</td>
</tr>
<tr>
<td>pear oil (artificial)</td>
<td>isoamyl acetate</td>
</tr>
<tr>
<td>pearl ash</td>
<td>potassium carbonate</td>
</tr>
<tr>
<td>permanent white</td>
<td>barium sulfate</td>
</tr>
<tr>
<td>plaster of Paris</td>
<td>calcium sulfate</td>
</tr>
<tr>
<td>plumbago</td>
<td>graphite</td>
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<tr>
<td>potash</td>
<td>potassium carbonate</td>
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<tr>
<td>potassa</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>precipitated chalk</td>
<td>calcium carbonate</td>
</tr>
<tr>
<td>Prussic acid</td>
<td>hydrogen cyanide</td>
</tr>
<tr>
<td>pyro</td>
<td>tetraboron pyrophosphate</td>
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<tr>
<td>quicklime</td>
<td>calcium oxide</td>
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<tr>
<td>quicksilver</td>
<td>mercury</td>
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<tr>
<td>red lead</td>
<td>lead tetraoxide</td>
</tr>
<tr>
<td>red liquor</td>
<td>aluminum acetate solution</td>
</tr>
<tr>
<td>red prussiate of potash</td>
<td>potassium ferrocyanide</td>
</tr>
<tr>
<td>red prussiate of soda</td>
<td>sodium ferrocyanide</td>
</tr>
<tr>
<td>Rochelle salt</td>
<td>potassium sodium tartrate</td>
</tr>
<tr>
<td>rock salt</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>rouge, jeweler's</td>
<td>ferric oxide</td>
</tr>
<tr>
<td>rubbing alcohol</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>sal ammoniac</td>
<td>ammonium chloride</td>
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<tr>
<td>sal soda</td>
<td>sodium carbonate</td>
</tr>
<tr>
<td>salt, table</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>salt of lemon</td>
<td>potassium binoxalate</td>
</tr>
<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>
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<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>
</tbody>
</table>
soluble glass   sodium silicate
sour water     dilute sulfuric acid
spirit of hartshorn    ammonium hydroxide solution
spirit of salt         hydrochloric acid
spirit of wine         ethyl alcohol
spirits of nitrous ether  ethyl nitrate
sugar, table        sucrose
sugar of lead        lead acetate
sulfuric ether      ethyl ether
talc or talcum       magnesium silicate
tin crystals         stannous chloride
trona                natural sodium carbonate
unslaked lime        calcium oxide
Venetian red         ferric oxide
verdigris            basic copper acetate
Vienna lime          calcium carbonate
vinegar              impure dilute acetic acid
vitamin C            ascorbic acid
vitriol              sulfuric acid
washing soda         sodium carbonate
water glass          sodium silicate
white caustic        sodium hydroxide
white lead           basic lead carbonate
white vitriol        zinc sulfate crystals
yellow prussiate of potash  potassium ferrocyanide
yellow prussiate of soda  sodium ferrocyanide
zinc vitriol         zinc sulfate
zinc white           zinc oxide

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

Colours of Compounds

$\text{Cr}_2\text{(SO}_4\text{)}_3$ - green
PbS – Black

[Fe(H2O)5NO]SO4 – brown

(CH3COO)3Fe – blood red
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)

Na₂CrO₄ + Pb(CH₃COO)₂ -> PbCrO₄ (yellow) + CH₃COONa

NaBr + AgNO₃ -> AgBr (pale yellow) + NaNO₃

AgI, AgBr, AgCl
Ammonia test for silver halides. Test tubes and the results of using concentrated ammonia to test for the presence of three silver halides. Each one of the silver halides is next to a fuller test tube that shows the result of adding concentrated ammonia. Halides are compounds containing halogens such as here, from left to right silver chloride, silver bromide and silver iodide. Adding dilute ammonia dissolves the chloride, while concentrated ammonia is needed to dissolve the bromide, but it fails to dissolve the iodide. The silver halides are themselves the results of standard tests using silver nitrate to test for the halide ions.

BrCl - pale yellow

NaI + AgNO₃ -> AgI (yellow ppt) + NaNO₃
Cu + 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
Na\textsubscript{2}S + CdCO\textsubscript{3} \rightarrow CdS (yellow) + Na\textsubscript{2}CO\textsubscript{3}

Na\textsubscript{3}[Co(NO\textsubscript{2})\textsubscript{6}] + KCl \rightarrow K\textsubscript{3}[Co(NO\textsubscript{2})\textsubscript{6}] (potassium cobalt nitrate - yellow ppt) + NaCl

AgCl, PbCl\textsubscript{2}, Hg\textsubscript{2}Cl\textsubscript{2} - white
PbCl₂ is white

Hg₂Cl₂ is white

H₂S, PbS, Bi₂S₃, CuS - black

H₂S is black
PbS is Black

Bi$_2$S$_3$ is Black

CuS - black

CdS, As$_2$S$_3$, SnS$_2$ - Yellow

CdS is Yellow
As$_2$S$_3$ is Yellow

SnS$_2$ is Yellow

Sb$_2$S$_3$ 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)₆]³⁻

6 C₆H₅OH + FeCl₃ → [Fe (OC₆H₅)₆]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 forms sodium halide on fusion with sodium metal. Sodium halide extracted with water can be easily identified by adding silver nitrate solution after acidifying with dil. HNO$_3$.

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

$$\text{Na} + \text{Cl} \rightarrow \text{NaCl}$$

$$\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$$

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 in to sodium ferrocyanide by the addition of sufficient quantity of ferrous sulphate. Ferric ions generated during the process react with ferrocyanide to form prussian blue precipitate of ferric ferrocyanide.

$$\text{Na} + \text{C} + \text{N} \rightarrow \text{NaCN}$$

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

Sodium ferrocyanide

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

Ferric ferrocyanide
FeCl₃ + K₄[Fe(CN)₆] –> Fe₄[Fe(CN)₆]₃ (prussian blue) + KCl

**Test for Sulphur:**

If sulphur is present in the organic compound, sodium fusion will convert it into sodium sulphide. Sulphide ions are readily identified using sodium nitroprusside.

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

\[
\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \rightarrow \text{Na}_4[\text{Fe(CN)}_5\text{NOS}]
\]

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 Fe³⁺ to form blood colour complex [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

\[ \text{Pentaamminechlorocobalt(III)Bromide} \]

\[ [\text{Co(NH}_3\text{)}_5\text{Cl}]^2+ \text{Pentaamminechlorocobalt(III)chloride} \]

Pentaamminesulphatocobalt(III)Bromide

Dark Yellow

Pale Yellow

Trans- \((\text{Pt(NH}_3\text{)}_2\text{Cl})^+\)

Cis- \((\text{Pt(NH}_3\text{)}_2\text{Cl})^+\)
Cis is Blue Violet  trans is green

Eta bonds - Also known as Hapticity - Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms.

