

# **Spoon Feeding Elements & Properties**



Simplified Knowledge Management Classes Bangalore

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

#### I am Life Member of ...

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

#### And also of

IACT (Indian Association of Chemistry Teachers)



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

- 1) **NSEP** (National Standard Exam in Physics) and **NSEC** (National Standard Exam in Chemistry) held around 24 rth November. Approx 35,000 students appear for these exams every year. The exam fees is Rs 100 each. Since 1998 the IIT JEE toppers have been topping these exams and they get to know their rank / performance ahead of others.
- 2 ) INPhO (Indian National Physics Olympiad ) and INChO (Indian National Chemistry Olympiad ). Around 300 students in each subject are allowed to take these exams. Students coming from outside cities are paid fair from the Govt of India.
- 3 ) The Top 35 students of each subject are invited at HBCSE (Homi Bhabha Center for Science Education) Mankhurd, near Chembur, BARC, Mumbai. After a 2-3 weeks camp the top 5 are selected to represent India. The flight tickets and many other expenses are taken care by Govt of India.

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

#### There are 3 kinds of Text Books

- The thin Books Good students who want more details are not happy with these. Average students who need more examples are not happy with these. Most students who want to "Cram" guickly 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.

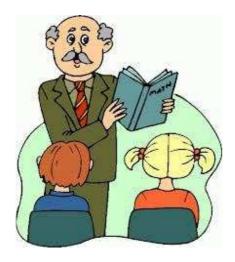
Printed books are not e-Books! Can't be downloaded and kept in hard-disc for reading "later"

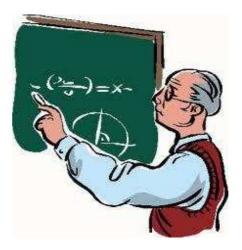
So if you read this book later, you will get all kinds of examples in a single place. This becomes a very good "Reference Material". I sincerely wish that all find this "very useful".

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.





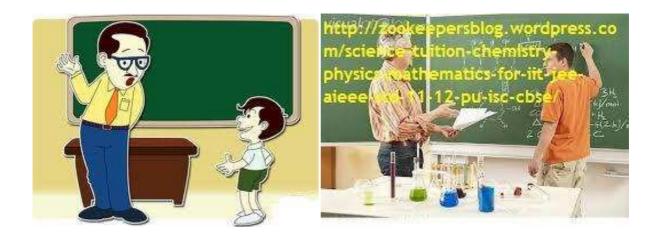
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#### A very polite request:

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

#### **Preface**

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

#### Random - 1

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









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

#### Random - 2

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









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

















Random - 3

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



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

Random - 4

The best Tabla Players are all Men.



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

Random - 5

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



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



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

#### Random - 6

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



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

#### Random - 7

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



Random - 8

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



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



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

#### Random - 9

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

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





#### Random - 10

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



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

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

#### Random - 11

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

#### Number 1

# Rupert & Anna Murdoch -- \$1.7 billion

One of the richest men in the world, Rupert

Murdoch developed his worldwide media empire
when he inherited his father's Australian
newspaper in 1952. He married Anna Murdoch in the '60s and they

remained together for 32 years, springing off three children

Wendi Deng, one of his employees.

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



## Ted Danson & Casey Coates --\$30 million

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

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

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

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

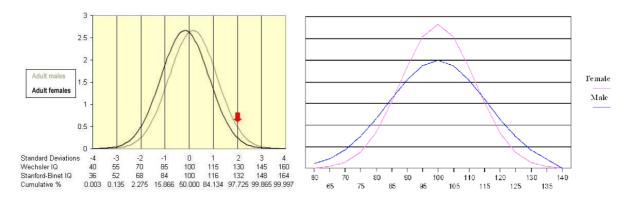
It was Boys and Men, who brought the girls / women home. The Laws are biased, completely favoring women. The men are paying for their own mistakes.

See <a href="https://zookeepersblog.wordpress.com/biased-laws/">https://zookeepersblog.wordpress.com/biased-laws/</a>

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

#### Random - 12

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



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

#### Random - 13

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



See <a href="http://skmclasses.kinja.com/progressively-daughters-become-monsters-1764484338">http://skmclasses.kinja.com/progressively-daughters-become-monsters-1764484338</a>

See <a href="http://skmclasses.kinja.com/vivacious-vixens-1764483974">http://skmclasses.kinja.com/vivacious-vixens-1764483974</a>

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 <a href="https://zookeepersblog.wordpress.com/iit-jee-iseet-main-and-advanced-results/">https://zookeepersblog.wordpress.com/iit-jee-iseet-main-and-advanced-results/</a>

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

Professor Subhashish Chattopadhyay

# HURT FEMINISM BY DOING NOTHING \* Don't HELP WOMEN

- **X** Don't fix things for women
- Don't support women's issues
- ✗ Don't come to women's defense¹
- Don't speak for women
- ✗ Don't value women's feelings
- **DON'T PORTRAY WOMEN AS VICTIMS**
- ✗ Don't PROTECT WOMEN²



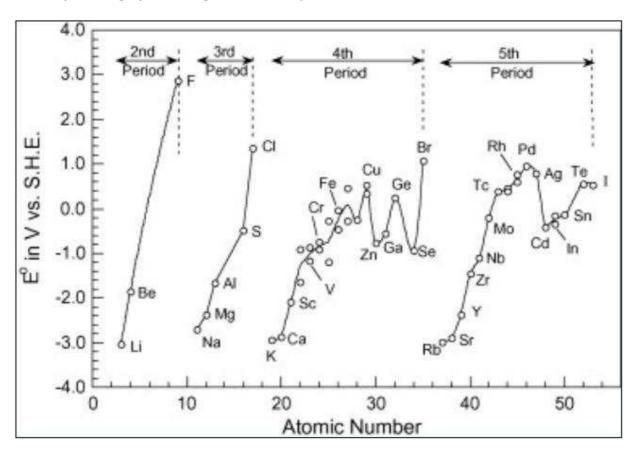
'Don't even nawalt ("Not All Women Are Like That")

<sup>2</sup> for example from criticism or insults



## Spoon Feeding Series - Elements & Properties in Chemistry

#### Most Important graph or Image of Chemistry



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

All chemical reactions happen because of this electrode potential difference. When a Solid is added to a solution of another compound such as a Gold Spoon in CuSO<sub>4</sub> Solution, of a Copper container having AgNO<sub>3</sub> Solution, then the displacement reaction happens or not is decided by these potential values. Battery and Electrochemistry chapter uses this knowledge. Oxidation-Reduction reactions, titrations etc all need this understanding.

The e.m.f of the standard cell Zn  $| Zn^{2+} | | Ag^+ | Ag^- | E^0_{cell} = 1.562 \text{ Volt}$ 

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

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

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

\_

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

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

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

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

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

		Half-Reaction			E (V)	
Ā	7	F <sub>2</sub> (g) + 2e <sup>-</sup>	2F-(aq)		+2.87	9 10
	1	$Cl_2(g) + 2e^-$	2Cl <sup>-</sup> (aq)		+1.36	
	1	$MnO_2(g) + 4H^+(a)$	aq) + 2e-	$Mn^{2+}(aq) + 2H_2O(l)$	+1.23	
4 4	1	$NO_3^-(aq) + 4H^+(aq)$	aq) + 3e-	$NO(g) + 2H_2O(I)$	+0.96	st
int	8		Ag(s)		+0.80	neng
agent		$Fe^{3+}(g) + e^{-}$	Fe2+(aq)		+0.77	pth o
strength of oxidizing		$O_2(g) + 2H_2O(I)$	+ 4e <sup>-</sup>	4OH-(aq)	+0.40	strength of reducing
cidiz		Cu2+(aq) + 2e-	Cu(s)		+0.34	duc
000		2H+(aq) + 2e-	$H_2(g)$		0.00	Sing
III C		$N_2(g) + 5H^+(aq)$	+ 4e <sup>-</sup>	$N_2H_5^+(aq)$	-0.23	agent
eng		Fe2+(aq) + 2e-	Fe(s)	THE PERSON THE LAND SALES IN	-0.44	127
str		2H <sub>2</sub> O(I) + 2e <sup>-</sup>	$H_2(g) +$	2OH-(aq)	-0.83	
		Na+(aq) + e-	Na(s)		-2.71	
k		Li+(aq) + e-	Li(s)		-3.05	V

#### A more detailed table

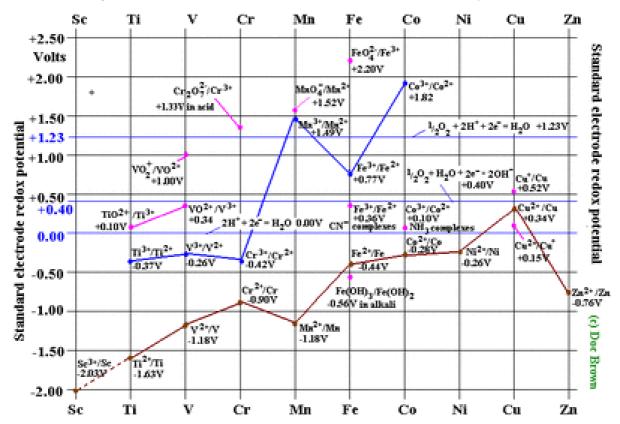
Half-Reaction	<b>ℰ</b> ° ( <b>v</b> )	Half-Reaction	&₀ (∧)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^{-} \rightarrow Cu$	0.34
$\text{Co}^{3-} + \text{e}^- \rightarrow \text{Co}^{2-}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^- + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^{-} \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^{-} + 2H^{+} + IO_{4}^{-} \rightarrow IO_{3}^{-} + H_{2}O$	1.60	$Fe^{3+} + 3e^{-} \rightarrow Fe$	-0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^{-} \rightarrow Pb$	-0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^{-} \rightarrow Sn$	-0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	-0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^{-} \rightarrow Cd$	-0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^{-} \rightarrow Fe$	-0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	-0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^{-} \rightarrow Zn$	-0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	-0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	-1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
$CIO_2 + e^- \rightarrow CIO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	-2.23
$2Hg^{2+} + 2e^{-} \rightarrow Hg_{2}^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^{-} \rightarrow La$	-2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	-2.71
$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^{-} \rightarrow Ca$	-2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	-2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	-2.92
$\rm I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	-3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

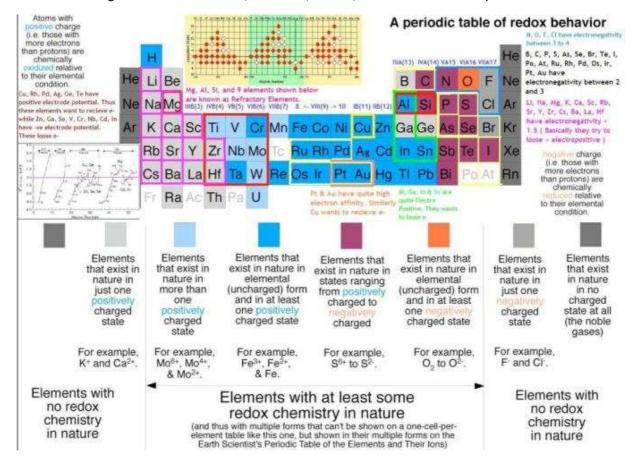
#### Spoon Feeding

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

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

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





Nernst Equation also uses Electrode potential

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

$$At \ 25^{0}C; E_{cell} = E_{cell}^{0} - \frac{0.059}{n} \log \frac{M}{[M^{n+}]} or \frac{1}{[M^{n+}]}$$
 Temperature (in Kelvin) Concentration Gas Constant RT [ion]o Constant RT [ion]o Ecell =  $E_{cell}^{0} - \frac{0.059}{n} \log [\frac{\text{Products}}{\text{Reactants}}] or Q.$  Equilibrium ZF [ion]i Potential Ion Charge Constant Concentration



Consider the following set of half-reactions

Reduction 
$$Fe^{2+} + 2e^{-} \longrightarrow Fe$$
  $E^{\circ}_{red} = -0.44 \text{ V}$ 

Oxidation  $Zn \longrightarrow Zn^{2+} + 2e^{-}$   $E^{\circ}_{ox} = +0.76 \text{ V}$ 

Overall 
$$Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$$
  $E^{\circ}_{cell} = 0.32 \text{ V}$ 

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 ( $E_{cell} = 0 \text{ V}$ ). If we add more  $Fe^{2+}$  to the reaction mixture, The equilibrium will shift to the right to use up the excess  $Fe^{2+}$ . This will, of course cause a positive cell potential to be measurable.

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

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

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

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

Substitute the new definition of  $\Delta G$  and we get

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

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

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

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

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

$$E = E^{\circ} - \frac{RT}{nF} \times \ln \frac{[Zn^{2+}]}{[Fe^{2+}]}$$

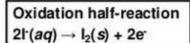
$$= 0.32V - \frac{8.3145 \frac{J}{mol K} \times 298.15K}{2 \times 96485 \frac{C}{mol}} \times \ln \frac{1.9}{0.10}$$

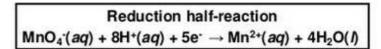
$$= 0.28V$$

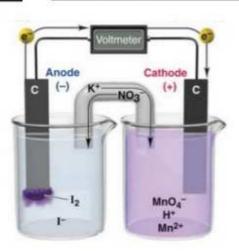
Although the reaction is 90% complete (from Standard Conditions initial) the cell potential has only dropped by a small amount (0.04 V). This is normal. For example, the batteries in your flashlight will put out almost full voltage until the last traces of chemical are almost used up at which point the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

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### A voltaic cell using inactive electrodes.







Overall (cell) reaction 
$$2\mathsf{MnO_4^-}(aq) + 16\mathsf{H}^+(aq) + 10\mathsf{l}^-(aq) \,\rightarrow\, 2\mathsf{Mn}^{2+}(aq) + 5\mathsf{l}_2(s) + 8\mathsf{H}_2\mathsf{O}(l)$$

graphite  $I^{-}(aq) \mid I_{2}(s) \parallel MnO_{4}^{-}(aq)$ ,  $H^{+}(aq)$ ,  $Mn^{2+}(aq) \mid graphite$ The inert electrode is specified.