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

Ferrocene - bis(η5-cyclopentadienyl)iron

Uranocene - bis(η8-1,3,5,7-cyclooctatetraene)uranium
W(CO)₃(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

\[ \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{FeCl}_3} \text{(C}_6\text{H}_5\text{O})_n\text{Fe} \]

Violet colour

\[ \text{Cu(NO}_3\text{)}_2 + \text{K}_4[\text{Fe(CN)}_6] \rightarrow \text{Cu}_2[\text{Fe(CN)}_6] \text{ (Chocolate brown)} + \text{KNO}_3 \]

\[ \text{Cd(NH}_3\text{)}_4(\text{NO}_3\text{)}_2 + \text{H}_2\text{S} \rightarrow \text{CdS} \text{ (yellow)} + \text{NH}_4\text{NO}_3 + \text{NH}_3 \]
HgCl₂ + SnCl₂ -> Hg₂Cl₂ (white) + SnCl₄

**Liebermann’s Nitroso Reaction**

\[ \text{C}_6\text{H}_5\text{OH} \rightarrow \text{Red colouration} \]

\[ \text{In H}_2\text{SO}_4 \rightarrow \text{Blue colouration} \]

\[ \text{OH} + \text{NaNO}_2 \rightarrow \text{Dil. H}_2\text{SO}_4 \rightarrow \text{N=O} \]

\[ \rightarrow \text{N—OH} \rightarrow \text{N—OH}_2 \rightarrow \text{N⁺} \]

\[ \text{Indophenol (blue)} \rightarrow \text{KOH (aq)} \rightarrow \text{Indophenol (red)} \]

SbCl₃ + H₂O -> SbOCl (white) + HCl

**SbOCl Antimony oxychloride**
Antimony Trioxide is white

Antimony Pentoxide is gray

Antimony Trichloride is white
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.

\[(\text{NH}_4)_2\text{Ce(NO}_3)_6\] + 2C₆H₅OH \rightarrow [\text{Ce(NO}_3]_4\text{(C}_6\text{H}_5\text{OH})_2\] + 2NH₄NO₃

Phenol gives blue colour with ammonia and sodium hypochlorite.

ZnCl₂ + 2NaOH –> Zn(OH)₂ (white ppt) + 2NaCl
Zn(OH)\(_2\) + NaOH → Na\(_2\)ZnO\(_2\) (soluble) + H\(_2\)O

Na\(_2\)ZnO\(_2\) + H\(_2\)S → ZnS (white) + NaOH

2KI + H\(_2\)O + O\(_3\) → 2KOH + O\(_2\) + I\(_2\)

Mn(NO\(_3\))\(_2\) + Pb\(_3\)O\(_4\) + HNO\(_3\) → HMnO\(_4\) (pink) + Pb\(_3\)O\(_4\) + H\(_2\)O
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 → NH₂HgOHgl (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. HNO₃ forming metastannic acid (H₂SnO₃).

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.

SnO₂ is an amphoteric oxide.

Stannous chloride (SnCl₂) acts as a good reducing agent. It reduces HgCl₂ to first Hg₂Cl₂ and then to Hg. It also reduces FeCl₃ to FeCl₂.

Stannic chloride (SnCl₄) is a liquid and fumes in air due to hydrolysis. It acts as a Lewis acid and dissolves in concentrated HCl forming H₂SnCl₆.

SnCl₄.5H₂O is called butter of tin.

SnS dissolves in yellow ammonium sulphide.

Aluminum Oxide is white

![Aluminum Oxide](image)

**Mercuric Iodide** HgI₂: It is a yellow solid below 400K but changes to red solid above 400K.

\[ \text{HgI}_2 \xrightarrow{400K} \text{Red} \xrightarrow{400K} \text{Yellow} \]

It dissolves in excess of KI forming K₂HgI₄;

\[ \text{HgI}_2 + 2\text{KI} \rightarrow \text{K}_2\text{HgI}_4 \]

Alkaline solution of \( \text{K}_2\text{HgI}_4 \) is called Nessler’s reagent.
Add NH₄OH excess and dimethylglyoxime to NiCl₂ then a rosy red ppt of nickel appears

\[
\text{Ni}^{2+} + 2 \text{NH}_4\text{OH} + 2 \text{OH}^- \rightarrow \text{Ni(OH)}_2 + 2 \text{NH}_4^+ + 2 \text{H}_2\text{O}
\]

CuO + B₂O₃ (Glassy bead) \rightarrow \text{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,

\[
\begin{align*}
\text{ZnSO}_4.7\text{H}_2\text{O} & \stackrel{375\text{K}}{\rightarrow} \text{ZnSO}_4.\text{H}_2\text{O} \stackrel{725\text{K}}{\rightarrow} \text{ZnSO}_4 \\
& \stackrel{1075\text{K}}{\rightarrow} \text{ZnO} + \text{SO}_2 + \text{O}_2
\end{align*}
\]
Verdigris – basic copper acetate

Verdigris

This pigment was used to the Middle Ages in paints. Until the nineteenth century this was the most vibrant shade of green available and it was used by artists widely. The color comes from copper acetate and you should know that it is highly toxic to humans.

Compounds of Mercury

(1) Mercuric oxide, \( \text{HgO} \) : It is obtained as a red solid by heating mercury in air or oxygen for a long time at 673 K

\[
2\text{Hg} + \text{O}_2 \rightarrow 2 \text{HgO} \text{ (red)} \text{ or by heating mercuric nitrate alone or in the presence of Hg}
\]

\[
\text{Heat}
\]

\[
2\text{Hg (NO}_3\text{)}_2 \rightarrow 2\text{HgO} + 4\text{NO}_2 + \text{O}_2 \text{ (red)}
\]
When $\text{NaOH}$ is added to a solution of $\text{HgCl}_2$, yellow precipitate of $\text{HgO}$ 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 $\text{HgO}$ differ only in their particle size. On heating to 673 $K$, yellow form changes to red form.

$$\text{HgO} \xrightarrow{673K} \text{HgO}\text{ red}$$

It is used in oil paints or as a mild antiseptic in ointments.

(2) Mercuric chloride, $\text{HgCl}_2$ : It is obtained by treating $\text{Hg}$ with $\text{Cl}_2$ or by heating a mixture of $\text{NaCl}$ and $\text{HgSO}_4$ in presence of small amount of $\text{MnO}_2$ (which oxidizes any $\text{Hg(I)}$ salts formed during the reaction).

Heat

$$\text{HgSO}_4 + 2\text{NaCl} \rightarrow \text{HgCl}_2 + \text{Na}_2\text{SO}_4$$

$\text{MnO}_2$
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.

\[ \text{HgCl}_2 + 2\text{NH}_3 \rightarrow \text{Hg} \ (\text{NH}_2) \ \text{Cl} + \text{NH}_4 \text{Cl} \]
dilute solution of \( \text{HgCl}_2 \) is used as an antiseptic.

(3) Mercuric iodide, \( \text{Hgl}_2 \): It is obtained when a required amount of \( \text{KI} \) solution is added to a solution of \( \text{HgCl}_2 \). \( \text{HgCl}_2 + 2\text{KI} \rightarrow \text{Hgl}_2 + 2\text{KCl} \)

Below 400 K, \( \text{Hgl}_2 \) is red but above 400 K, it turns yellow

\[ \text{Hgl}_2 \] readily dissolves in excess of \( \text{KI} \) solution to form the \( (\text{Hgl}_4)^2- \) complex ion.

\[ 2\text{K}_2[\text{Hgl}_4] + \text{NH}_3 + 3\text{KOH} \rightarrow \text{NH}_2\cdot\text{HgO} \cdot \text{Hgl} + 7\text{KCl} + 2\text{H}_2\text{O} \]

It is used in ointments for treating skin infections.

(4) Mercurous chloride, \( \text{Hg}_2\text{Cl}_2 \): It is obtained as under:

(a) \( \text{Hg}_2 \ (\text{NO}_3) \ 2\text{NaCl} \rightarrow \text{Hg}_4\text{Cl}_2 + 2\text{NaNO}_3 \)

white ppt.

Heat in an iron retort
(b) HgCl₂ + Hg → Hg₂Cl₂ (condenses on cooling)

It is purified by sublimation.

Mercurous chloride is also called calomel. It is a white powder insoluble in H₂O. On heating, it decomposes to give HgCl₂ and Hg.

Heat

Hg₂Cl₂ → HgCl₂ + Hg

It dissolves in chlorine water forming mercuric chloride.

HgCl₂ + Cl₂ → 2HgCl₂

With ammonia, it turns black due to the formation of a mixture of finely divided black Hg and mercuric amino chloride.