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

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

$$Br_2(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2Br(aq)$$
  $E_{cell} = 1.83 \text{ V}.$   
Calculate  $E_{bromine}$ , given that  $E_{zlnc} = -0.76 \text{ V}$ 

Solution:

$$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$$
 [reduction; cathode]  $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$  [oxidation; anode]  $E^{\circ}_{zinc} = -0.76 \text{ V}$ 

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

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

-

What is the equilibrium constant for the reaction of copper metal with bromine to form copper(II) ions and bromide ions in aqueous solution at  $25^{\circ}$ C?

Cathode 
$$Br_2 + 2e^- \longrightarrow 2 Br^ E^\circ_{red} = 1.09 V$$

Anode  $Cu \longrightarrow Cu^{2+} + 2e^ E^\circ_{ox} = -E^\circ_{red} = -0.34 V$ 

Cell  $Cu + Br_2 \longrightarrow Cu^{2+} + 2 Br^ E^\circ_{cell} = 0.75$ 

$$\ln K = \frac{nFE^{\circ}}{RT} = \frac{2 \times 96458 \frac{c}{\text{mol}} \times 0.75 \text{ V}}{8.31451 \frac{J}{\text{mol K}} \times 298.15 \text{ K}} = 58.38_{208}$$
$$K = e^{58.38_{208}} = 2.2 \times 10^{25}$$

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Using half reactions write the spontaneous Redox reactions

$$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$$
  $E^{\circ}_{tin} = -0.14 \text{ V}$   
 $Ag^{+}(aq) + e^- \rightarrow Ag(s)$   $E^{\circ}_{silver} = 0.80 \text{ V}$ 

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

Note: This does not change the voltage obtained

**2**Ag<sup>+</sup>(aq) + **2**e<sup>-</sup> → **2**Ag(s) 
$$E_{silver}^{\circ} = 0.80 \text{ V}$$

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

$$Sn(s) \to Sn^{2+}(aq) + 2e^{-} \qquad E^{\circ}_{tin} = -0.14 \text{ V}$$

$$2Ag^{+}(aq) + 2e^{-} \to 2Ag(s) \qquad E^{\circ}_{silver} = 0.80 \text{ V}$$

$$Sn(s) + 2Ag^{+}(aq) \to 2Ag(s) + Sn^{2+}(aq) \qquad E^{\circ}_{cell} = 0.94 \text{ V}$$

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

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

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#### Zinc and Magnesium Oxide Battery

Anode (oxidation):  $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_{2}O(l) + 2e^{-}$   $Cathode \ (reduction): \quad MnO_{2}(s) + 2H_{2}O(l) + 2e^{-} \rightarrow Mn(OH)_{2}(s) + 2OH^{-}(aq)$   $Overall \ (cell) \ reaction: \\ Zn(s) + MnO_{2}(s) + H_{2}O(l) \rightarrow ZnO(s) + Mn(OH)_{2}(s) \quad E_{cell} = 1.5 \text{ V}$ 

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#### Zinc and Magnesium Oxide Battery

Anode (oxidation):  $Zn(s) + 2OH^{-}(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^{-}$ Cathode (reduction):  $Ag_2O(s) + H_2O(l) + 2e^{-} \rightarrow 2Ag(s) + 2OH^{-}(aq)$ Overall (cell) reaction:  $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$  $E_{cell} = 1.6 \text{ V}$ 

The mercury battery uses HgO as the oxidizing agent instead of Ag<sub>2</sub>O and has cell potential of 1.3 V.

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

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Anode (oxidation): 
 3.5 \text{Li}(s) \rightarrow 3.5 \text{Li}^+ + 3.5 \text{e}^-

Cathode (reduction): 
 \text{AgV}_2\text{O}_{5.5} + 3.5 \text{Li}^- + 3.5 \text{e}^- \rightarrow \text{Li}_{3.5}\text{V}_2\text{O}_{5.5}