Hg₂Cl₂ + 2NH₃ → Hg + NH₂HgCl + NH₄Cl

(white)

It is used to prepare standard calomel electrode and as a purgative in medicine.

(5) Mercuric sulphide, HgS: The solubility product of HgS is lower than that of ZnS and hence it gets precipitated as black solid when H₂S is passed through an acidic solution of any mercury (II) salt.

HgCl₂ + H₂S → HgS + 2HCl

It is insoluble in water and HCl but dissolves in aqua regia (1 part conc. HNO₃ + 3 parts conc. HCl)

3HCl + HNO₃ → NOCl + 2H₂O + 2Cl⁻

Aqua regia Nitrosyl chloride Nacent chlorine

HgS + 2Cl⁻ → HgCl₂ + S↓

(Soluble)

On sublimation, its colour changes to red and hence it is used as a red pigment.

(6) Mercuric sulphate, HgSO₄: It is obtained when HgS is treated with conc. H₂SO₄.

Hg + 2H₂SO₄ → HgSO₄ + SO₂ + 2H₂O

It is a white solid which decomposes on heating to give mercurous sulphate.

₃HgSO₄ → Δ Hg₂SO₄ + Hg + 2SO₂ + 2O₂
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 Vermillion 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 (CO3^2-)
- Bicarbonate (HCO3-)
- Nitrite (NO2-)
- Sulphide (S^2-)
- Sulphite (SO3^2-)
- Thiosulphate (S2O3^2-)

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 (NO3-)

Those which do not react with either dilute hydrochloric acid or concentrated sulphuric acid:

- Phosphate (PO4^3-)
- Borate (B4O7^2-)
- Sulphate (SO4^2-)

A Radical is an atom, or group of atoms that behaves like a single atom. Examples: H, K, Na, Cu, Pb, simple radicals; NH4, SO2, NO2, compound radicals.
A Basic Radical is a metal, or any radical behaving like a metal. Examples: Ag, Cu, Ca, Na, and NH₄ the last so classified because it behaves like such simple radicals as Na, K, and Li.

An Acid Radical is a nonmetal, or any radical behaving like a nonmetal. Examples: Cl, Br, I, SO₂, NO₂.

An Acid is a substance containing H that may be replaced by a basic radical. When a nonmetal is combined with H only, as in HCl, HBr, H₂S, the compound is said to be a binary (i.e. composed of two elements) acid, or an 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, Fe₂Cl₆, Co(NO₃)₂, Ba(NO₃)₂, NaCl.

Take about 2 c.c. of each solution, and add HCl.

Points to be Observed Whether a precipitate is formed.

Whether the precipitate is soluble in an excess of the reagent.

* Always use dilute acids unless otherwise directed.

GROUPING THE BASES

The color of each precipitate.

Whether there is change in color of the precipitate.

Change in color of solutions.

Chemical equations.

Tabulate all results carefully in your notebook, according to the following scheme:

HCl was added to the seven solutions with the following results:

Typical of Gr. I AgNO₃ + HCl = AgCl w. pp. + I IN ( ) 8 .
Typical of Gr. II A Cu(NO₃)₂ + II Cl = No change.
Typical of Gr. II B AsCl₃ + HCl = No change.
Typical of Gr. III Fe₂ Cl₆ + HCl = No change.
Typical of Gr. IV Co(NO₃)₂ + IIICl = No change.
Typical of Gr. V: $\text{Ba(NO}_3\text{)}_2 + \text{HCl} = \text{No change.}$
Typical of Gr. VI: $\text{NaCl} + \text{HCl} = \text{No change.}$

### 1) Anions which react with dilute hydrochloric acid

<table>
<thead>
<tr>
<th>Carbonates ($\text{CO}_3^{2-}$)</th>
<th>Bicarbonates ($\text{HCO}_3^-$)</th>
<th>Nitrites ($\text{NO}_2^-$)</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 nitrites are water soluble except that of silver.</td>
</tr>
<tr>
<td><strong>Solid salt + dil. HCl</strong></td>
<td>Effervescence and a colourless gas is evolved. Carbon dioxide ($\text{CO}_2$). $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$</td>
<td>Effervescence and a colourless gas is evolved. Carbon dioxide ($\text{CO}_2$). $\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2$</td>
</tr>
</tbody>
</table>

### To differentiate between $\text{CO}_3^{2-}$ and $\text{HCO}_3^-$

<table>
<thead>
<tr>
<th>Carbone</th>
<th>Bicarbonate</th>
<th>Nitrites</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1) Salt solution + magnesium sulphate solution</strong></td>
<td>White precipitate of magnesium carbonate. $\text{Na}_2\text{CO}_3 + \text{MgSO}_4 \rightarrow \text{MgCO}_3\cdot\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$</td>
<td>No ppt. in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained: $2\text{NaHCO}_3\cdot\text{H}_2\text{O} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ $\text{Mg(HCO}_3\text{)}_2 \rightarrow \text{MgCO}_3\cdot\text{CO}_2 + \text{H}_2\text{O}$ No ppt. in the cold, but on heating a reddish brown ppt of mercuric carbonate is obtained: $2\text{NaHCO}_3 + \text{HgCl}_2 \rightarrow 2\text{NaCl} + \text{HgCO}_3\cdot\text{H}_2\text{O}$ $\text{Hg(HCO}_3\text{)}_2 \rightarrow \text{HgCO}_3\cdot\text{CO}_2 + \text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
Is \( \text{HgCO}_3 \) reddish Brown?

<table>
<thead>
<tr>
<th>Sulphites ((\text{SO}_3^{2-}))</th>
<th>Thioureas ((\text{S}_2\text{O}_3^{2-}))</th>
<th>Sulphides ((\text{S}_2^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>All sulphonates are slightly soluble in water except the amyl and stearic acid.</td>
<td>Sodium thiosulphate is readily soluble in water, other thioureas are slightly soluble.</td>
<td>All sulphides, except those of alkali, alkaline earth metals and the ammonium ion, are slightly soluble in water.</td>
</tr>
</tbody>
</table>

**Solid salt + dilute HCl**

Sulphur dioxide gas \((\text{SO}_2)\) is evolved, which is recognized 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.

\[
3\text{SO}_2 + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 \rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}
\]