Overall (cell) reaction: 
 \text{AgV}_2\text{O}_{5.5} + 3.5 \text{Li}(s) \rightarrow \text{Li}_{3.5}\text{V}_2\text{O}_{5.5}
```

#### The most commonly used Battery is Lead-Acid Battery

Anode (oxidation):  $Pb(s) + HSO_4(aq) \rightarrow PbSO_4(s) + H^+(aq) + 2e^-$ Cathode (reduction):  $PbO_2(s) + 3H^+(aq) + HSO_4(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$ Overall (cell) reaction (discharge):  $PbO_2(s) + Pb(s) + H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$   $E_{cell} = 2.1 \text{ V}$ Overall (cell) reaction (recharge):  $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + Pb(s) + H_2SO_4(aq)$ 

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#### Nickel Metal Hydride Battery

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#### Laptops, Cell-phones most commonly use Lithium ion Batteries

Anode (oxidation):  $\begin{array}{l} \operatorname{Li}_x C_6(s) \to x \operatorname{Li}^+ + x \operatorname{e}^- + C_6(s) \\ Cathode \ (reduction): \\ \operatorname{Li}_{1-x} \operatorname{Mn}_2 O_4(s) + x \operatorname{Li}^+ + x \operatorname{e}^- \to \operatorname{LiMn}_2 O_4(s) \\ Overall \ (cell) \ reaction: \\ \operatorname{Li}_x C_6(s) + \operatorname{Li}_{1-x} \operatorname{Mn}_2 O_4(s) \to \operatorname{LiMn}_2 O_4(s) \\ E_{cell} = 3.7 \ \operatorname{V} \end{array}$ 

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#### Hydrogen Fuel Cell

Anode (oxidation):  $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$ Cathode (reduction):  $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(g)$ Overall (cell) reaction:  $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$   $E_{cell} = 1.2 \text{ V}$ 

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

We could calculate this by breaking the overall K<sub>sp</sub> reaction into a series of redox reactions as follows:

Anode 
$$Ag(s) \xrightarrow{*} Ag^{+} + e^{-}$$
  $E^{\circ}_{ox} = -0.80 \text{ V}$ 

Cathode  $AgCl + e^{-} \xrightarrow{*} Ag(s) + Cl^{-}$   $E^{\circ}_{red} = 0.22 \text{ V}$ 

Overall  $AgCl \xrightarrow{*} Ag^{+} + Cl^{-}$   $E^{\circ}_{cell} = -0.58 \text{ V}$  (not very spontaneous)

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

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

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Ion Concentrations can also be calculated...

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

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

The Nernst equation is

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

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

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

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

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

$$E = E^{\circ} - 0.0257 \text{ V ln } [H^{+}]$$
 (Note: ln  $Y = 2.303 \times \log Y$  and .-257×2.303=.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<sup>+</sup> ions to pass through.

Electrochemical Cell

The electrochemical cell shown below is a concentration cell.

M|M<sup>2+</sup>(saturated solution of a sparingly soluble salt, MX<sub>2</sub>) || M<sup>2+</sup>(0.001 mol dm<sup>-3</sup>)|M

The emf of the cell depends on the difference in concentration of M2+ ions at the two electrodes. The emf of the cell at

- The solubility product (K<sub>sp</sub>) of MX<sub>2</sub> at 298 K based on the information available for the given concentration cell (take 2.303 RT/F = 0.059 V at 298 K) is
  - (a)  $1 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$ (c)  $1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

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

- 1 The value of  $\Delta G$  for the given cell reaction (take  $1F = 96\,500\,\mathrm{C}\,\mathrm{mol}^{-1}$ ) is
  - (a) −5.7 kJ mol<sup>-1</sup>

- (b) 5.7 kJ mol<sup>-1</sup> (c) 11.4 kJ mol<sup>-1</sup> (d) -11.4 kJ mol<sup>-1</sup>

#### Solutions:

The cell reaction may be obtained as follows.

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

The cell potential is

$$E = -\frac{RT}{2F} \ln \left\{ \frac{\left[M^{2+}\right]_L / \, \text{mol dm}^{-3}}{\left[M^{2+}\right]_R / \, \text{mol dm}^{-3}} \right\} \quad \text{i.e.,} \quad 0.059 \, \text{V} = -\left(\frac{0.059 \, \text{V}}{2}\right) \, \log \, \left\{ \frac{\left[M^{2+}\right]_L / \, \text{mol dm}^{-3}}{0.001} \right\} \\ \text{This gives} \quad \log \left( \left[M^{2+}\right]_L / \, \text{mol dm}^{-3} \right) = -2 + \log \left(0.001\right) = -2 - 3 = -5 \quad \text{i.e.,} \quad \left[M^{2+}\right]_L = 1.0 \times 10^{-5} \, \, \text{mol dm}^{-3}$$

From the reaction

$$\begin{split} \text{MX}_2(\text{s}) &\rightleftharpoons \text{M}^{2^+}(\text{aq}) + 2 \ \ \text{X}^-(\text{aq}); \\ K_{\text{sp}} &= \ [\text{M}^{2^+}][\text{X}^{2^-}] = (s)(2s)^2 = 4s^3 = 4 \ (1.0 \times 10^{-5} \ \text{mol dm}^{-3})^3 = 4 \times 10^{-15} \ \text{mol}^3 \ \text{dm}^{-9} \end{split}$$

The  $\Delta G$  of the cell reaction is

$$\Delta G = -nFE = -$$
 (2) (96500 C mol<sup>-1</sup>) (0.059 V) = -11 387 J mol<sup>-1</sup> = -11.4 kJ mol<sup>-1</sup>

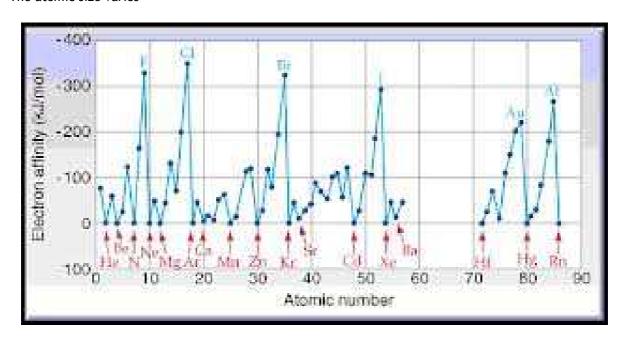
Hence, we have

The choice (b) is correctin first Question

The choice (d) is correct in the second Question

# **Elements & Properties**

The atomic size varies



<u>Elements are divided into s-Block elements, p-Block elements, d-Block elements and f-Block elements</u>

We know that electrons are arranged in the shells of atoms around the nucleus. These shells are arranged according to their energy and can be represented as K, L, M, and N.... The atomic shells can be further classified as s, p, d and f sub-shells. Each sub-shell is divided into orbitals which are denoted as s, p, d, and f-orbitals. The long form of the periodic table is also based in these orbital and sub-shells.

The s-block of the periodic table consists of the first two groups i.e the groups IA and IIA namely the Alkali Metals and the Alkaline Earth Metals along with Hydrogen and Helium.

s-block elements include hydrogen (H), helium (He), lithium (Li), beryllium (Be), sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), rubidium (Rb), strontium (Sr), cesium (Cs), barium (Ba), francium (Fr) and radium (Ra). The Group IA of the Periodic Table consists of elements like Lithium (Li), Sodium (Na), Potassium(K), Rubidium (Rb), Cesium (Cs) and Francium (Fr) which are collectively known as Alkali Metals. These are so called because they form hydroxides on reaction with water which are strongly alkaline in nature.

All of the s-block elements are metals. In general, they are shiny, silvery, good conductors of heat and electricity and lose their valence electrons easily. In fact, they lose their trademark s orbital valence electrons so easily that the s-block elements are considered to be some of the most reactive elements on the periodic table. The Group IIA consists of elements like Beryllium(Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium(Ra) which are collectively known as Alkaline Earth Metals (except Beryllium). They are so called because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust. In s-block elements the last electron enters the outermost s-orbital and as the s-orbital can accommodate only two electrons, that is why only two groups i.e group 1 & 2 belong to the s-block of the Periodic Table. Thus the outermost orbital of s block

elements consists of one or two electrons and the orbital next to the outermost shell i.e the penultimate shell has either 2 or 8 electrons. This is the reason why the s-block elements show a fixed valency which depends on the number of electrons present in the outermost shell. The last element of both the groups i.e, Francium(Fr) and Radium (Ra) are radioactive and possess different properties than the other elements of the same group.

The periodic table can be divided into blocks; s, p, d and f according to their valence shell electronic configuration. The elements of s-block have their valence electron in s-sub shell. A first and second group of the periodic table is part of s-block. From 3rd group, the valence electrons are filled in d-sub shell therefore these elements are part of d-block and continue till 12th group of the periodic table. Form 13th group, again valence electrons are again filled in p-sub shell, therefore these elements are known as p-block elements. p-block elements are placed from 13th to 18th group of the periodic table. They include metals, non-metals and metalloids. This block is better explained group wise and each group is known with its 1st element such as carbon family, nitrogen family, boron family etc. Let's have a look at some more features of p-block of elements.

The elements in column 1, known collectively as the alkali metals (except hydrogen), always lose their one valence electron to make a +1 ion. These metals are characterized by being silvery, very soft, not very dense and having low melting points. These metals react extremely vigorously with water and even oxygen to produce energy and flammable hydrogen gas. They are kept in mineral oil to reduce the chance of an unwanted reaction or worse, an unwanted explosion.

The elements in column 2, known as the alkaline earth metals (except helium), always lose their two valence electrons to make a +2 ion. Like the alkali metals, the alkaline earth metals are silvery, shiny and relatively soft. Some of the elements in this column also react vigorously with water and must be stored carefully.

S-block elements are common for being ingredients in fireworks. The ionic forms of potassium, strontium and barium make appearances in firework displays as the brilliant purples, reds and greens.

Francium is considered to be the most rare naturally occurring element on earth. It is estimated that there is only a few grams of Francium present on earth at a time. Francium has a very unstable nucleus and undergoes nuclear decay rapidly. As soon as it is created it vanishes.

- 1) Electronic Configuration :- The general electronic configuration of s-block elements is ns 1 for Alkali metals and ns 2 for Alkaline earth metals where n=2 to 7. All the Alkali metals have one valence electron and these loosely held s-electron in the outermost valence shell of these elements makes them the most electropositive metals. The Alkaline Earth Metals have two electrons in the s-orbital of the valence shell. Like Alkali Metals, these elements are also electropositive ( Electronegativity value less than 1).
- 2) Metallic character: All the Alkali metals are silvery white, soft and light metals. The Alkaline Earth metals, in general, are silvery white, lustrous and relatively soft but harder than the Alkali metals. Beryllium and magnesium appear to be somewhat greyish. The Metallic character increases as we go down both groups. Both the Alkali metals and the Alkaline Earth metals are highly malleable and ductile and have a very high tendency to loose electrons to form positive ions and hence they are highly electropositive (Meaning in Pauling scale electronegativity values less than 1).
- 3) Atomic Density: The Alkali metals and the Alkaline Earth metals both have low density. This is because they have large ionic size due to which their atomic nuclei are widely separated in their crystal lattices. The density increases down both groups.

- 4) Melting and Boiling Points: The melting and boiling points of the Alkali metals are low indicating weak metallic bonding due to the presence of only a single valence electron in them. The melting and boiling points of Alkaline Earth metals are higher than the corresponding alkali metals due to their smaller sizes. The trend is, however, not systematic but it slightly decreases down the group.
- 5) Oxidation state: The Alkali metals show only +1 oxidation state, while Alkaline Earth metals show +2 oxidation state only.
- 6) Atomic and Ionic radii: Both the Alkali metals and the Alkaline Earth metals have large atomic and ionic radii. The Atomic and the Ionic radii increases as we move down both groups. But as we go from group I to group II in the same period the Atomic and the Ionic radii decreases.
- 7) Electrode potential: The Alkali metals are strong reducing agents. The Standard Electrode Potentials of all alkali metals lie between -2.7V and -3.0V, indicating a strong tendency to form cations in solution. The Alkaline Earth Metals also have negative values of their Standard Electrode potentials.
- 8) Ionisation Energies: The ionization energies of the Alkali metals are considerably low and decreases down the group from Lithium (Li) to Cesium (Cs). This is due to the increasing size, increasing nuclear charge, and the outermost electron is very well screened from the nuclear charge. The Alkaline Earth metals have low ionization energies due to their large size of the atoms. Since the atomic size increases down the group, their ionization energies decreases down the group. But as we go from group I to group II in the same period Ionisation Energies increases. The first ionisation energies (means the energy required to remove the first electron from the atom) of the alkaline earth metals are higher than those of the corresponding Group I metals. This is due to their small size as compared to the corresponding alkali metals. But the second ionisation energies (means the energy required to remove the second electron from the atom) of the alkaline earth metals are smaller than those of thecorresponding alkali metals.
- 9) Magnetic Properties: Alkali metals are attracted by the applied magnetic field and hence are Paramagnetic in nature whereas the Alkaline Earth metals are repelled by the magnetic field and hence are diamagnetic in nature.
- 10) Complex Formation: Both the Alkali metals and the Alkaline earth metals show weak tendency to form complexes because they have no low energy vacant orbital available for bonding with lone pair of ligands. This is due to large size, low nuclear charge and poor ability to attract electrons.
- 11) Chemical Reactivity: The alkali metals are highly reactive metals and the reactivity increases down the group. The reactivity is due to:-
- (a) Low value of first ionization energy
- (b) Large size
- (c) Low heat of atomization

#### Reactivity of Alkali Metals:-

- 1) Alkali metals lose their luster very easily upon exposure to air.
- 2) Alkali metals react with water and form hydroxides along with liberation of hydrogen.
- 3) Alkali metals react with hydrogen and form ionic hydrides and these metal hydrides in turn react with water to give back the hydrogen.
- 4) Alkali metals react with halogens very easily forming halides.

- 5) All alkali metals are readily soluble in liquid ammonia.
- 6) The alkali metals are good reducing agents and the reducing property increases from Li to Cs.
- 7) Alkali metals can form alloys with other elements in the same period or with metals in other groups.
- 8) Alkali metals react with sulphur and phosphorus on heating to form sulphides and phosphides.
- 9) Alkali metals combine with mercury to form amalgams.

#### Reactivity of Alkaline Earth Metals :-

The alkaline earth metals are less reactive than the alkali metals. Reactivity of alkaline earth metals increases as we move down the group.

- 1) Beryllium and magnesium are kinetically inert to oxygen and water because of the formation of an oxide film on their surface.
- 2) All the alkaline earth metals combine with halogen at elevated temperatures forming their halides.
- 3) All the elements except beryllium combine with hydrogen upon heating to form their hydrides.
- 4) The alkaline earth metals readily react with acids liberating dihydrogen.
- 5) Like alkali metals, the alkaline earth metals are strong reducing agents.
- 6) Like alkali metals, the alkaline earth metals dissolve in liquid ammonia to give deep blue black solutions forming ammoniated ions.
- 7) The alkaline earth metals burn in oxygen to form the monoxide.
- 8) The alkaline earth metals also form salts of oxoacids like carbonates, sulphates and nitrates.
- 9) They directly combine with carbon and form carbides .
- 10) Conductivity :- Both the Alkali metals and the Alkaline Earth metals are good conductors of heat and electricity.
- 11) Colour: All the alkali elements are silvery white solid. When freshly cut, they have a bright lusture which quickly fades due to surface oxidation. The silvery luster of alkali metals is due to the presence of highly mobile electrons of the metallic lattice.

The alkaline earth metals, in general, are silvery white and lustrous.

12) Flame coloration: This property is due to the ease of excitation of the valence electrons. When elements or their compounds are introduced to flame, the electrons absorbs energy from the flame and gets excited to higher energy levels. When these electrons return to their ground state, they emit absorbed energy in form of visible light having characteristic wavelengths. Depending upon the wavelength of light emitted, different colours are imparted to the flame. Salts (generally chlorides) impart characteristic colours to the Bunsen flame.

The alkali metals and their salts impart a characteristic colour to flame.

For eg:-

Lithium - Crimson Red

Sodium - Golden Yellow

Potassium - Pale Violet

Rubidium - Violet

The alkaline earth metals also imparts colours to flame.

For eg:-

Strontium - Bright crimson

Calcium - Brick red

Barium - Apple green

Radium - Carmine - red

13) Photoelectric Effect: Alkali metals (except Li) and the Alkaline Earth metals exhibit photoelectric effect (A phenomenon of emission of electrons from the surface of metal when light falls on them). The ability to exhibit photoelectric effect is due to low value of ionization energy of alkali and alkaline earth metals. Li does not emit photoelectrons due to high value of ionization energy.

#### Description of Helium (group I element):-

Helium is named for the Greek god of the Sun, Helios. It was first detected as an unknown yellow spectral line signature in sunlight during a solar eclipse in 1868 by French astronomer Jules Janssen. Janssen is jointly credited with detecting the element along with Norman Lockyer. Jannsen observed during the solar eclipse of 1868 while Lockyer observed from Britain. Lockyer was the first to propose that the line was due to a new element, which he named. The formal discovery of the element was made in 1895 by two Swedish chemists, Per Teodor Cleve and Nils Abraham Langlet, who found helium emanating from the uranium ore cleveite. In 1903, large reserves of helium were found in natural gas fields in parts of the United States, which is by far the largest supplier of the gas today.

Helium is an element with symbol He and atomic number 2. It is a colorless, odourless, tasteless, non-toxic, inert and monatomic gas. It is the second lightest element and is the most abundant element in the universe. Helium is the least water soluble monoatomic gas. It's the less reactive element and doesn't essentially form chemical compounds. The density and viscosity of helium vapour are very

low.It has low boiling point, low density and high thermal conductivity.Natural gases contain higher helium concentrations than the atmosphere.

#### Description of Hydrogen (group II element):-

Hydrogen is an element with symbol H and atomic number 1. It is a colourless, odorless, tasteless, flammable and nontoxic gas atmospheric temperatures and pressures. It is the most abundant element in the universe. Hydrogen is the lightest of all gases. Hydrogen burns in air with a pale blue colour, almost invisible flame. Hydrogen has the highest combustion energy, This property makes it the fuel of choice for multi-stage rockets. Hydrogen has the lowest boiling point of any element except helium. Hydrogen was Discovered by H. Cavendish and named by A. Lavoisier . It's Density is about 0.08988 g/l . It's Melting point is about 14.01 K and Boiling point is about 20.28 K . It has dimagnetic magnetic properties. Hydrogen gas can form explosive mixtures with air. The destruction of the Hindenburg airship was an famous example of hydrogen combustion. Hydrogen is the only element that has different names for its isotopes i.e Deuterium , Protium and tritium . The electrolysis of water is a simple method of producing hydrogen. Hydrogen can be prepared in several different ways, but economically the most important processes involve removal of hydrogen from hydrocarbons.

#### P Block elements

The p-block of the periodic table consists of the elements of groups 13,14, 15, 16, 17 and 18. These elements are characterised by the filling up of electrons in the outermost p-orbitals of their atoms. Some of these elements and their compounds play an important role in our daily life. For example:

Nitrogen is used in the manufacture of ammonia, nitric acid and fertilizers. Trinitrotoluene (TNT), nitroglycrine, etc., are compounds of nitrogen, which are used as explosives.

Oxygen present in air is essential for life and combustion processes.

Carbohydrates, proteins, vitamins, enzymes, etc., which contain chain of carbon atoms, are responsible for the growth and development of living organism.

P block chemistry is a little complicated compared to the s block chemistry. The reason behind this is that P block not only has non metals, but metalloids and metals too.

Every group, the boron group, Carbon group, Nitrogen group, Chalcogens, halogens and the noble gases have different physical and chemical properties.

Some of the common properties of 'P' block elements are

#### 1. Atomic size

Atomic size of all elements in the 'P' block, decreases as we move from IIIA to VIIA. When we move down a group, say, for example, from carbon to lead in group IV A, the elements increase in size, due to the additional shell added.

#### 2. Ionization energy

Ionization energy, or the energy to remove an electron from the outermost shell of an element, increases as we move along from IIIA to VIIA. It is maximum for a noble gas because noble gases have completely filled configuration. Ionization energy decreases as we move down a group. Some elements

at the bottom of a group like Lead, tin, Thallium, Bismuth, etc. behave almost as like metals with very low ionization energies.

#### 3. Electronegativity

The property of acquiring an electron or the ability to withdraw electrons from an electropositive element increases as we move from III A to VII A. Elements of VII A have maximum electronegativity, with fluorine being the most electronegative atom present, due to its smaller size.

#### 4. Allotropy

Allotropy is a phenomenon by which one element can exist in many forms. Most elements of IV A, V A, and VI A show allotropy. For example, phosphorus exist in many forms like red phosphorus, white phosphorus, etc. Similarly, many forms of sulfur like monoclininc sulfur, rhombic sulfur, etc., are known. There are many forms of carbon too, like graphite, diamond, etc. Halogens do not show allotropy.

#### 5. Catenation

Catenation is the ability to form compounds in which the atoms are linked to each other in chains or rings.

Carbon has the greater tendency to combine with other carbon atoms to form quite large carbon structures.

Other elements like silicon undergo catenation in IV A group. V A group also exhibits this property. Nitrogen and phosphorus have a tendency to form M-M links.

Catenation can be seen in the case of Oxygen group too. S8 is an example of catenation.

Catenation is not shown among halogens and noble gases.

#### 6. Chemical Properties of P block elements

Since P block elements are all non metals, covalent bond is seen in compounds such as hydrides, oxides, halides, etc.

The usual trends (vertical as well as horizontal) in various properties observed in the s-block are observed in this block, too. As we move from top to bottom through a vertical column (group) some similarities are observed in the properties. However, this vertical similarity is less marked in the p-block than that observed in the s-block, especially in groups 13 and 15; vertical similarity is increasingly shown by the later groups. As far as the horizontal trend is concerned, the properties vary in a regular fashion as we move from left to right across a row (period).

Elements belonging to the group 13 ( i.e group IIIA ) to group 17 (i.e group VIIA ) of the periodic table along with the group 18 i.e the zero group elements together form the p-block of the periodic table.

In the p-block elements the last electron enters the outermost p orbital. They have 3 to 8 electrons in the outermost shell. As we know that the number of p orbitals is three and, therefore, the maximum number of electrons that can be accommodated in a set of p orbitals is six. Hence there are six groups of p-block elements in the periodic table numbering from 13 to 18. The First group of the p-block i.e

the group IIIA is commonly called as Boron group, the second group i.e the group IVA is called Carbon group, the third group i.e the group VI is called Nitrogen group, the fourth group i.e the group VIA is called Chalcogens ,the fifth group i.e the group VIIA is called Halogens and the sixth group i.e the zero group or group 18 is called Inert or Noble gases group. In the p-block all the three types of elements are present, i.e. the Metals, Non-Metals and Metalloids .The zigzag line in the p-block separates all the elements that are metals from those that are non-metals. Metals are found on the left of the line, and non-metals are those on the right. Along the line we find the metalloids. Due to the presence of all types of elements the p-block show a lot of variation in properties.

Classification of elements in the p-block of the Periodic Table :-

The elements in the p-block of the periodic table consists of all types of elements i.e metals , non-metals and metalloids.

- a) Metals:-
- 1) Aluminium, 2) Gallium, 3) Indium, 4) Thallium, 5) Tin, 6) Lead, 7) Bismuth.
- b)Non-Metals:-
- 1) Helium, 2) Carbon, 3) Nitrogen, 4) Oxygen, 5) Fluorine, 6) Neon, 7) Phosphorus, 8) Sulphur, 9) Chlorine, 10) Argon, 11) Selenium, 12) Bromine, 13) Krypton, 14) Iodine, 15) Xenon, 16) Radon.
- c) Metalloids:-
- 1)Boron, 2) Silicon, 3) Germanium, 4) Arsenic, 5) Antimony, 6) Tellurium, 7) Polonium, 8) Astatine.

Characteristic Properties of elements in p-block of Modern Periodic Table :-

1) Electronic Configuration: The general valence shell electronic configuration of p-block elements is ns 2 np 1-6 (except for He). The inner core of the electronic configuration may, however, differ.

The General electronic configuration shown by elements from group13 to 18 of p-block is as given below:-

```
Group 13 (Boron family) :- ns 2 np 1.
```

Group 14 (Carbon family) :- ns 2 np 2.

Group 15 (Nitrogen family):- ns 2 np 3.

Group 16 (Oxygen family) :- ns 2 np 4.

Group 17 (Halogen family) :- ns 2 np 5.

Group 18 (Noble gases) :- ns 2 np 6 (except Helium).

The general electronic configuration of Helium is 1s 2. Due to their distinct electronic configuration pblock elements show a lot of variation in properties.

- 2) Metallic Character: As stated earlier p-block contains all types of elements i.e metals,non-metals and metalloids. The p-block is the only region of the periodic table to contain metalloids. The non metallic character decreases down the group whereas there is a gradual increase in non-metallic character from left to right in the p-block. The metallic character tends to increase down each group whereas it decreases as we go from left to right across a period. In fact, the heaviest element in each p-block group is the most metallic in nature.
- 3) Atomic Density: The Atomic Density of elements in p-block increases down the group, this is due to increase in the size of the atom down the group.

Whereas it decreases as we move from left to right across the period, this is due to the decrease in atomic size of all elements in the p- block across the period. Of all the elements, aluminum is of very low density and is widely used as a structural material.

- 4) Melting and Boiling points: The Melting and Boiling points gradually increases down the group because the molecular mass increases down the group and hence the intermolecular forces increases.
- 5) Oxidation state :- The p-block elements show a variable oxidation state . The oxidation states increases as we move from left to right in the periodic table. The maximum oxidation state shown by a p-block element is equal to the total number of valence electrons . According to this, the oxidation states

shown by different groups is as follows:-

```
Boron family (Group 13) :- +3
```

Carbon family (Group 14):-+4

Nitrogen family (Group 15):-+5

Oxygen family (Group 16):-+6

Halogen family (Group 17) :- +7

Noble gases (Group 18):-+8

But in addition to this p-block elements may also show other oxidation states which normally , but not necessarily , differ from total number of valence electrons by unit of two. The other oxidation state two unit less than the group oxidation state shown by different groups is as follows:-

```
Boron family (Group 13) :- +1
```

Carbon family (Group 14):- +2, -4

Nitrogen family (Group 15):-+3, -3

Oxygen family (Group 16):- +4, +2, -2

Halogen family (Group 17):- +5, +3, +1, -1

Noble gases (Group 18):-+6,+4,+2.

However, the relative stabilities of these two oxidation states i.e the group oxidation state and the other oxidation state two unit less than the group oxidation state , may vary from group to group .

- 6) Atomic and Ionic radii :- As we move down the group in the p-block one extra shell than the preceding element gets added into the next element. This ultimately increases the atomic and the ionic radius of every next element down the group , which finally shows that the atomic and the ionic radii increases down the group. The trend is not same across the period. As we move from left to right in a period the Atomic radii and the Ionic radii of p-block elements decreases . The Atomic radius increases greatly from Boron to Aluminum. This increase is due to greater screening effect caused by the eight electrons present in the penultimate shell.
- 7) Electrode Potential :- The p-block elements generally have a positive electrode potential. It generally decreases down the groups.

For eg. Consider the electrode potentials of the halogen group:-

Fluorine = 2.87 V

Chlorine = 1.36 V

Bromine = 1.09 V

Iodine = 0.53 V

From the above analytical data we can say that the electrode potential in the p-block decreases down the groups .

8) Ionisation Energies: The p-block elements have high ionization potentials. The ionisation energies of p-block elements increases from left to right in a period due to increasing effective nuclear charge.

According to the general trends the ionisation energy values decreases down the group but do not decrease smoothly as expected. Non-metals have high Ionisation Energies than metals. It is maximum for a noble gas because noble gases have completely filled configuration. Some elements at the bottom of a group like Lead, Tin, Thallium, Bismuth, etc. behaves almost as a metal with very low ionization energies.

- 9) Magnetic Properties: The elements Radon, Astatine, Iodine and Polonium of the p-block are Non-Magnetic in nature. The element Tin is Paramagnetic and the rest all elements of the p-block are Diamagnetic in nature.
- 10) Complex Formation: The smaller size and the greater charge of the elements of different groups of p-block enable them to have a greater tendency to form complexes than the s-block elements. The complex formation tendency decreases down the group as the size of the atoms increases down the group.
- 11) Chemical Reactivity: The Chemical Reactivity of elements in the p-block increases as we move from left to right in a period. But as we move down in a group the chemical reactivity of elements decreases down the group.

#### i) Reactivity of Noble gases:-

All the orbitals of the noble gases are completely filled by electrons and it is very difficult to break their stability by the addition or removal of electrons. Thus the noble gases exhibit very low chemical

reactivity. Because of their low reactivity noble gases, are often used when an nonreactive atmosphere is needed, such as in welding.

Preceding the noble gas family there are two chemically important groups of non-metals. They are the halogens (Group 17) and the chalcogens (Group 16).

These two groups of elements have high electron gain enthalpies and can readily add one or two electrons forming an anion to attain the stable noble gas configuration thus showing good chemical reactivity.

#### ii) Reactivity of Halogens:-

- a) All halogens are naturally found in a combined state.
- b) Fluorine reacts readily with almost any substance coming in contact with it.
- c) Chlorine, Bromine, and Iodine are progressively less reactive but still form compounds with most other elements, especially metals.
- d) All the halogens are strong oxidising agents. The halogens oxidize other Substances, but themselves get reduced.
- e) All halogens combine directly with sodium to form sodium halides.
- f) All halogens react with red phosphorus to form phosphorus halides.
- g) Halogens react readily with alkali metals forming salts.
- h) The presence of Chlorine, Bromine and Iodine can be tested by the treatment of acidified silver nitrate solution.

#### iii) Reactivity of group VIA Elements (Chalogens):-

- a) As we approach to the right-hand side of the periodic table, similarities among the elements within a group become greater. This is true for the group VIA. Except Polonium, which is radioactive and usually omitted from all discussions.
- b) All members of the group VIA form X 2- ions when combined with highly electropositive metals.
- c) The tendency to be reduced to the 2 oxidation state decreases significantly from top to bottom.
- d) At ordinary temperatures and pressures, oxygen is a gas. It exists in either of the two allotropic forms :- 0.2, which makes up 21 percent of the earth's atmosphere, or 0.3 (ozone), which slowly decomposes to 0.2.
- e) The ozone itself absorbs longer-wavelength ultraviolet radiations , preventing these harmful rays from reaching the earth's surface which would otherwise increase the probability of human skin cancer and can also cause other environmental problems.

f) The Compounds of selenium and tellurium are of little commercial importance as they are toxic.

#### iv) Reactivity of Metalloids:-

- a) The chemical reactivity of the metalloids depends on the substance with which it is reacting. For example:- Boron behaves as a nonmetal when reacting with sodium, but it acts as a metal when reacting with fluorine.
- b) Thus from the above example we can say that Metalloids show variable chemical properties.
- c) They act like non-metals when they react with metals whereas they act like metals when they react with non-metals.
- d) Due to their low electronegativity, they are usually oxidized in reactions. The oxides of metalloids are usually amphoteric .

#### v) Reactivity of group VA Elements:-

- a) All the group VA elements form trihydrides when reacted with hydrogen.
- b) The reactivity decreases down the group.
- c) The elements in the group VA either form trioxides or pentoxides when reacted with oxygen.
- d) Also they form trihalides or pentahalides when reacted with halogens.
- e) All the group VA elements react with metals to form binary compounds.
- f) The most important compounds of the group VA elements are those of nitrogen and phosphorus.
- g) Nitrogen and phosphorus are most commonly used as fertilizer.

#### vi) Reactivity of group IIIA Elements:-

1) Unlike groups IA and IIA, none of the group IIIA elements react directly with hydrogen to form hydrides.

Also all the group IIIA elements react with halogens to form trihalides instead of simply halides like group IA and IIA elements.

#### vii) Reactivity of group IVA elements:-

- a) Carbon have a ability to form strong bonds with other carbon atoms and thus form a tremendous variety of organic compounds
- b) In the +4 oxidation state lead acts as a strong oxidizing agent, gaining two electrons and after gaining electrons it gets reduced to the +2 oxidation state.
- c) Also in the +4 oxidation state lead forms covalent compounds and bonds strongly to carbon.
- d) Besides the metals themselves, some tin and lead compounds are of commercial importance. For eg:-

Tin(II) fluoride (stannous fluoride), is added to some toothpastes to inhibit dental cares.

- e) Lead is also found in two main commercial applications. One, the lead-acid storage batteries used to start cars and the other is in the automobile fuel.
- 12) Conductivity: The conductivity of elements in p-block increases down the group. Generally the metals in the p-block are good conductors of heat and electricity whereas the non-metals are poor conductors of heat and electricity. The conductivity of metalloids lies in between the metals and non-metals.

## 13) Colour :-

### Colour of group IIIA elements:-

All the group IIIA elements are silvery solids except boron which is brown solid.

Colour of group IVA elements:-

Carbon is black in colour whereas silicon and germanium have reddish brown or dull grey or black colour. Lead has a bluish-white colour.

Colour of group VA elements:-

Nitrogen is a colourless.

Phosphorus exists in white colour.

Arsenic is found in yellow and grey solid form.

Antimony is found in a amorphous grey form.

Bismuth is silvery white in colour.

Colour of group 16 elements:-

Oxygen is a gas and is colourless.

Sulphur is pale yellow in colour.

Tellurium is Silvery-white in colour .

All the Halogens are coloured. They have following colours :-

Fluorine: - Pale yellow.

Chlorine: - Greenish yellow.

Bromine: - Reddish brown.

Iodine :- Violet black.

### Noble Gases have following colours:-

Helium is red, Neon is orange, Krypton is purple whereas Xenon is white in colour. Radon is colourless. Helium is used for filling air ships and weather balloons because they are light and non-inflammable.

Neon is used as Beacon lights.

Argon is used for filling electric bulbs because of its inert nature.

Krypton is used in discharge tubes, filament lamps and decorative sign tubes.

Radon finds its use in the treatment of cancer along with radium. It is used in radiotherapy.

14) Flame colouration: Not all but a few p-block elements impart characteristic colour to the flame. Arsenic impart Blue colour to the flame. Boron impart Bright green Colour to the flame. Copper (I) impart Blue colour whereas Copper(II) (non-halide) impart Green colour to flame whereas Copper(II) (halide) impart Blue- green colour to flame. Indium and selenium impart Blue colour to flame. Phosphorus impart Pale bluish green colour whereas Lead impart Blue/White colour to flame. Antimony and Tellurium impart Pale green colour. Thallium impart Pure green colour to flame.

#### d Block Elements

The elements in the groups from 3 to 12 or The elements in the groups IB, IIB, IIB, IVB, VB, VIB, VIB and, VIIIB of the periodic table are called as d-block elements. The 4th, 5th, 6th and 7th period consists of 10 elements each and are called as d-block elements. Thus, In all there are 40 d-block elements. The d-block elements have partially filled d-orbitals. They are placed in between the s-block and p-block elements in the periodic table. They are also called as Transition elements. The name "Transition" originates from their place between s and p-block elements in the periodic table. The d-block elements are all metals with their last two shells incompletely filled. The elements which have partially filled d-orbitals either ground state or in one or more of their ions, are called d-block elements or outer transition elements. Their properties are intermediate between s-block elements and

p-block elements. They are more electropositive than p-block elements but less electropositive than s-block elements. They form ionic compounds in their lower oxidation state and covalent compounds in higher oxidation states. They are all metals and have electronic configuration ns2, (n-1)d1 to 10 Characteristic Properties of elements in d-block of Modern Periodic Table:

The properties of d-block elements are intermediate between s-block and p-block elements.

1) Electronic Configuration :- The general electronic configuration of d-block elements is ns 2 ( n - 1 ) d1 to 10 . But in the elements of the 12th group i.e Zn, Cd and Hg ,the incoming electron occupy the ns shell instead of ( n - 1 ) d subshell which are already saturated and they should therefore, be excluded from d-block elements , But, since they posses properties similar to those of d-block elements, for all practical purposes they are placed with d-block elements.

## The d-block elements are classified into 4 series:-

a) 3d series containing 10 elements:-

They have incomplete 3d-orbital. Elements starting from Sc (21) to Zn (30) are present in these series.

For first series (Sc z=21) to (Zn z=30) Sc (z=21): 1s2, 2s2, 2p6, 3s2, 3p6, 4s2, 3d1.