**K_2SO_4 is white**

Cr_2(SO_4)_3 is green
**Redox Reactions**

<table>
<thead>
<tr>
<th>Sulphites</th>
<th>Thiouosphates</th>
<th>Sulphites</th>
</tr>
</thead>
<tbody>
<tr>
<td>A white precipitate forms (silver sulphide Ag₂SO₄) which dissolves in excess of sulphite due to the formation of soluble complex.</td>
<td>A white precipitate forms (silver thiouosphate Ag₂S₂O₆) which is soluble in excess of the thiouosphate due to the formation of complex, which is unstable it changes to yellow; brown and finally to black Ag₂(S).</td>
<td>A black precipitate of silver sulphide, (Ag₂S) is formed.</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_3 + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{SO}_4 + 2\text{NaNO}_3 ) (BRS)</td>
<td>( \text{Na}_2\text{S}_2\text{O}_7 + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{S}_2\text{O}_7 + 2\text{NaNO}_3 ) White ppt.</td>
<td>( \text{Na}_2\text{S} + 2\text{AgNO}_3 \rightarrow \text{Ag}_2\text{S} + 2\text{NaNO}_3 ) Black ppt.</td>
</tr>
<tr>
<td>( \text{Ag}_2\text{SO}_4 + \text{Na}_2\text{SO}_3 \rightarrow 2\text{Na}[\text{Ag}_2\text{S}] ) Soluble complex.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2) Salt solution + lead acetate solution ( \text{Pb(CH}_3\text{COO)}_2 ) A white ppt of lead sulphate (( \text{PbSO}_4 )) is formed.</td>
<td>A white ppt of lead thiouosphate (( \text{PbS}_2\text{O}_6 )) is formed, the ppt turns black (( \text{PbS} )) on boiling.</td>
<td>A black ppt of lead sulphate. (( \text{PbSO}_4 )) is formed.</td>
</tr>
<tr>
<td>( \text{Na}_2\text{SO}_3 + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbSO}_4 \cdot \text{H}_2\text{O} + 2\text{CH}_3\text{COONa} ) BRS</td>
<td>( \text{Na}_2\text{S}_2\text{O}_7 + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbS}_2\text{O}_7 \cdot 2\text{CH}_3\text{COONa} ) White ppt.</td>
<td>( \text{Na}_2\text{S} + \text{Pb}(\text{CH}_3\text{COO})_2 \rightarrow \text{PbS} + 2\text{CH}_3\text{COONa} ) Black ppt.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>* Salt solution + drops of acidified solution of ( \text{K}_2\text{MnO}_4 ). The purple colour of the permanganate will disappear. The sulphite reduces the permanganate ion ( \text{MnO}_4^{2-} ) which is almost colourless.</td>
<td>* Salt solution + sodium nitroprusside solution : A violet colour is formed.</td>
<td></td>
</tr>
<tr>
<td>( 5\text{Na}_2\text{SO}_3 + 2\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow 5\text{Na}_2\text{SO}_4 + 2\text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 3\text{H}_2\text{O} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sulphites</th>
<th>Thiouosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>The brown colour of the iodine solution disappears. ( \text{Na}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{HI} )</td>
<td>The brown colour of the iodine solution disappears, because the iodine is reduced to the iodide ion, which is colourless. At the same time, the thiouosphate is oxidized to tetraiodochrome: ( 2\text{Na}_2\text{S}_2\text{O}_7 + \text{I}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_5 + 2\text{NaI} )</td>
</tr>
</tbody>
</table>
### 2) Anions which react with concentrated sulphuric acid

**Note:** Do these tests in fuming rooms 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>Nitrates (NO₃⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>All chlorides are water soluble except the chlorides of silver, mercurous and cuprous.</td>
<td>Bromides resemble chlorides in their solubility.</td>
<td>Iodides resemble chlorides and bromides in their solubility. However, bisulfite iodide is insoluble.</td>
<td>All nitrates are soluble in water except some basic nitrates.</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 concentrated 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: \( HCl \rightarrow NH₃ + HNO₂ \)

- **Reddish fumes evolve and the solution turns orange due to liberation of bromine (Br₂).**
  
  \[ 2NaBr + H₂SO₄ → 2HBr + Na₂SO₄ \]
  
  **2HBr + H₂SO₄ → 2H₂O + SO₂ + Br₂**

- **If a small piece of copper metal and drops of water are added, dense brown fumes of nitrogen dioxide (NO₂) will be given off.**

  **If no result, heat carefully.**

  \[ 2KNO₃ + H₂SO₄ → K₂SO₄ + 2HNO₂ \]
  
  \[ 4HNO₂ + Cu → Cu(NO₃)₂ + 2H₂O + 2NO₂ \]

#### Confirmation tests:

1. **Salt solution + silver nitrate (AgNO₃).**

   - A dense white ppt. of silver chloride (AgCl) slowly turns a violet colour when exposed to bright light.
   - \( NaCl + AgNO₃ \rightarrow AgCl + NaNO₃ \)

2. **Salt solution + lead acetate (Pb(CH₃COO)₂).**

   - A white precipitate of lead chloride (PbCl₂) appears which is soluble in hot water and precipitates on cooling.
   - \( 2NaCl + Pb(CH₃COO)₂ → PbCl₂ + 2NaCH₃COO \)

   **Salt solution + Mercuric chloride:**

   - A reddish precipitate of mercuric iodide is formed which dissolves in excess of KI.
   - \( HgCl₂ + 2KI → HgI₂ + 2KCl \)

   **Salt solution + Copper sulphate:**

   - A brown ppt. of copper(I) iodide CuI and iodine I₂.
   - \( 4KI + CuSO₄ → CuI₂ + 2K₂SO₄ + I₂ \)
AgCl is white

Cul Cuprous Iodide

Brown Ring Test
### 3) Anions which do not react with acids:

<table>
<thead>
<tr>
<th>Phosphates (H₂PO₄⁻, HPO₄²⁻, PO₄³⁻)</th>
<th>Borates (BO₄³⁻, BO₂⁻, B₃O₅⁻)</th>
<th>Sulphates (SO₄²⁻)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Most phosphates are insoluble in water except those of ammonium and alkal metals.</td>
<td>Ammonium and alkal 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 metal e.g. calcium, strontium, barium and lead.</td>
</tr>
<tr>
<td><strong>Salt solution + Barium chloride solution (BaCl₂)</strong></td>
<td>A white precipitate of barium phosphate (Ba₃(PO₄)₂) is produced, soluble in dilute acids e.g. HNO₃ or HCl and insoluble in excess of barium chloride. ( \text{Na}_2\text{HPO}_4 + \text{BaCl}_2 \rightarrow \text{Ba}_3(\text{PO}_4)_2 + 2\text{NaCl} )</td>
<td>A white precipitate of barium borate from concentrated solutions ( \text{Ba}(\text{BO}<em>3)</em>{2} \cdot \text{H}_2\text{O} ) is produced, soluble in dilute acids and in excess of barium chloride. ( \text{Na}_2\text{H}_2\text{BO}_3 + 3\text{H}_2\text{O} + \text{BaCl}_2 \rightarrow \text{Ba}(\text{BO}<em>3)</em>{2} \cdot \text{H}_2\text{O} + 2\text{NaCl} )</td>
</tr>
<tr>
<td><strong>Confirmation tests:</strong></td>
<td></td>
<td>A white precipitate of barium sulphate ( \text{BaSO}_4 ) is formed which is insoluble in dilute acids and in excess of barium chloride. ( \text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{NaCl} )</td>
</tr>
<tr>
<td>1) Salt solution + silver nitrate ( (\text{AgNO}_3) )</td>
<td>A yellow precipitate of silver phosphate ( (\text{Ag}_3\text{PO}_4) ) is formed, which is readily soluble in dil. HNO₃ and ammonia.</td>
<td>A white precipitate of silver borate ( (\text{Ag}_2\text{BO}_3) ) is formed, which is also a brown ppt. formed with diluted solution. ( \text{Na}_2\text{H}_2\text{BO}_3 + 3\text{H}_2\text{O} + 2\text{AgNO}_3 \rightarrow 2\text{Ag}_2\text{BO}_3 + 2\text{H}_2\text{BO}_3 + 2\text{NaNO}_3 ) ( 2\text{AgBO}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ag}_2\text{O} + 2\text{H}_2\text{BO}_3 )</td>
</tr>
</tbody>
</table>

**BaSO₄ is white**
For phosphates:

0.5 ml of salt solution + 4 ml of ammonium molybdate solution + 0.5 ml of conc. HNO₃

Form a canary yellow precipitate of ammonium phosphomolybdate (NH₄)₂(H₂MoO₄)₂·H₂O in the cold or by gentle warming.

(Notes: the volume needed in this test).

For sulphates:

Sulfate solution – lead acetate:

A white precipitate of lead sulphate is formed, which is readily soluble in hot concentrated ammonium acetate or conc. H₂SO₄.

K₂SO₄ + Pb(CH₃COO)₂ → PbSO₄ + 2CH₃COOK

PbSO₄ + H₂SO₄ → Pb(H₂SO₄)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 odourless gas is evolved.</td>
<td>The gas is CO₂, The anion is carbonate or bicarbonate.</td>
</tr>
<tr>
<td>Pungent brown fumes are evolved.</td>
<td>The gas is NO₂, The anion is Nitrite.</td>
</tr>
<tr>
<td>Colourless gas with Pungent odour, which turns an acidified dichromate paper green, is evolved.</td>
<td>The gas is SO₂ and the green colour is Cr₂(SO₄)₃, The anion is sulphite.</td>
</tr>
<tr>
<td>Colourless gas with pungent odour, which turns an acidified potassium dichromate paper green, is evolved, and a yellow precipitate of sulphur appears.</td>
<td>The gas is SO₃, the ppt. is S and the green colour is Cr₂(SO₄)₃, The anion is thiosulphate.</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 H₂S, and the black colour is PbS. The anion is sulphide.</td>
</tr>
</tbody>
</table>

**To differentiate between carbonate and bicarbonate**

1) **Salt solution - magnesium sulphate solution:**
   - **For carbonate:** White precipitate of magnesium carbonate (MgCO₃).
   - **For bicarbonate:** No ppt. in the cold, on heating, a white ppt. of magnesium carbonate is obtained.

2) **Solid salt + conc. H₂SO₄:**
   - **Observation:** Effervescence with the evolution of a colourless gas which forms white fumes with NH₃OH.
   - **Reddish fumes evolve and the solution turns orange.**
   - **Violet fumes are evolved, and a brown or black precipitate is formed in the test tube.**
   - **If a small piece of copper metal and drops of water are added, dense brown fumes will be given off.**
   - **No results, heat carefully.**
   - **The salt does not react with conc. H₂SO₄.**

   - **Results:** The gas is HCl and the white fumes are NH₃Cl, The anion is chloride.
   - The gas is Br₂, The anion is Bromide.
   - The gas is I₂, The anion is iodide.
   - The gas is NO₂, The anion is Nitrate.
   - The anion is not from group 1. (Go to step 2).

3) **Salt solution - BaCl₂:**
   - **Observation:** A white precipitate is produced, soluble in dilute acids e.g. HNO₃ or HCl and insoluble in excess of barium chloride.
   - A white ppt. from concentrated solutions is produced, soluble in dilute acids and in excess of barium chloride.
   - A white precipitate is formed which is insoluble in dilute acids and in excess of barium chloride.

   - **Results:** The white precipitate is barium phosphate (BaHPO₄), The anion is phosphate.
   - The white ppt. is barium borate Ba₃(BO₃)₂, The anion is Borate.
   - A white precipitate is barium sulphate (BaSO₄), 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><strong>Observation</strong></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><strong>Results</strong></td>
<td>The yellow ppt. is silver phosphate (Ag₃PO₄). The anion is phosphate.</td>
<td>The white ppt. is silver borate (Ag₂BO₄). The anion is borate.</td>
<td>The white ppt. is silver sulphate (Ag₂SO₄). The anion is sulphate.</td>
</tr>
</tbody>
</table>

Which one of the following is the smallest in size?
(a) N³⁻   
(b) O²⁻   
(c) F⁻   
(d) Na⁺

Ans: (d)

Na⁺ will have the smallest size

**Group 14 Elements—Carbon Family**

Group 14 contains carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). Their outer electronic configuration is (n-1)s² (n-2)p³, where n varies from 2 to 6. The metallic character of elements increases on descending the group; C and Si are nonmetals, Ge is a nonmetal but also has some metallic characteristics, and Sn and Pb are metals. The melting points decrease on descending the group, with the exception of Pb whose melting point is slightly higher than that of Sn. Carbon has extremely high melting point. This is due to the stronger C—C bonds in the network of carbon atoms.

The ionization energies decrease from C to Si, but then change in an irregular way because of the effects of filling d and f sub-shells.

Carbon forms single, double and triple bonds with carbon itself and with other elements. The tendency to form multiple bond by other elements is rare. However, silicon can form double bond due to back bonding in which the lone pair in p orbitals of an atom is extended to an empty orbital of Si. One of the examples of back bonding is trisilamidine, N(SiH₃)₁₂.

The chemical reactivity of elements decreases down the group. The inert pair effect becomes increasingly effective on descending the group.

The stability of +4 oxidation state decreases while that of the +2 oxidation state increases on descending the group. C, Si and Ge are unaffected by dilute acids. Sn and Pb react with dilute nitric acid.

4Sn + 10HNO₃ → 4Sn(NO₃)₂ + NH₄NO₃ + 3H₂O
3Pb + 8HNO₃ → 3Pb(NO₃)₂ + 2NO + 4H₂O

C is not affected by alkalis, Si reacts forming silicates while Sn and Pb form stannite, [Sn(OH)₄]²⁻, and plumbate, [Pb(OH)₄]²⁻, respectively.
The size of Zr is very similar to Hf due to Lanthanide contraction
The size of Nb is very similar to Tantalum (Ta) due to Lanthanide contraction.

Oxygen Family

Group 16 Elements—Oxygen Family

Group 16 contains oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their electronic configuration is \((ns)^2 (np)^4\), where \(n\) varies from 2 to 6.

The metallic character of these elements increases on descending the group; O and S are nonmetallic, Se and Te are weaker nonmetallic and Po is metallic.

Electron affinity of sulphur is larger than that of oxygen, this is due to the more repulsion experienced by the incoming electron from the smaller, more compact electronic cloud of oxygen atom.

Oxygen is diatomic with two unpaired electrons. Sulphur exists in two allotropic forms—rhombic and monoclinic sulphur. Rhombic sulphur is stable at room temperature while monoclinic sulphur is stable above 369 K. Selenium exists in six allotropic forms. Tellurium has only one crystalline form and polonium has two allotropic forms (cubic and rhombohedral).

Ozone is another allotrope of oxygen. It is very reactive. It is formed in the upper layer of atmosphere (about 20 km from the earth) by the action of ultraviolet radiation on oxygen. Ozone is a strong oxidizing agent. In organic chemistry, ozone is used to locate the carbon-carbon double and triple bonds. The ozone molecule is angular with bond angle about 117° and bond length 127.8 pm.

The melting and boiling points of hydrogen compounds of elements of Group 16 follow the order \(H_2O > H_2S < H_2Se < H_2Te\). The exceptional high values of \(H_2O\) is due to hydrogen bonding.

\(H_2O\) is a strong oxidizing agent. With stronger oxidizing agents such as \(KMnO_4\), \(KIO_5\), \(O_3\), hydrogen peroxide acts as a reducing agent.

Amongst Co, Ni, Cu and Zn; Zn has maximum size.

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CBSE Standard 12 Chemistry Survival Guide - Redox Reactions by Prof. Subhashish Chattopadhyay
SKMClasses Bangalore Useful for IIT-JEE, I.Sc. PU-II, Boards, IGCSE IB AP-Chemistry and other exams
The monohydrogen and dihydrogen phosphates have very important uses in real-world analytical laboratories. Mostly, these uses center around the control of the acidity of solutions. Solutions of these partially neutralized acids resist changes in acidity level even when strong acids or bases are added. For this reason they are called “buffer solutions.” For example, dilute solutions of potassium dihydrogen phosphate, \( \text{KH}_2\text{PO}_4 \), will maintain an acidity level near the neutral point between acids and bases. Solutions of sodium monohydrogen, \( \text{Na}_2\text{HPO}_4 \), will maintain an acidity level that is considerably below the neutral point, which means that base-like properties predominate.

The size of Mo is very similar to W due to
(a) the difference of atomic number by one
(b) the contraction in size in the first transition series elements
(c) lanthanide contraction
(d) actinide contraction

Mo belongs to 5\(^{th}\) period and 6\(^{th}\) group. W belongs to 6\(^{th}\) period and 6\(^{th}\) group. Their sizes are more or less identical due to intervening lanthanides.