```
\begin{array}{l} \text{Ti } (z=22): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d2. \\ \text{V } (z=23): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d3. \\ \text{Cr } (z=24): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s1, \, 3d5. \\ \text{Mn } (z=25): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d5. \\ \text{Fe } (z=26): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d6. \\ \text{Co } (z=27): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d7. \\ \text{Ni } (z=28): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d8. \\ \text{Cu } (z=29): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s1, \, 3d10. \\ \text{Zn } (z=30): 1s2, \, 2s2, \, 2p6, \, 3s2, \, 3p6, \, 4s2, \, 3d10. \\ \end{array}
```

b) 4d series containing 10 elements:-

They have incomplete 4d-orbital. Elements starting from Y (39) to Cd(48) are present in these series.

c) 5d series containing 10 elements:-

They have incomplete 5d-orbital. Elements starting from La (57) to Hf (72) to Hg (80) are present in these series.

d) 6d series containing 10 elements:-

They have incomplete 6d-orbital. This is the incomplete series.

- 2) Metallic Character: All the d-block elements have 1 or 2 electrons in their outermost shell and thus all are metals. All are hard, ductile and malleable solids with strong bonding due to their greater effective nuclear charge and large number of valence electrons (except Hg which is liquid).
- 3) Atomic and Ionic Radii: The Atomic and Ionic Radii of transition elements are smaller than their corresponding s-block elements and are greater than their corresponding p-block elements. The Atomic and Ionic Radii of transition elements for a given series show a decreasing trend for first 5 elements and then becomes almost constant for next 5 elements of the series. For eg: In 3d series atomic radius decreases from Sc(21) to Mn(25) and then becomes constant for next five, i.e. Fe(26) to Zn(30). This is due to the combined effect of increasing effective nuclear charge and increasing screening effect along the period.
- 4) Atomic volume and density: The size decreases along the period and therefore atomic volume also decreases along the period. Atomic volumes are smaller than group 1 and 2 members, i.e. s-block elements. The density, however, increases along the period.
- 5) Boiling and Melting points: All the transition elements have high M.P. and B.P., as compared to s-block elements due to their strong metallic bonding and unpaired d-electrons. M.P. of transition elements of a given series increases on moving from left to right in a period and attains a maximum value and after that M.P. goes on decreasing towards the end of period. These higher values are due to small atomic radii of transition elements which provides greater inter atomic forces of attraction. However Zn, Cd, Hg have relatively low values of M.P. and B.P. Due to their completely filled d-orbitals.

Melting and boiling point of these elements are very high (except Zn). These higher values are due to small atomic radii of transition elements which provides greater inter atomic forces of attraction. They are very hard .

6) Ionisation Energy: The Ionisation energy of d-block elements lies in between the of s-block and p-block elements. Thus they are more electropositive than p-block elements and less electropositive than s-block elements. Since smaller being atomic size, thus high Ionisation Energy is noticed for transition elements. Ionization Energy values first increases upto Mn(25) and then becomes irregular or constant due to irregular trend of atomic size after Mn(25) in 3d series, also similar trend is noticed in 5d and 6d series. However Zn, Cd, Hg have abnormally high values of Ionization Energy on account of greater stability of s-subshell.

7) Oxidation state: The Transition elements show variable oxidation state in their compounds. Reason for this variable oxidation state is that there is a very small energy difference in between (n-1)d and ns orbitals. As a result, electrons of (n-1)d orbitals as well as ns-orbitals take part in bond formation. Variation in oxidation state is related to their electronic configuration.

### For e.g:-

```
Ti : +2, +3, +4.

Cr : +1, +2, +3, +4, +5, +6.

Mn : +2, +3, +4, +6, +7.

Fe : +2, +3.

Cu : +1, +2
```

- 8) Standard Electrode Potential and Reducing properties: Expect Cu and Hg, the standard reduction potential of d-block elements in acid solution is generally negative, but however Cu and Hg are having positive electrode potential. The d-block elements are not good reducing agents in comparision to s-block elements due to their high heats of sublimation, high ionisation potential and low heats of hydration of their ions.
- 9) General Chemical Reactivity: The d-block elements have been unreactive in comparision to s-block elements due to their high ionisation energy, high heats of sublimation and low heats of hydration.

But however Transition metals vary widely in their chemical reactivity. Many of them are sufficiently electropositive to dissolve in mineral acids, although a few are 'noble', that is, they areunaffected by simple acids. The metals of the first series with the exception of copper are relatively more reactive and can be oxidised.

Transition metals form alloys among themselves. The alloys of transition metals are hard and have high melting point as compared to other metal.

- 10) Conductivity: All the Transition elements are good conductors of heat and electricity.
- 11) Colour :- Except zinc all the transition metals complex ions are colourless due to presence of unpaired electrons.

The colours exhibited by some transition metal ions are :-