The solution from which excess \( \text{Br}_2 \) is removed by heating must be acidic, otherwise a portion of Br, shall be fixed in the form of potassium hypobromite (\( \text{KBrO} \)).

With alcalies it forms a hypobromite in cold dilute solution and a bromate in a hot solution

\[
2\text{KOH} + \text{Br}_2 \rightarrow \text{KBr} + \text{KBrO} + \text{H}_2\text{O}
\]

Cold and dilute          Potassium hypobromite

\[
6\text{KOH} + 3\text{Br}_2 \rightarrow 5\text{KBr} + \text{KBrO}_3 + 3\text{H}_2\text{O}
\]

Hot and concentrated          Potassium bromate

The first compound of xenon, \( \text{XePtF}_6 \), was discovered in 1962. Xenon reacts with fluorine to give three compounds they are \( \text{XeF}_2 \), \( \text{XeF}_4 \) and \( \text{XeF}_6 \). Other known compounds of xenon are \( \text{XeO}_3 \), \( \text{XeO}_4 \), \( \text{XeOF}_2 \), \( \text{XeO}_2\text{F}_2 \), etc. No compound of He, Ne and Ar has been prepared.
Many salts of ternary acids are used in medicine. Lithium carbonate, Li$_2$CO$_3$, has been used successfully to combat severe jet lag. Lithium carbonate is also useful in the treatment of mania, depression, alcoholism, and schizophrenia. Magnesium sulfate, MgSO$_4$, sometimes helps to prevent convulsions during pregnancy and to reduce the solubility of toxic barium sulfate in internally administered preparations consumed before gastrointestinal X-ray films are taken.

Other salts of ternary acids that you may find in your home include potassium chlorate, KClO$_3$, in matches as an oxidizing agent and oxygen source; sodium hypochlorite, NaClO, in bleaches and mildew removers; and ammonium carbonate, (NH$_4$)$_2$CO$_3$, which is the primary ingredient in smelling salts.

The tips of “strike anywhere” matches contain tetraphosphorus trisulfide, red phosphorus, and potassium chlorate. Friction converts kinetic energy into heat, which initiates a spontaneous reaction.

$$P_4S_3(s) + 8O_2 \rightarrow P_4O_{10}(s) + 3SO_2(g)$$

The thermal decomposition of KClO$_3$ provides additional oxygen for this reaction.

**Group 17 Elements—Halogen Family**

Group 17 contains fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Their outer electron configuration is $(n-1)d^5(ns)^x$, where $n$ varies from 2 to 6. The trends in this group are as follows.

- Covalent and ionic radii—\textit{increase down the group}.
- Electronegativity and ionization energy—\textit{decrease down the group}.
- Electron affinity—\textit{increases from F to Cl} followed by a \textit{decrease}.
- Melting and boiling points—\textit{increase down the group}.
- Bond enthalpy $\Delta H(X-X)$—\textit{increases from F to Cl} followed by a \textit{decrease}.
- Oxidizing ability—\textit{decreases down the group}.
- Halogens are very reactive and do not occur in free state. Fluorine is most electronegative atom, there exists hydrogen bonding in gaseous HF.
- HF is a weak acid and HCl, HBr and HI behave as strong acids. In the glacial acetic acid medium, the acid strength follows the order HI > HBr > HCl > HF.
Halogenoacids—hypohalous acids (HOX), halous acids (HXL), halic acid (HXO₂), and perhalic acid (HXO₃). The acid strength follows the order HXO₄ > HXO₃ > HXO₂ > HXO. Fluorine forms only hypofluorous acid (HOF).

Halogens also form interhalogen compounds AX₁, AX₂, AX₃, and AX₄. The compounds AX₁ and AX₂ are formed where the electronegativity is not very large. The compounds AX₃ and AX₄ are formed by large Br and I atoms surrounded by small atom F. The molecule AX₃ is T-shaped with two lone pair of electrons at the equilateral positions. The orientations of five pair of electrons around the atom A is trigonal bipyramidal.

The six pairs of electrons around atom A in AX₄ acquire octahedral orientation. The seven pairs of electrons around atom A in AX₅ acquire pentagonal bipyramidal orientation.

Halogens are nonmetallic and have high electron affinity. The nonmetallic character decreases down the group and iodine shows some metallic character. With metals, they form ionic compounds by accepting one electron and with nonmetals covalent compounds are formed by sharing an electron.

All halogens exhibit −1 oxidation state. Except fluorine, rest of the halogens also exhibit 1, +3, +5 and +7 oxidation states. Fluorine is the most electronegative and thus there exists hydrogen bonding in HF with the result that it has exceptionally high melting and boiling points as compared to those of HCl, HBr and HI.

Because of high reactivity, halogens do not exist in the free state.

## Oxides of Chlorine

Chlorine reacts with oxygen to form a number of oxides like Cl₂O, ClO₂, Cl₂O₃, and Cl₂O₄. All these oxides are highly reactive and very unstable.

### Dichloro Oxide (Cl₂O)

#### Preparation

- It can be prepared by passing dry chlorine over a fresh precipitate of yellow mercuric oxide as follows:

\[ \text{HgO} + 2\text{Cl}_2 \text{ (dry)} \rightarrow \text{HgCl}_2 + \text{Cl}_2 \text{O} \]

#### Physiochemical Properties

1. **It is a brownish yellow gas with a penetrating odour.**
2. **It can be condensed to an orange coloured liquid in a freezing mixture (boiling point = 275 K).**
3. **Decomposition:** It decomposes on heating or in sunlight as follows:

\[ 2\text{Cl}_2\text{O} \rightarrow 2\text{Cl}_2 + \text{O}_2 \]
Group 18 Elements—Noble Gases

The group 18 contains helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). Their outer electronic configurations is \((n\pi)^2\) \((n\pi)^6\) with the exception of the electronic configuration of He which is \((1s)^2\). All elements exist as monatomic gas.

Xenon forms a number of fluorides—XeF₂, XeF₄ and XeF₆. The other compounds are XeO₂, XeOF₄, XeO₃F₂, XeOF₄ and \([\text{XeO}_4]^2^-\)

4. **With Water:** It dissolves in water forming a golden yellow solution of hypochlorous acid (HClO) i.e., it is an anhydride of hypochlorous acid.

\[ \text{Cl}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HClO} \]

5. **Oxidizing Action:** Being a strong oxidizing agent, it oxidizes HCl to Cl₂ as follows:

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

6. **With Ammonia:** Its reacts with ammonia with an explosion as follows:

\[ 3\text{Cl}_2\text{O} + 10\text{NH}_3 \rightarrow 2\text{N}_2 + 6\text{NH}_3\text{Cl} + 3\text{H}_2\text{O} \]

**Structure** It has angular or V-shaped structure.

Here oxygen atom is sp³ hybridized. Cl – O – Cl bond angle is 110.9° and O – Cl bond length is 1.71 Å
**Chlorine Dioxide (ClO₂)**

**Preparation**

1. Pure ClO₂ can be obtained by passing dry Cl₂ over AgClO₃ heated to 363 K as follows:

   
   \[ 2\text{AgClO}_3 + \text{Cl}_2 \text{(dry)} \rightarrow 2\text{AgCl} + 2\text{ClO}_2 + \text{O}_2 \]

2. It can also be prepared by the action of Cl₂ on sodium chlorite as follows:

   \[ 2\text{NaClO}_2 + \text{Cl}_2 \rightarrow 2\text{NaCl} + 2\text{ClO}_2 \]

**Physiochemical Properties**

1. It can be condensed by cooling to a coloured liquid (boiling point 284 K).
2. It is a powerful oxidizing and bleaching agent.
3. Decomposition: It explodes and decomposes to Cl₂ and O₂ by an electric spark.
4. With H₂O: It dissolves in water to give a mixture of chlorous acid and chloric acid.
From the X-ray diffraction of nitric oxide it is found to be present in a dimeric orientation. It has a resonating dimeric structure.