```
    Cu2+ (Blue).
    Fe2+ (Green).
    Ti3+ (Purple).
    Mn3+ (Violet).
    Fe3+ (Yellow).
```

12) Flame colouration: The d-block elements impart no characteristic colour to the flame. We know that when an electron gains energy, it gets excited to a higher energy level, and when it looses that energy, it again comes back to the same level, by giving out some amount of radiation. This released energy appears in the form of colour. The d-block elements do not impart colour to the flame as their electron don't jump to the higher energy level when brought in the flame.

#### f Block Elements

14 elements from atomic number 58 (Cerium) to 71(Lutetium) are called as Lanthanides and the another 14 elements from atomic number 90 (Thorium) to 103 ( Lawrencium ) are called as Actinides. These 28 elements are arranged in the 2 series placed below the Modern Periodic Table and the elements in these 2 series are collectively called as f-block elements. These elements have outermost three shells incomplete . In these elements the last or differentiating electron enters in to the f-orbital of anti-penultimate shell or the 3rd shell from the outermost shell, Thus the f-orbital is partially filled and hence they are called as f-block elements. They are also called as " Inner Transition elements ". They are so called because the last electron enters in the f-orbital of anti-penultimate shell, which is inner and these elements are present between strongly electropositive s-block elements and strongly electronegative p-block elements . The general electronic configuration of the f-block elements is given as :-

(n-2) f1-14, (n-1) s2, p6, d0-1, ns2.

F- block elements are also called Inner transition elements. The last electron of these elements enters the 'f' sub shell. They are mostly radioactive elements. They are present beneath the main periodic table, in the form of two rows, one row belonging to lanthanides and the other row belonging to actinides.

### Lanthanides

The group of 14 elements from Cerium(58) to Lutetium(71) are placed alongwith lanthanum in IIIB group and in the 6th period of the periodic table in a series below the periodic table called as Lanthanides. They are also called as Lanthanoids or Lanthanones and are represented as Ln. In Lanthanoids the last or differentiating electron enters into 4f orbital of the anti-penultimate shell and hence the series of 14 elements in lanthanoids is called as 4f series.

Europium and gadolinium has half-filled f-orbital. Ytterbium and lutetium has fully filled f-orbital.

### Properties of Lanthanides:-

1) Electronic Configuration :- The General electronic configuration of Lanthanides is [Xe] 4f1-14 5d1 6s2

The complete electronic configuration of Lanthanides can be given as 1s2 2s2 2p6 3s2 3p6 3d10 4s2 4p6 4d10 5s2 5p6 . The Lanthanoids have partially filled 4f-orbital.But, However ,the first member Lanthanum and the last member Lutetium of the lanthanide series have no partially filled 4f-orbital and they should therefore, be excluded from Lanthanoids, But, since they posses properties similar to those of Lanthanoids, for all practical purposes they are placed with Lanthanoids . We know that 4f orbital is filled only after completing 5s, 5p and 6s orbitals. It is found that when the f-orbital contains 0, 7 or 14 electrons it is stable. The electronic configuration of Lanthanum which is followed by 14 lanthanides is 2,8,18,18,9,2 . In Lanthanum 4f subshell is vacant and 5d subshell contains one electron. Thus in Lanthanides 4f orbitals are successively filled,means from Cerium(58) to Lutetium(71) ,the Additional electron should occupy vacant 5f orbital and 5d orbital should remain singly filled up. Thus the electronic configuration of Lanthanides should be 2,8,18,19-32,9,2 .

But in observed electronic configuration, 5d1 electron gets shifted to 4f orbital and 5d orbital remains vacant. It is because energies of 5d and 4f orbitals are closely similar.

- 2) Metallic Character: Lanthanides are silvery white metals having tensile strength.
- 3) Atomic Density: Lanthanides have lighter density values ranging from 6.77 to 9.74 gm/cm3. Density increases with increase in atomic number.

- 4) Melting and Boiling Points: These elements posses high M.P. and B.P., but no regularity is seen with the increase in atomic number.
- 5) Oxidation state: All Lanthanides show a common stable oxidation state +3. It is because there are two electrons in the outermost shell and one electron in next to outermost shell i.e penultimate shell. Some Lanthanides show +2 and +4 oxidation states, these are observed in those elements, which by losing electrons attain the stable 4f0,4f7 and 4f14 configuration. Only +3 state is exhibited by La, Gd and Lu which is due to extract-ability of empty, completely half filled or completely filled 4f orbitals. Along with +3, other two oxidation states, +2 and +4 are exhibited by some members of this series.

Example: Eu and Yb can acquire +2 state as it provides them with extra stability.

The Ce4+ ion is stale and it can convert easily to Ce3+ thereby making the 4+ ion a very strong oxidizing agent.

- 6) Atomic and Ionic radii: In Lanthanide series, there is regular decrease in atomic size as well as atomic radii as the atomic number increases from Cerium to Lutetium. This decrease in size of atoms and ions is known as Lanthanide Contraction. On moving from Cerium to Lutetium, the atomic radii decreases from 165 pm to 156 pm and the ionic radii decreases from 103 pm to 85 pm.
- 7) Electrode Potential :- Due to Lanthanide Contraction the value of standard electrode potential increases regularly from La to Lu.
- 8) Ionisation Energies: Lanthanides have very low ionisation energies. Ionisation energy values are similar to alkaline earth metals, particularly calcium. Due to low ionisation energies, Lanthanides are highly electropositive in nature.
- 9) Magnetic Properties: Elements with paired electrons does not show any magnetism due to cancellation of the opposite spins due to pairing. Lanthanide ions having unpaired electrons and hence are paramagnetic, while those having all the orbitals with paired electrons are diamagnetic in nature. Lanthanum and Lutetium have all paired electrons and hence are diamagnetic in nature.
- 10) Complex Formation: Lanthanides do not have much tendency to form complexes due to their low charge density because of their large size. However, they form complexes with few chelating agents such as EDTA. The tendency to form complexes increases with increase in atomic number.
- 11) Chemical Reactivity: As all the Lanthanides show a similar electronic configuration and common +3 oxidation state, they show similar Chemical Reactivity. They react with carbon, hydrogen, oxygen and sulfur and form carbides, hydrides, oxides and sulphides respectively. The oxides formed are M2O3 oxides. They react with water and form insoluble hydroxides. The oxides and hydroxides react with CO2 and form carbonates, M2(CO3)3.
- a) All lanthanides react readily upon exposure to air and tarnish.
- b) They readily dissolve in hot water liberating hydrogen. They can also dissolve in cold water.
- c) They react with nitrogen and hydrogen forming the corresponding nitrides and hydrides.
- d) Lanthanides react with other non-metals such as halogens, sulphur, phosphorus, carbon and silicon and form corresponding compounds.

- e) The high oxidation potentials indicate their strong electro positive nature to act as strong reducing agents.
- f) Lanthanides react with acids and liberate hydrogen.
- 12) Conductivity:- Lanthanides are good conductors of heat and electricity.
- 13) Colour :- All Lanthanides are silvery white metals . The trivalent lanthanide ions are coloured both in solid state and in aqueous solution, this colour change is seen only in case of cations. The colour of a cation depends on the number of unpaired f electrons.

Lanthanides with either half-filled or completely filled orbitals are colourless.

In moving along the lanthanide series from Ce(58) to Lu (71) a regular decrease in the size of the atom/ion with increase in atomic number is observed.

This decrease in size is called the Lanthanide contraction. In this series the size of Lanthanum is maximum and that of Lu, lutetium is minimum. The decrease is size, though continuous, is not regular.

### **Reason for Lanthanide Contraction**

The cause of lanthanide contraction can be traced to the imperfect shielding of one 4f electron by another in the same sub-shell. On moving along the lanthanide series the number of 4f electrons increases by one unit at each step and the imperfect shielding increases, causing the contraction in electron cloud of the 4f sub-shell. Ionic radii changes from 1.06 A to 0.85A.

## **Important Consequences**

The lanthanide contraction plays a significant role in the chemistry of lanthanides. The important consequences of it are:

There is a steady decrease in ionic size.

There is a slight increase in electronegativity of the trivalent ions.

The Eo values for M3+ + 3e  $\rightarrow$  M(g) increases regularly from Lanthanum -252V to 2.25 V for Lutetium.

Since there is a very small change in the size of ions in the lanthanide series and there is no change in the outermost shell, there is a close resemblance in chemical properties.

Lanthanide contraction plays a significant role in the chemistry of lanthanides and heavier transition elements. The atomic radii of 5d transition elements are very close to those of the corresponding 4d transition elements.

Due to this the crystal structure and other properties of lanthanides are very similar.

## **Applications of Lanthanides**

Metallurgical applications: Some of the alloys of lanthanide elements find important metallurgical applications as reducing agents. Example: Misch meals (Ce- 30 to 35%)

Ceramic applications: Ce(III) and Ce(IV) oxides find use in glass polishing powders whereas Nd and Pr oxides are extensively used in coloring glass and in the production of standard light filters.

Catalytic applications: Some lanthanide compounds are used as catalysts. Example: Cerium phosphate is used in petroleum cracking as a catalyst.

Electronic applications: The ferromagnetic garnets of 3Ln2O3.5Fe2O3 type are used in microwave devices.

Nuclear applications: These elements and some of their compounds are used in nuclear control devices, shielding devices and fluxing devices. Sm - 140, Eu - 153, Gd- 155, Gd- 157 and Dy - 164 are some of the important isotopes used in nuclear technology.

### **Actinides**

The group of 14 elements from Thorium(90) to Lawrencium(103) are placed alongwith Actinum in IIIB group and in the 7th period of the periodic table in a series below the periodic table called as Actinides. They are also called as Actinoids or Actinones and are represented as An. In Actinoids the last or differentiating electron enters into 5f orbital, hence the series of 14 elements in Actinoids is called as 5f series. All Actinides are radioactive in nature.

Elements beyond Uranium are prepared synthetically in labouratory through nuclear reactions. The starting element for this purpose is always Uranium. Hence the elements from Neptunium to Lawrencium are called Transuranic elements ar Urenides.

# **Properties of Actinides:-**

1) Electronic Configuration: The general electronic configuration of Actinides is [Rn] 5f1-14 6d0-1 7s2. The Actinoids have partially filled 5f-orbitals.

The electronic configuration of Actinum which is followed by 14 Actinides is 2,8,18,32,18,9,2. In Actinum 5f subshell is vacant and 6d subshell contains one electron. Thus in Actinides 5f orbitals are successively filled, means the Additional electron should occupy vacant 5f orbital and 6d orbital should remain singly filled up. Thus the electronic configuration of Actinides should be 2,8,18,32,19-32,9,2.

But since it is not sure whether the last electron enters the 5f orbital or the 6d orbital as both have the same energy. Hence, there are two views regarding the electronic configuration of actinides. According to Seaborg view, the 5f orbital is filled from thorium, while in Dawson view the 5f orbital is filled from uranium and are called uranides.

- 2) Metallic Character: Actinides are silvery metals.
- 3) Atomic Density: All Actinides except Thorium and Americium have high Atomic density.
- 4) Melting and Boiling Points: These elements posses high M.P. and B.P. than the Lanthanides, but no regularity is seen with the increase in atomic number.

5) Oxidation state :- All Lanthanides show a common stable oxidation state +3 . The most stable oxidation state for first 3 elements

Thorium, Protactinium and Uranium is +4, +5 and +6.

Plutonium(Pu)shows all oxidation states from +3 to +7 but most stable is +4. Americium shows oxidation state from +2 to +6.

- 6) Atomic and lonic radii :- In the Actinide series ,there is regular decrease in atomic size as well as atomic radii as the atomic number increases from Actinium to Lawrencium. The size of ions decreases gradually along the series because extra charge of the nucleus is poorly shielded by f-electrons. It is called as Actinide Contraction and is similar to Lanthanide Contraction.
- 7) Electrode Potential :- Due to Actinide Contraction the value of standard electrode potential increases regularly from Ac to Lw.
- 8) Ionisation Energies: Actinides have lower ionisation energies than lanthanides because 5f is more effectively shielded from nuclear charge than 4f.

Due to low ionisation energies, Actinides are highly electropositive in nature.

- 9) Magnetic Properties: All Actinides have unpaired electrons and hence are paramagnetic in nature.
- 10) Complex Formation: Actinides have higher tendency to form complexes than Lanthanides. It is because of their higher charge and smaller sizes of cations. Halides of actinides form complexes with alkali metals. Theses elements form chelates with organic compounds such as EDTA and oxime.
- 11) Chemical Reactivity :- Actinides are highly reactive metals in fine state and very strong reducing agents.

### A few properties are given below.

- a) They react with boiling water to give oxide and hydride.
- b) They combine with most of non-metals at moderate temperature.
- c) All these metals are attacked by HCl acid but the effect of nitric acid is very small.
- d) They react with tarnish in air forming oxide coating.
- 12) Conductivity: Actinides are good conductors of heat and electricity.
- 13) Colour :- Actinide ions are coloured . It depends upon the number of electrons in 5f orbitals. Ions having no electron in f orbital or 7 electrons in 5f orbital are colourless. The ions with 2 or 6 electrons in 5f orbitals are coloured in both the crystalline and in solution state due to f-f transition of electrons.

We know that the periodic table is divided into four blocks, depending upon the sub shell the last electron enters. The arrangement of elements in the periodic property is such that some properties follow a definite pattern. The repetition of the elements with similar properties in the order of increasing atomic number as in the periodic table is called as Periodicity of properties.

## Cause of periodicity

The properties of an element are reflected in its electronic configuration. In the long form of the periodic table, atoms having similar outermost electronic configuration appear after regular intervals. Therefore, the properties are repeated after a regular interval. All elements belonging to a particular group have similar electronic configuration and hence they exhibit similar properties.

Atomic size: Size of an atom Decreases along the period

Along a Group Increases with addition of a main orbital

## Various Details of Chemical Elements, origin of their names and uses are given here

Tc - Technetium - ( p - 43, M - 98 ) ( Radioactive ) The first element in the periodic table which is radioactive. So lightest Radioactive and Naturally Radioactive elemement. Medically used for identifying blockages in the body.

( Left of Ru - Ruthenium ). Tc was synthesized.

### **Uses of Tantalum**

Ta - Tantalum - ( p - 73, M - 181 ) Ta was named after " Torments of Tantalus " which mean useless futile work. Tantalum was discovered after lot of try and lot of hard work ( Many false predictions in between ). Is used for making capacitors that are used in Mobile phones.

Nb - Niobium - ( p - 41, M - 93 ) Nb was discovered along with Tantalum. Niobium was daughter of Tantalus so the name! Niobium as an element and compounds have very similar properties as Vanadium and Tantalum.

F - Fluorine - ( p - 9, M - 19 ) F was last of the nonmetals discovered / separated in free state. Named after Greek Fluros meaning very destructive. Almost 30 scientists lost their lives and many more sustained burns and loss of laboratory equipments while trying to purify Fluorine. O2F2 , HF are some of the compounds.

Li - Lithium - ( p - 3, M - 7 ) From Greek Lithios meaning stone. Li was discovered in mineral kingdom while Na (Sodium) and K (Potassium) in plant kingdom. All Alkali elements are Silvery white Solid. When freshly cut has a bright luster. Li is more harder and lighter than other Alkali metals. Not affected by air easily and does not loose its lusture even after melting. Li reacts with H2O slowly to liberate H2. Li does not react with O2 below 0 deg C. Li when burnt in air gives monoxide Li20 while other alkali metals gives peroxides or super-oxides. Li20 is much less basic than oxides of other alkali metals. LiOH is much weaker base than NaOH or KOH. Li is the only Alkali metal which directly reacts with N2 to give Li3N. LiOH decomposes on heating to give Li2O. Hydroxides of other alkaline metals do not decompose. LiHCO3 is known in solution but not in solid state. While bicarbonates of other Alkali metals are known in solid state. Li2CO3 is less stable compared to carbonates of other Alkali metals. LiNO3 on heating gives mixture of NO2 and O2, 4LiNO3 -> 2Li2O + On heating gives li20 + CO2. 4NO2 + O2 while nitrates of other alkali metals yield only O2, 2NaNO3 -> 2NaNO2 + O2 the only alkali metal sulphate which does not form double salts e.g. alum. Li reacts with Br very slowly while all other alkali metals react violently. LiF, Li3PO4, Lithium Oxalate Li2C2O4, Li2CO3 are sparingly soluble in water. The corresponding salts of other alkali metals are freely soluble in water. LiCl is highly deliquescent (becoming liquid by absorbing moisture from the air) and soluble in Alcohol and pyridine. LiCl separates out from aqueous solutions as hydrated crystals LiCl.2H2O whereas Chlorides of other alkali metals are insoluble in organic solvents and do not form hydrated crystals under ordinary temperatures. Li when heated in NH3 forms imide Li2NH while other alkali metals form amides MNH2

Li shows lot of similarity with Mg known as diagonal relationship due to similarity in size, electronegativity and high polarizing power (Ionic Potential). (Ionic Chrage / (Ionic Radius)^2) [Cations with large Ionic potentials have a tendency to polarize the anions and to give partial covalent character to compounds] Li gives Crimson Red colour in flame test. Highest reducing power of Li in solution is due to its large heat of hydration.

Si - Silicon - ( p - 14, M - 28 ) The most abundant element on the Earth's crust ( after oxygen ). Si is 28% of Earth's crust. Latin name Silicium comes from Silex meaning hard stone. CO2 and SiO2 are acidic while GeO2, SnO2 and PbO2 are amphoteric in nature.

Al - Aluminium - ( p - 13, M - 27 ) 3rd most abundant element in Earth's crust. Diaspore Al2O3.H2O Gibbsite Al2O3.3H2O Bauxite Al2O3.2H2O Cryolite Na3AlF6 Alunite K2SO4.Al2(SO4)3.4Al(OH)3 Torquoise AlPO4.Al(OH)3.H2O is usually blue coloured due to presence of copper phosphate. Felspar KalSi3O8 . It is a good reflective material so used in front coating of mirrors in an experiment in contrast to normal bathroom mirrors where the reflective coating is in the back. Aluminium foils are widely used for packing medicines, or food etc. In 19 th century when it was isolated for the first time, it was very costly and was displayed in museums.

Th - Thorium - ( p - 90, M - 232 ) Named after Thor. The ancient Scandinavian God of Thunder. Thorium in air burns very intensely. When mixed with glass gives very high Refractive index and very low dispersion, so used for making high quality lenses. Solid Solutions of Thorium Di-oxide and Yttrium oxide is transparent like glass for visible region. With a melting point around 2200 C this is used for peep windows for high temperature furnaces.

V - Vanadium - ( p - 23, M - 51 ) Named after Godess Vanadis. Scandinavian Godess of Beauty. It is used to make certain types of Catalysts. There are certain mushrooms which are rich in Vanadium.

Xe - Xenon - (p - 54, M - 131) From Greek Xenos meaning stranger.

Hf - Hafnium and Re - Rhenium were last to be discovered even though these are stable. Hafnium oxide is being used as top layer of some computer chips and shows better properties than some other oxides which are being used. Hf (p - 72, M - 178.5) and Re (p - 75, M - 186.2) Rhenium is used in the alloy form in steel blades of aircrafts, as it gives good high temperature and stress properties. Rhenium is used as a catalyst. The name Rhenium is derived from river Rhine. Rhenium is one of the most rarest of the elements. Similar to Tungsten its boiling point is close to 6000 C. The only element which can form 8 different oxides. Rhenium is the only element that can form negatively charged univalent ions.