Structure of (NO)₂

Group 12 - Electrode potential of Mercury is +ve, 1st ionisation Energy higher than Cd

5. With Alkalis: It gives a mixture of chlorite and chlorate with alkalis as follows:

\[ 2\text{ClO}_2 + \text{H}_2\text{O} \rightarrow \text{HClO}_2 + \text{HClO}_3 \]

Structure: It is an odd electron molecule and paramagnetic in nature. It is an angular molecule with sp³ hybridization of chlorine. Here O – Cl – O bond angle is 118° and Cl – O bond length is 1.47 Å.
Dichlorine Hexoxide (Cl₂O₆)

Preparation
1. It can be prepared by mixing chlorine dioxide with ozonized air at 273 K.
   \[2\text{ClO}_2 + 2\text{O}_3 \rightarrow \text{Cl}_2\text{O}_6 + 2\text{O}_2\]

Physiochemical Properties
1. It is a dark red unstable liquid.
2. Decomposition: It is quite unstable and decomposes into ClO₂ and O₂.
3. It is a strong oxidizing agent.
4. With Water: It reacts with water to give chloric acid and perchloric acids.
   \[\text{Cl}_2\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{HClO}_3 + \text{HClO}_4\]
5. With HF: It gives HClO₄ and chloryl fluoride with HF as follows:
   \[\text{Cl}_2\text{O}_6 + \text{HF} \rightarrow \text{HClO}_4 + \text{ClO}_2\text{F}\]
6. With Alkalis: It reacts with alkalis to give chlorates and perchlorates.

5. With HF: It gives HClO₄ and chloryl fluoride with HF as follows:
   \[\text{Cl}_2\text{O}_6 + \text{HF} \rightarrow \text{HClO}_4 + \text{ClO}_2\text{F}\]
6. With Alkalis: It reacts with alkalis to give chlorates and perchlorates.
\[ \text{Cl}_2\text{O}_6 + 2\text{KOH} \rightarrow \text{KClO}_3 + \text{KClO}_4 + \text{H}_2\text{O} \]

**Structure:** In liquid state it is a diamagnetic molecule with uncertain structure which is not known so far.

\[ 2\text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_6 \]

In the vapour state it exists as \( \text{ClO}_3 \) molecule which has odd number of electrons and hence paramagnetic. In solid state it has \( \text{ClO}_4^- \), \( \text{ClO}_2^- \) ions. Although the exact structure is unknown for it yet the following structure having Cl – Cl linkage is proposed for it in which each chlorine atom is \( \text{sp}^3 \) hybridized.

![Structure of Cl₂O₆](image)

**Chlorine Heptoxide \( (\text{Cl}_2\text{O}_7) \)**

**Preparation**

It can be formed by the dehydration of perchloric acid with \( \text{P}_2\text{O}_5 \) at 263 K.

\[ 2\text{HClO}_4 \xrightarrow{\text{P}_2\text{O}_5} \text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \]

**Physiochemical Properties**

1. It is a colourless oily explosive liquid.
2. With Water: It slowly dissolves in water to form perchloric acid i.e., it is an anhydride of perchloric acid.

\[ \text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HClO}_4 \]

**Structure:** In it two \( \text{ClO}_4^- \) units are joint through oxygen at an angle of 118.5° or 118°36’ giving tetrahedral look. Here Cl – O₅ bond length is 1.72 Å while Cl – O₂ is 1.42 Å.
### (1) Oxoacids of Nitrogen

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<tr>
<th>Oxoacid</th>
<th>Formula</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyponitrous acid</td>
<td>$\text{H}_2\text{N}_2\text{O}_2$</td>
<td>+1</td>
</tr>
<tr>
<td>Hydronitrous acid</td>
<td>$\text{H}_2\text{NO}_2$</td>
<td>+2</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>$\text{HNO}_2$</td>
<td>+3</td>
</tr>
<tr>
<td>Hyponitric acid</td>
<td>$\text{H}_2\text{N}_2\text{O}_3$</td>
<td>+5</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>$\text{HNO}_3$</td>
<td>+5</td>
</tr>
<tr>
<td>Pernitric acid</td>
<td>$\text{HNO}_4$</td>
<td>+7</td>
</tr>
</tbody>
</table>

### (2) Oxoacids of Phosphorous

<table>
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<tr>
<th>Oxoacid</th>
<th>Formula</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hypophosphorous acid</td>
<td>$\text{H}_3\text{PO}_2$</td>
<td>+1</td>
</tr>
<tr>
<td>Phosphorous acid</td>
<td>$\text{H}_3\text{PO}_3$</td>
<td>+3</td>
</tr>
<tr>
<td>Hypophosphoric acid</td>
<td>$\text{H}_3\text{P}_2\text{O}_6$</td>
<td>+4</td>
</tr>
<tr>
<td>Orthophosphoric acid</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>+5</td>
</tr>
<tr>
<td>Pyrophosphoric acid</td>
<td>$\text{H}_4\text{P}_2\text{O}_7$</td>
<td>+5</td>
</tr>
<tr>
<td>Metaphosphoric acid</td>
<td>$\text{HPO}_3$</td>
<td>+5</td>
</tr>
<tr>
<td>Peroxophosphoric acid</td>
<td>$\text{H}_3\text{PO}_5$ or $\text{H}_4\text{P}_2\text{O}_8$</td>
<td>+7 or +6</td>
</tr>
<tr>
<td>Tripolyphosphoric acid</td>
<td>$\text{H}_3\text{P}<em>3\text{O}</em>{10}$</td>
<td>+5</td>
</tr>
<tr>
<td>Tetra polyphosphoric acid</td>
<td>$\text{H}_6\text{P}<em>4\text{O}</em>{13}$</td>
<td>+5</td>
</tr>
</tbody>
</table>
Oxy-acids of Chlorine

Chlorine forms all the four oxy-acids, which are hypochlorous acid (HClO), chlorous acid (HClO₂), chloric acid (HClO₃) and perchloric acid (HClO₄). It may be noted that Cl-atom is in +1, +3, +5 and +7 oxidation state respectively in these acids.

\[
\text{HClO, HClO}_2, \text{HClO}_3, \text{HClO}_4
\]

The acidic strength of these acids increases as follows:

\[
\text{HClO} < \text{HClO}_2 < \text{HClO}_3 < \text{HClO}_4
\]

Hypochlorous Acid (HClO)

Preparation

1. From Chlorine

(i) It can be prepared by passing Cl₂ into H₂O or into a suspension of CaCO₃ in water or into an aqueous solution of potassium hypochlorite (KClO) or bleaching powder (CaOCl₂).

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HClO}
\]

\[
\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{Cl}^- + \text{ClO}^- + 2\text{H}^+
\]
Co-ordination Complexes

2. It can be prepared by the action of atmospheric CO$_2$ on sodium hypochlorite, NaOCl as shown.

NaOCl + CO$_2$ + H$_2$O $\rightarrow$ NaHCO$_3$ + HClO

3. From bleaching powder Hypochlorous acid can be prepared by distilling the aqueous solution of bleaching powder (CaOCl$_2$) with a calculated quantity of 5 per cent HNO$_3$ or by passing CO$_2$ into aqueous solution of CaOCl$_2$ and then distilling it.

2CaOCl$_2$ + 2HNO$_3$ $\rightarrow$ CaCl$_2$ + Ca(NO$_3$)$_2$ + 2HClO
CaOCl$_2$ + H$_2$O + CO$_2$ $\rightarrow$ CaCO$_3$ + 2HClO

Physiochemical properties

1. The dilute solution of hypochlorous acid is colourless while its concentrated solution is yellow in colour.

2. It is a weak acid, even weaker than H$_2$CO$_3$, with a dissociation constant of $3 \times 10^{-8}$ at 20°C.

3. Acidity nature: (Monobasic nature) HClO is a monobasic acid as its aqueous solution on ionization gives only one H$^+$ ion.