Sg - Seaborgium - ( p - 106, M - 263 ) The first element named after a living person, Glenn Seaborg who headed the team to make 6 artificial elements.

O - Oxygen - ( p - 8, M - 16 ) Oxus means acid. Gennas means maker. So Oxygen was "acid maker". Oxygen differs from other elements of group 6A due to small size, High electronegativity, and non availability of d-orbitals in the valence shell. Oxygen is a gas while other elements are solid. O2 is diatomic while S8, Se8 etc are complex molecules. Oxygen is 2 nd most electronegative element and thus highly non-metallic. Oxygen di-negative O(-2) is pretty common but for other elements it is less common. Oxgen shows oxidation state of only -2 ( except OF2 and peroxides ). It does not show +4 and +6 oxidation states as shown by others. Most abandunt element on Earth's crust with Si. Metals like Cu, Ag, Hg show lesser affinity with O2 to form oxide than with Sulphur to form Sulphide. ( This isdue to polarizing power of Cu(+2), Ag(+1), Hg(+2) ion. This gives strong bonds with S(-2).

## **Elements known since Antiquity -**

- C Carbon (p 6, M 12) 17 th most abundant element. Catenation is the tendency to form long open or closed chains by the combination of same atoms. Carbon shows maximum catenation tendencies. Only Carbon can form double and triple bonds due to small size. Si, Ge, Sn and Pb are too big for the p orbitals to overlap and form bonds. Also Carbon chains can be very large while Si or Ge chains are max of 6 atoms. Graphite is prepared by Acheson process. CO2 and SiO2 are acidic while GeO2, SnO2 and PbO2 are amphoteric in nature.
- S Sulphur ( p-16, M-32 ) Chemosynthesis is oxidation of element by bacteria. Nitrogen, Sulphur, Iron, Hydrogen and Antimony are the only elements which can undergo Chemosynthesis.

Au - Gold - (p - 79, M - 197)

- Ag Silver ( p 47, M 108 ) Argentite Ag2S Horn Silver AgCl . Siver has the higest electrical conductivity amongst all elements.
- Fe Iron (p 26, M 55.8) Ferrous Ammonium Sulphate (Mohr's salt) (NH4)2SO4.FeSO4.6H2O Haematite Fe2O3 Magnetite Fe3O4 Limonite F2O3.3H2O Siderite FeCO3. Steel rods are used in Nuclear reactors for slowing down and absorbing Neutrons. Because Iron atom is a very stable atom, and after absorbing Neutrons does not convert to Radioactive elements. Chemosynthesis is oxidation of element by bacteria. Nitrogen, Sulphur, Iron, Hydrogen and Antimony are the only elements which can undergo Chemosynthesis.
- Pb Lead ( p 82, M 207 ) Galena PbS. Ionisation energy decreases regularly from C to Sn. Pb however shows a higher value than Sn due to poor shielding of f-orbitals. Electronegativity of Pb is higher ( or almost same ) than Sn. Pb(+2) compounds are more stable than Pb(+4) compounds. Thus Pb(+4) compounds actas oxidizing agents. Lead shows no tendency of catenation. ( The tendency to form long open or closed chains by the combination of same atoms ). Carbon shows maximum catenation tendencies. CO2 and SiO2 are acidic while GeO2, SnO2 and PbO2 are amphoteric in nature. PbCrO4 Chrome Yellow is used as Yellow Pigment. Lead Chromate PbCrO4.PbO is Red, also used as pigment. 2PbCO3.Pb(OH)2 in linseed oil is used as white paint. In electrolysis Lead cathode vanishes and gets deposited in Anode. Bismuth, Lead, Tin and Antimony settle in Anode in an eletrolysis experiment.
- Sn Tin (p 50, M 118.7) Cassiterite SnO2. CO2 and SiO2 are acidic while GeO2, SnO2 and PbO2 are amphoteric in nature. Tin produces a peculiar sound when bent known as Tincry. Tin is not attacked by organic acids. So is used to make protection layer in cooking vessels and cooking oil containers. Solder 67% Sn 33% Pb , Bronze 75-90% Cu 25-10% Sn , Bell metal 80% Cu 20% Sn. Named from latin Stanum. Bronze swords were stronger than copper swords. Tin is used in alloy to make solders for electronic circuits / boards. In electrolysis Tin cathode vanishes and gets deposited in Anode. Bismuth, Lead, Tin and Antimony settle in Anode in an eletrolysis experiment.
- Hg Mercury ( p 80, M 200.6 ) Alkaline solution of K2HgI4 ( Nessler's reagent ) gives Brown precipitate with NH3 called iodide of Millon's base ( H2NhgOHgI) Calomel Hg2Cl2 Calomel. Cinnabar HgS HgCN precipitates Pd but not other Platinum metals. Mercury boils at 357 C.

## Elements Discovered in Middle Ages -

- P phosphorus ( p 15, M 31 ) Greek Phos means Light. Phero means " I carry ".So Phosphorus means " I carry light ". Minerals Phosphorite Ca3(PO4)2, Flourapatite 3Ca3(PO4)2.CaF2, Chlorapatite 3Ca3(PO4)2.CaCl2 Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth are collectively known as pnicogens. Their compounds are known as pnictides.
- As Arsenic (p 33, M 75) Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth are collectively known as pnicogens. Their compounds are known as pnictides.
- Sb Antimony (p 51, M 122) Indium and Antimony together as an alloy is used for Electronics, because it is a semiconductor. Antimony is used as a catalyst to make Chloro Fluoro carbons. Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth are collectively known as pnicogens. Their compounds are known as pnictides. Antimony is very toxic. Similar to Gallium and Bismuth, Antimony increases in volume when solidifies from liquid. Chemosynthesis is oxidation of element by bacteria. Nitrogen, Sulphur, Iron, Hydrogen and Antimony are the only elements which can undergo Chemosynthesis. In electrolysis Antimony cathode vanishes and gets deposited in Anode. Bismuth, Lead, Tin and Antimony settle in Anode in an eletrolysis experiment.
- Bi Bismuth (p 83, M 209) Nitrogen, Phosphorus, Arsenic, Antimony and Bismuth are collectively known as pnicogens. Their compounds are known as pnictides. Similar to Antimony and Gallium, Bismuth increases in volume when solidifies from liquid. In electrolysis Bismuth cathode vanishes and gets deposited in Anode. Bismuth, Lead, Tin and Antimony settle in Anode in an eletrolysis experiment.
- Zn Zinc (p 30, M 65) Zinc Sulphate (White Vitriol) ZnSO4.7H2O Zinc Blende ZnS Calamine ZnCO3 Zincite ZnO. Many enzymes in body have Zinc and is vital for the reactions to happen. Zinc helps in absobing chemicals in the body. So many medicines come along with Zinc to increase absorbtion. Zinc coated steel sheets are known as galvanised sheets, used for roofs. Zinc washers are used in underwater equipments or in boats to localize corrosion.

# **Elements Discovered by Chemical Analysis -**

- Co Cobalt (p 27, M 59) Used to make very small powerful magnets, which are particularly used in Colour Televisions speakers, as big magnet would affect the electrons from the guns and distort the colours. Powdered Cobalt is used for catalytic reactions.
- Ni Nickel (p- 28, M 58.7) Found in Canada. It is pretty toxic and has melting point within room temperature. Some people can be allergic to Nickel. Is used for plating Tin containers, steel plates etc.
- Mn Manganese (p 25, M 55)
- Ba barium ( p 56, M 137 ) Barytes BaSO4. BaO is an excellent drying agent especially for Organic bases such as Pyridine. BaO2 is used for preparation of H2O2. Ba(OH)2 is used for preparation of standard alkali solution for titrating acids. BaCl2 is used as a laboratory reagent for test of sulphate radical. Ba(ClO3)2 is used for producing Green fire and preparation of Chloric acid. Barium absorbs X-rays very well, so used for observing certain parts of body by giving the patient a Barium milk or Barium Anema ( as the case may be ). First named as Barot, then Barite from Greek Barus Heavy. As it is a heavy Earth metal so Barium. Many types of spark plugs were made with Barium Nickel alloy.
- Mo Molybdenum ( p 42, M 96 ) Mo is essential for life to exist as it is part of an enzyme called nitrogenase, which is responsible to absorb Nitrogen from atmosphere and convert it to proteins. A type of Bacteria that exists in the roots of beans, have Nitrogenase, convert the atmospheric Nitrogen to compounds which become part of the beans, and thus as food, become part of our body as Proteins.

W - Tungsten - (p - 74, M - 184) - Tungsten has a boiling point close to 6000 C similar to Rhenium.

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Te - Tellurium - (p - 52, M - 177.6)
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Sr - Strontium - (p - 38, M - 87.6) Mineral Celestine SrSO4, Strontianite SrCO3. Strontium 90 is radioactive which is produced in Nuclear Reaction experiments. In 1950s and 60s Strontium 90 got dispersed in the atmosphere quite widely to be ultimately seen in bones and teeth of people, resulting in lot of fear and protests. Named after a small village Strontian, in Scotland, where Strontianite mineral was found. Used in Asia for Pyroworks, and later for signaling ships. Was used to extract Sugar from molasses before Calcium started being used for the same. Radioactive Strontium-90 cells of the size of a matchbox can emit electrons which can be converted to electricity for 20 years.

Zr - Zirconium - ( p - 40, M - 91 ) Used for coating / cladding of Nuclear Fuel rods, used in Reactors. Used in cutting tools and instruments as it is very hard. Oxide known as Zirconia, is use for catalysts.

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U - Uranium - ( p - 92, M - 238 )

Ti - Titanium - ( p - 22, M - 48 )

Cr - Chrimium - ( p - 24, M - 52 )
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Be - Beryllium - ( p - 4, M - 9 ) Be is more chemically similar to Al being amphoteric than Mg - Magnesium of Group 2A. Berylium was hiding behind Alumina and was very difficult to be identified. The standard oxidation potential values of Be and Al are very close to each other. Electronegativity values are same. Mineral Beryl 3BeO.Al2O3.6SiO2 Be does not decompose in water due to low value of oxidation potential. Has tendency to form covalent compounds. Does not react directly with Hydrogen. (BeH2)n is a polymeric solid. BeCO3 is not stable towards heat. Sulphate is soluble in water due to high degree of solvation of small Be(2+) ions. Its compounds do not impart any colour in the flame, due to very high energy needed to excite the electron to higher states. It forms many chelate complexes.

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Ni - Niobium - ( p - 28, M - 58.7 )

Ta - Tantalum - ( p - 73, M - 181 )
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## **Elements Discovered by Electrochemical Methods -**

Na - Sodium - ( p - 11, M - 23 ) 7 th most abundant. All Alkali elements are Silvery white Solid. Most abundant Alkali metal. Chile Saltpeter NaNO3, Glauber's Salt Na2SO4.10H2O , Trona Na2CO3.2NaHCO3.3H2O , Natron Na2CO3.H2O , Tincal ( Borax ) Na2B4O7.10H2O , Cryolite Na3AlF6 , Soda Felspar NaAlSi3O8 Na gives Golden Yellow colour in flame test. Yellow colour of Na2O2 is probably due to presence of small amount of superoxides.

K - Potassium - ( p - 19, M - 39 ) 8 th most abundant. Carnallite KCl.MgCl2.6H2O , Kainite KCl.MgSO4.MgCl2.3H2O , Indian Saltpeter KNO3 , Feldspar K2O.Al2O3.6SiO2 , Polyhalite K2SO4.MgSO4.CaSO4.6H2O , Sylvine kCl All Alkali metals are paramagnetic. While their salts are diamagnetic. K gives pale violet colour in flame test.

Mg - Magnesium - ( p - 12, M - 24 ) Minerals - Magnesite MgCO3, Dolomite MgCO3.CaCO3, Carnallite KCl.MgCl2.6H2O, Epsomite MgSO4.7H2O, Asbestos CaMg3(SiO3)4 Kieserite MgSO4.H2O. Mg is an essential constituent of Chlorophyll.

Ca - Calcium - (p - 20, M - 40) Gypsum CaSO4.2H2O, Fluorspar CaF2, Limestone CaCO<sub>3</sub>

### **Elements Predicted from Periodic Table -**

Ga - Gallium - ( p - 31, M - 69.7 ) - Mendelev predicted this as Eka-Aluminium. Gallium was the first element discovered amongst the Mendelev's more than a dozen predictions in around 1870. Named after Gallia the Latin of France. Has a low melting point 29.8 C, close to body temperature; so in some hot countries it is a liquid. This low melting point of Gallium and certain Alloys of it help making Fire alarms, so that these melt easily, and complete an electrical circuit to raise the alarm. The mineral Hallite in a mines of South-East Africa contains upto 37% Gallium. Coal Ash of some places are very rich in Gallium ( a few grams per tons of Ash ). Similar to Sodium it can be cut by knife. Similar to Antimony and Bismuth, Gallium grows in volume when solidifies from liquid. Gallium thermometers can be used for temperatures over 1000 C and over. ( A level Mercury thermometers cannot even approach as Mercury boils at 357 C ).

Sc - Scandium - (p - 21, M - 45) - Mendelev had predicted Scandium as Eka-Boron from his periodic table. It is a shiny light metal. Its ability to store Hydrogen for car fuels is being explored.

Ge - Germanium - ( p - 32, M - 72.6 ) Named after Germany. CO2 and SiO2 are acidic while GeO2, SnO2 and PbO2 are amphoteric in nature. Ge is not attacked by dilute HCl. But when heated in HCl gas Germanium Chloroform GeHCl3 is formed. Can be used for polished mirrors.

### The 6 Platinum metals -

Ru - Ruthenium - ( p - 44, M - 101 ) Named after Ruthenia ( old named of Russia ). As first element discovered by a Russian Scientist.

Rh - Rhodium - ( p - 45, M - 103 ) Named due to Red colour of 1st Salt produced. Greek Rodon means Rose. ( Are all Roses Red? ). Rh is least abundant amongst Pt metals. Very widely used in Catalysts. Is very costly. Industrially Methanol ( CH3OH ) and Carbon Monoxide ( CO ) is joined togather to synthesize Ethanoic acid ( C2H5OH ) using Rhodium Catalysts.

Pd - Palladium - ( p - 46, M - 106.42 ) HgCN precipitates Pd but not other Platinum metals. Palladium is most abundant amongst these 6 metals but was discovered the last. Palladium was named in honour of Pallas Athena ( Greek Goddess of Wisdom, War, Civilisation ).

Os - Osmium - ( p - 76, M - 192 ) From Greek Osme, meaning smell. Osmium oxide is volatile and has peculiar smell.

Ir - Iridium - (p - 77, M - 192) Got its name due to variety of colour of its salts. Greek Iris means Rainbow. The Iridium catalysts are more effective than Rhodium catalysts. So chemical engineers get more yield of compounds in the same plant using Iridium catalysts.

Pt - Platinum - (p - 78, M - 195) The 2nd most abundant element amongst the 6 elements.

# Elements named after Asteroids / Gods -

Pd - Palladium - ( p - 46, M - 106 ) HgCN precipitates Pd but not other Platinum metals. Palladium is most abundant amongst 6 Platinum metals but was discovered the last. Palladium was named in honour of Pallas Athena ( Greek Goddess of Wisdom, War, Civilisation ).

Ce - Cerium - (p - 58, M - 140) Named after a "recently" discovered asteroid Ceres (1801)

### Elements named after colour -

- Cr Chromium ( p 24, M 52 ) Greek Chroma means colour. Almost all compounds of Cr are of some colour. Siberia is the birthplace of Cr. One of the quite abundant element in the Earth's crust. ( 0.02% of Earth's crust by mass ). Crocoite is PbCrO<sub>4</sub>
- Cl Chlorine ( p 17, M 35.5 ) Named after Greek Chloros meaning Yellow-Green. [ The word Halogen in Greek means Salt Producing i.e. Salt + Produce ]
- I Iodine (p 53, M 127) From Greek Iodes meaning Violet Colour.
- Rh Rhodium (p 45, M 103) Named due to Red colour of 1st Salt produced. Greek Rodon means Rose. (Are all Roses Red?). Rh is least abundant amongst Pt metals.
- Cs Cesium (p 55, M 133) From Latin Caesius. Blueness of the upper part of the firmament (Celestial Sphere The apparent surface of the imaginary sphere on which celestial bodies appear to be projected). Cs had Blue vapor. Also Blue spectral lines. All Alkali elements are Silvery white Solid. In flame test gives sky Blue colour. Melting point 28.5 C. Cesium has the best photo-electric effect, so very widely used for Photocells.
- Rb Rubidium (p 37, M 85.5) 2nd element discovered by spectroscopy. Latin Rubidius means deep red colour. Rb had red spectral lines. All Alkali elements are Silvery white Solid. In flame test gives Reddish Violet colour. Rubidium also gives out electrons very easily, but not as good as Cesium.
- Tl Thallium (p 81, M 204) 3rd element discovered by spectroscopy. Greek Thallos (new Green Branch) Tl had Green spectral lines. Thallium salts are very poisonous. Thallium salts of Bromine and Iodine as a combination (Red in coulur) is used for making windows used in infrared experiements.
- In Indium ( p 49, M 115 ) Extremely bright Blue spectral lines. Named after Indigo meaning Bright Blue.
- Ir Iridium ( p 77, M 192 ) Got its name due to variety of colour of its salts. Greek Iris means Rainbow.
- Sc Scandium and Y Yttrium are considered as part of "Rare Earth elements" along with Lanthanides. Rare Earth elements are almost 1/3 rd of the total elements, but took 113 years to discover all mainly due to rare availability and very similar chemical behavior. Y Yttrium was the first to be discovered. Lu Lutetium being the last. Pm Promethium was prepared artificially. La Lanthanum in Greek means to lie hidden. Solid Solutions of Thorium Di-oxide and Yttrium oxide is transparent like glass for visible region. With a melting point around 2200 C this is used for peep windows for high temperature furnaces.
- La Lanthanum ( p 57, M 139 ) Is the biggest by size amongst all Lanthanides, so most reactive. Is very soft and can be cut by a knife. La with Cu as a compound ( Lanthanum-Cuprate ) is used for catalysts. Lathanum has the property to absorb Hydrogen like a sponge and thus has application in Hydrogen fueled cars. Lanthanum has also been used for special lighting in Hollywood studios.

### Elements named after smell -

Br - Bromine - (p - 35, M - 80) Named after Greek Bromos which means stinking.

Os - Osmium - ( p - 76, M - 190 ) From Greek Osme, meaning smell. Osmium oxide is volatile and has peculiar smell.

# **Elements discovered by Spectroscopy -**

Cs - Cesium - (p - 55, M - 133) From Latin Caesius. Blueness of the upper part of the firmament (Celestial Sphere - The apparent surface of the imaginary sphere on which celestial bodies appear to be projected). Cs had Blue vapor. Also Blue spectral lines. 1st element established by spectroscopy. Cs is the strongest reducing agent amongst all the Alkali metals because ionization energy decreses down the group.

Rb - Rubidium - (p - 37, M - 85) 2nd element discovered by spectroscopy. Latin Rubidius means deep red colour. Rb had red spectral lines. All the Alkali metals are Silvery white elements. Can be cut by knife except Li. Softness increases down the group due to longer bond length. In flame test the salts of Rb gives violet colour. Reducing property increases down the group, because ionization energy decreases down the group.

Tl - Thallium - (p - 81, M - 204) 3rd element discovered by spectroscopy. Greek Thallos (new Green Branch) - Tl had Green spectral lines.

In - Indium - ( p - 49, M - 115 ) Extremely bright Blue spectral lines. Named after Indigo meaning Bright Blue.

He - Helium - ( p - 2, M - 4 ) New spectral lines were first observed in Sun rays ( So discovered outside Earth ). Later discovered in Hot springs and Alpha-particles trapped inside rocks as He, produced due to Radio activity.

## **Elements named after Places -**

Y - Ytterbium - (p - 39, M - 89) Ytterby is Swedish village where the mineral Ytterbite is available. Ytterbium was discovered from Ytterbite so the name!

Lu - Lutetium - ( p - 71, M - 175 ) Named after old name of Paris - Lutetia. Is used to date the meteorites. Used for treatment of cancer.

Ho - Holmium - ( p - 67, M - 165 ) Named after old name of Stockholm. It has the Highest Magnetic Moment amongst all the elements. ( Due to a large number of unpaired electrons )

Tm - Thulium - ( p - 69, M - 169 ) Named after a legendary country tale Thule the world's end. Tm was so difficult to purify and discover. In beginning of 1900s Charles James, purified Thulium Chloride, by a record of 15,000 recrystalisations. So it is very expensive.

Se - Selenium - (p - 34, M - 79 ) Se was discovered late because it was hiding behind S (Sulphur) and Te (Telurium). Selenium is named after Greek Selenus meaning moon.

### Radioactive Elements -

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Po - Polonium - ( p - 84, M - 209 ) ( Radioactive )
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Ra - Radium - (p - 88, M - 226) (Radioactive)
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Ac - Actinium - ( p - 89, M - 227 ) ( Radioactive ) The actinides have been named after Actinium. Actinium glows with a light bluish tinge in dark. It is more lethal and toxic than Polonium which was considered to be most lethal once upon a time.

 $\mbox{Rn}$  - Radon - (  $\mbox{p}$  -  $\mbox{86}$  ,  $\mbox{M}$  -  $\mbox{222}$  ) ( Radioactive ) Radon is produced by Radioactive decomposition of other elements. So houses made above Granite deposites often contain more than average level of Radon. This Radioactive gas can cause lung cancer.

Pa - Protactinium - (p - 91, M - 231) (Radioactive) Only 125 kg was purified from 60 tons of nuclear waste after 12 costly steps. This being radioactive, has not much of use.