HClO (aq) $\rightarrow$ H$^+$ (aq) + ClO$^-$ (aq)

Hypochlorite ion

The monobasic nature shows that this molecule has one –OH group attached directly with the central Cl atom.
Being an acid it reacts with alkalis to give salts which are called hypochlorites.

NaOH + HClO → NaOCl + H₂O

OH⁻ + HClO → OCl⁻ + H₂O

4. Disproportion

(i) The dilute solution of hypochlorous acid is quite stable in the dark but when the concentrated solution is exposed to light, it becomes unstable and undergoes disproportionation to form Cl₂ and HClO₄.

5HClO → 2Cl₂ + HClO₄ + 2H₂O

(ii) When aqueous solution of HClO is heated, it undergoes disproportionation into HCl and HClO₃.

3HClO → 2HCl + HClO₃

(iii) On distillation it decomposes into H₂O and Cl₂O.

2HClO → Cl₂O + H₂O

5. Reaction with metals: HClO reacts with Mg with the evolution of H₂.

Mg + 2HClO → MgOCl₂ + H₂

It reacts with Fe and Al with the evolution of H₂ and Cl₂, while with Co, Ni and Cu, Cl₂ and O₂ are evolved.
6. **Reaction with mercury:** When it is shaken with Hg, a light brown precipitate of basic mercuric chloride, HgCl(OH) is formed which is soluble in HCl.

\[ 2\text{Hg} + 2\text{HClO} \rightarrow 2\text{HgCl} (\text{OH}) \]  
Light brown ppt.

7. **Oxidizing and bleaching properties:** The aqueous solution of HClO and its salts (like, NaOCl) are oxidizing and bleaching agents. It is due to the fact that HClO or NaOCl decomposes to give nascent oxygen as follows.

\[ \text{HClO} \xrightarrow{\text{Reduction}} \text{HCl} + [\text{O}] \]
\[ \text{NaOCl} \xrightarrow{\text{Reduction}} \text{NaCl} + [\text{O}] \]
\[ \text{ClO}^- + 2\text{H}^+ + 2\text{e}^- \xrightarrow{\text{Reduction}} \text{Cl}^- + \text{H}_2\text{O} \]  
(ion electron equation)

8. **Action of AgNO\textsubscript{3}:** It reacts with AgNO\textsubscript{3} to give silver hypochlorite (AgClO) which is unstable and undergoes disproportionation into AgCl and AgClO\textsubscript{3}.

\[ \text{HOCl} + \text{AgNO}_3 \rightarrow \text{AgClO} + \text{HNO}_3 \]
\[ 3\text{AgClO} \rightarrow 2\text{AgCl} + \text{AgClO}_3 \]

**Uses**

(i) Hypochlorous acid is used for bleaching paper pulp etc.


**Structure**  It is a linear molecule in which chlorine atoms is \( sp^3 \) hybridized.

![Structure of Hypochlorous Acid](image)

**Chlorous acid (HClO₂)**

**Preparation**

1. *From Barium hypochlorite*  It is prepared in the aqueous solution by treating a suspension of barium hypochlorite, \( \text{Ba(ClO}_2\text{)}_2 \), with dil. \( \text{H}_2\text{SO}_4 \) and filtering off the precipitate of \( \text{BaSO}_4 \).
   
   \[
   \text{Ba(ClO}_2\text{)}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{HClO}_2 + \text{BaSO}_4
   \]

2. *From \( \text{ClO}_3 \)*  It can also be obtained by the action of \( \text{ClO}_3 \) on \( \text{H}_2\text{O}_2 \).
   
   \[
   2\text{ClO}_3 + \text{H}_2\text{O} \rightarrow 2\text{HClO}_2 + \text{O}_2
   \]

**Physicochemical properties**

1. The freshly prepared solution of chlorous acid is colourless but it soon decomposes to \( \text{ClO}_2 \) which colours the solution yellow.
2. It gives a violet colour with \( \text{FeSO}_4 \).
3. **Decomposition:** \( \text{In acid solution, HClO}_2 \) rapidly decomposes as shown.
4. Disproportion: \( \text{HClO}_3 \) and its salts undergo disproportionation on heating in an alkaline solution as shown.

\[
\begin{align*}
3\text{HClO}_3 & \rightarrow 2\text{HClO}_2 + \text{HCl} \\
(\text{Cl} = +3) & \quad (\text{Cl} = +5) \\
3\text{ClO}_2^- & \rightarrow 2\text{ClO}_3^- + \text{Cl}^- \\
\end{align*}
\]

It undergoes auto-oxidation.

\[
2\text{HClO}_2 \rightarrow \text{HClO} + \text{HClO}_3
\]

5. Oxidizing properties: Both \( \text{HClO}_3 \) and its salts show oxidizing properties due to nascent oxygen.

\[
\begin{align*}
\text{HClO}_3 & \rightarrow \text{HCl} + 2 \text{[O]} \\
\text{ClO}_2^- + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{Cl}^- + 2\text{H}_2\text{O} \\
\text{HClO}_3 \text{ and its salts liberate I}_2 \text{ from KI solution.} \\
\text{HClO}_3 + 2\text{H}_2\text{O} + 4\text{Kl} & \rightarrow 4\text{KOH} + \text{HCl} + \text{I}_2 \\
4 \text{I}^- + \text{ClO}_3^- + 4\text{H}^+ & \rightarrow \text{Cl}^- + 2\text{H}_2\text{O} + 2\text{I}_2
\end{align*}
\]

**Structure**: \( \text{ClO}_2^- \) is angular in shape as chlorine atom is sp\(^3\) hybridized.

Parke’s process-Pyrometallurgical extraction of Ag (Silver) from Pb (Lead) Chemistry

MaC Arthur Forrest cyanide process to extract Au, Ag by KCN, Na Cyanide Chemistry

Deacon’s process-Obtaining \( \text{Cl}_2 \) from HCl passed on hot saturated slag Chemistry

\( \text{Cu}_2\text{Fe(CN)}_6 \) Chocolate Brown Precipitate

\( \text{Cd(CN)}_2, \text{K}_2\text{SO}_4, \text{KCN} \) are all white - \( \text{Cd(CN)}_2 \) white precipitate

\( \text{Ag}_2\text{SO}_3 \) White Precipitate

2\( \text{FeSO}_4 + 2\text{H}_2\text{SO}_4 \) green vitriol, ZnSO\(_4\) White Vitriol, CuSO\(_4\) Blue Vitriol

Ti\(^+3\) Violet, V\(^+3\) Grey, Fe\(^+3\) yellow, Co\(^+2\) Pink - ion colours

Silver nitrate (Lunar caustic) \( \text{AgNO}_3 \)
### Oxidation States and Colors

<table>
<thead>
<tr>
<th>Metal</th>
<th>+1</th>
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<th>+4</th>
<th>+5</th>
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<tr>
<td>V</td>
<td>Violet</td>
<td>Green</td>
<td>blue</td>
<td>Yellow</td>
<td>(CrO$_2^-$)</td>
<td>orange</td>
<td>(Cr$_2$O$_7^{2-}$)</td>
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<tr>
<td>Cr</td>
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<td></td>
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<tr>
<td>Mn</td>
<td>Pale pink</td>
<td>Brown</td>
<td></td>
<td>Dark green</td>
<td>(MnO$_2^{2+}$)</td>
<td>Intense purple</td>
<td>(MnO$_4^-$)</td>
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<tr>
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<td>Pale green</td>
<td>Yellow or brown</td>
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<tr>
<td>Co</td>
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</table>
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