```
Fr - Francium - (p - 87, M - 223) (Radioactive)
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Rf - Rutherfordium - ( p - 104, M - 261 ) - ( Radioactive ) Rutherford in 1919 bombarded Nitrogen with Alpha particles to produce some Oxygen atoms. This was amongst the first examples of transformation of elements.

# **Synthesized Elements -**

 $\mbox{Tc}$  - Technetium - ( p - 43, M - 98 ) ( Radioactive ) The first element in the periodic table to be radioactive.

Pm - Promethium - ( p - 61, M - 145 ) ( Radioactive ) The only Lanthanide which is radioactive. So its chemistry is hardly studied.

At - Astatine - ( p - 85, M - 210 ) ( Radioactive ) No particular use, as it is radioactive. The atoms and the compounds decay very fast, so chemists could not study Astatine much.

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Fr - Francium - (p - 87, M - 223) (Radioactive)
```

# **Transuranium Elements -**

Np - Neptunium - ( p - 93, M - 237 ) ( Radioacive ) Was the first synthetic element. Also found in traces in Nuclear Bomb experiement sites.

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Pu - Plutonium - (p - 94, M - 244) (Radioactive)
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Am - Americium - ( p - 95, M - 243 ) ( Radioactive ) The only synthetic elements used widely in households. This is part of the "smoke Detectors", due to its ability to detect various ions in air, as it happens in case of smoke.

Cm - Curium - ( p - 96, M - 247 ) ( Radioactive ) Named after Marie Curie and Pierre Curie. Can be used for thermoelectric generators, but practical / commercial use is shunned because highly radioactive and has be produced artificially.

Bk - Berkelium - (p - 97, M - 247) A 3 billionth of a gram was made in Berkeley, and was just enough to observe some spectroscopical data.

Cf - Californium - ( p - 98, M - 251 ) ( Radioactive ) It is used to detect metal fatigue and stress, as the instruments for observing these have Californium. Also used in metal detectors. Similar to Americium it is commonly used in household appliances.

Es - Einsteinium - ( p - 99, M - 252 ) ( Radioactive ) First found in the debri site of an Nuclear Bomb experiment.

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Fm - Fermium - ( p - 100, M - 257 ) ( Radioactive )
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Md - Mendelevium - (p - 101, M - 258) (Radioactive)

No -Nobelium - (p - 102, M - 259) (Radioactive)

Bh - Bohrium - (p - 107, M - 262) (Radioactive)

Db - Dubnium - ( p - 105, M - 262 ) ( Radioactive ) Named after Russian atomic research centre at Dubna.

Uuu - Unununium - Rg - Roentgenium - ( p - 111, M - 272 ) Artificially made. Named after Roentgen the 1st Nobel Laureate in Chemistry.

Uub - Ununbium - ( p - 112, M - ) Copernicium was synthesized in 1996 at GSI

Uut - Ununtrium - (p - 113, M - ) Sythesized in accelerator facility at RIKEN, Japan.

Uup - Ununpentium - ( p - 115 , M - ) Made artificially. Belongs to VA group.

Uus - Ununseptium - ( p - 117, M - ? ) Very difficult to synthesize as 117 proton number seems to be highly unstable.

B - Boron - ( p - 5, M - 11 ) Boron has maximum covalency of 4 due to non-availability of d-electrons. While all other elements of Group 3A have max covalency as 6.

Boron alone exhibits allotropy in the group. Boron shows +3 oxidation state while others in 3A shows +1 and +3. Boron does not form cations in aqueous solutions as the hydration energy is less than sum of the 3 successive ionization energies. Boron halides are monomeric while other halides of 3A are dimeric. Boron does not show iner pair effect. Boron forms a number of volatile hydrides which are electron deficient compounds. Others form only one polymeric hydride. Thallium does not form hydride. Boron does not decompose water or steam, while other elements of 3A decompose water or steam. B2O3 is acidic in nature. Other oxides of 3A are either amphoteric or basic. B(OH)3 is a weak acid, Al(OH)3 is amphoteric in nature. Boron is not attacked by non-oxidising acids, while other elements are attacked. Boron dissolves in conc. HNO3 forming H3BO3. The other elements become passive esp. Al, Ga. Boron combines with metals and form borides while other elements do not combine. They can form alloys. BCl3 is fuming liquid, while AlCl3 is a solid.

Minerals - Borax (Tincal ) Na2B4O7.10H2O Colemanite Ca2B6O11 5H2O Panderinite Ca2B6O11.3H2O Boracite 2Mg3B8O15.MgCl2 Boronatro Calcite CaB4O7.NaBO2.8H2O Kernite ( Rasorite ) Na2B4O7.4H2O Boric Acid H3BO3

#### Boron Banana Bond

- B2O3 Boron Trioxide is also called Sesquioxide. Borax Sodium Tetraborate Na2B4O7.10H2O
- N Nitrogen (p 7, M 14) Nitrogen is a gas while other members of Group 5A are solids. Catenation property of N is known. Chains upto 8 Nitrogen atoms are known. Chile Saltpeter NaNO3 Indian saltpeter KNO3. Chemosynthesis is oxidation of element by bacteria. Nitrogen, Sulphur, Iron, Hydrogen and Antimony are the only elements which can undergo Chemosynthesis.
- Pr Praseodymium (p 59, M 141) Praseodymium has lots of uses. Added in some types of Silicates, produces a material with very high refractive index that can reduce the speed of light to mere 300 m/sec. Also used in the coils, that were used to produce very low temperature close to 0 Kelvin. (1 billionth of a degree away from Zero kelvin). Is used in welder's goggles to filter out harmful UV lights.
- Kr Krypton ( p 36, M 83 ) Can make compounds with Fluorine. A very high energy UV light is needed to break the F-F bond and make Kr Fluoride. Kr Fluoride is used to make very high energy UV pulse LASERS.
- Eu Europium (p 63, M 152) This Lanthanide is not radioactive and its salts are used for getting various colours in the Picture / cathode ray tube when bombarded by electron guns. Europium salts were particularly used for getting Red and Blue colour in the beginning of colour television sets.
- Tb Terbium (p 65, M 159) Similar to Europium the salts of Terbium is used to give Green and Yellow colours in the Picture / cathode ray tube when bombarded by electron guns. Used as a marker in Biochemistry experiments due to its fluorescence nature. In certain magnetic materials, which contain Terbium the size changes with direction of Magnetic field, giving rise to many technical applications.
- Sm Samarium (p 62, M 150) Samarium is known to change its oxidation states very easily and thus has quite a few uses. It is a good Neutron absorber so has uses in Nuclear power plants for slowing down and controlling the Nuclear reactions. Samarium is used to date the old samples of rocks such as moon rocks.
- Ar Argon ( p 18, M 40 ) Nearly 1% of Earth's Atmosphere is Argon ( 0.93% ). It is widely used for packaging pure elements and compounds to avoid oxidation by atmospheric Oxygen. Purged and blown around liquid metals, such as Aluminium or Iron to stop action of Oxygen, Nitrogen etc. Neon lights made of Argon gives nice Blue colour.
- Dy Dysprosium ( p 66, M 162.5 ) This lanthanide is very good in absorbing Neutrons. So used as coatings of Nuclear rods and control the Nuclear reactions. When mixed with Sulphur and Cadmium can produce Infrared when irradiated with EM waves. This Infrared is used to study structure of molecules by studying the absorption spectra.
- Cd Cadmium (p 48, M 112) Used in batteries. As a metal it is toxic but various compounds of Cadmium are used for colouring, such as Plastic pipes. Cadmium Sulfide has Orange colour and commonly used as a dye. Cadmium was named after Cadmea in Greek which meant Zinc Ore. An alloy of 99% Cd and 1% Ni is used in bearings as antifriction.

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## Topic wise grouping of information kind of Dictionary of General Chemistry

Graphite and Diamond comparison

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

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

#### Solution :

The given facts about graphite and diamond are as follows.

Graphite is less hard than diamond. Graphite has higher electrical and thermal conductivities than diamond. This is due to highly delocalized nature of  $\pi$  electrons. Graphite has higher C—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:

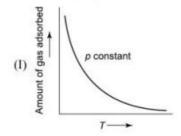
The stability of lyophobic colloidal particles is due to the preferential adsorption of common ion from the solution. Each colloidal particle has the same charge and are thus kept away from each other due to electronic repulsion (choice a).

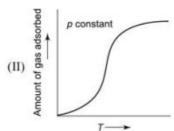
There exists potential difference between the fixed and diffused layer of opposite charge (choice d).

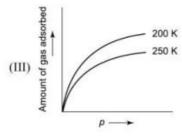
Therefore, the choice (a) and (d) are correct.

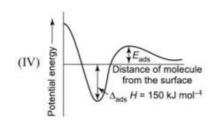
Physiorption and Chemisorption comparison

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









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

#### Solution:

We have the following facts.

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

With these guidelines, we will have

Graph I represents physisorption

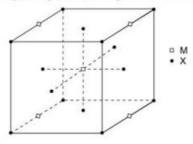
Graph III represents physisorption

Graph II represents chemisorption Graph IV represents chemisorptions

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

-

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



The empirical formula of the compound is

- (a) MX
- (b) MX<sub>2</sub>
- (c) M<sub>2</sub>X
- (d) M<sub>5</sub>X<sub>14</sub>

### Solution .

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

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

unit cell is

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

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

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

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

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

Which of the following halides react(s) with AgNO<sub>3</sub>(aq) to give a precipitate that dissolves in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq)?

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

## Solution:

The precipitates of AgCl, AgBr and AgI are soluble in Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>(aq) forming the complex Na<sub>3</sub>[Ag(S<sub>2</sub>O<sub>3</sub>)<sub>2</sub>]. 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)  $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$



We will have

 $T_1 = T_2$  as the expansion is isothermal.

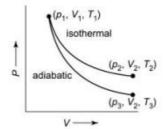
 $T_3 < T_1$  as the adiabatic expansion involves cooling.

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

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

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

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



Acid Ionization Constant 
$$K_a = \frac{[H^+] [A^-]}{[HA]}$$
 Adibiatic change 
$$PV = k$$
 Base Ionization Constant 
$$K_b = \frac{[OH^-] [HB^+]}{[B]}$$
 Bohr Radius 
$$a_0 = \frac{\hbar^2}{m_e k e^2}$$
 Boiling Point Elevation 
$$\Delta T_b = iK_b \times molality$$
 Buffer Design Equation 
$$pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$$
 Cell Voltage 
$$E_{cell} = E_{cell}^\circ - \frac{RT}{n\Im} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q$$
 Charles' Law

## **Atomic Structure**

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

Rydberg Equation 
$$\Delta E=R_H\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right)$$
 Speed of Light to Wavelength and Frequency Relationship 
$$c=\lambda\nu$$

# Electrochemistry

DESCRIPTION	EQUATION
Cell Voltage	$E_{cell} = E_{cell}^{\circ} - rac{RT}{n\Im} \ln Q = E_{cell}^{\circ} - rac{0.0592}{n} \log Q$
Electric Current	$I=rac{q}{t}$
Reaction Quotient	$egin{aligned} Q &= rac{[C]^c[D]^d}{[A]^a[B]^b} \ where & aA + bB  ightarrow cC + dD \end{aligned}$
Relationship between Equilibrium Constant and Cell Voltage	$\log K = \frac{nE^\circ}{0.0592}$

# Equilibrium

DESCRIPTION	EQUATION
Acid Ionization Constant	$K_{oldsymbol{a}} = rac{\left[H^{+} ight]\left[A^{-} ight]}{\left[HA ight]}$
Base Ionization Constant	$K_b = \frac{\left[OH^-\right]\left[HB^+\right]}{\left[B\right]}$
Buffer Design Equation	$pH \approx pK_a - \log \frac{[HA]_0}{[A^-]_0}$
Gas Pressure and Concentration Relationship	$K_{p}=K_{c}\left( RT\right) ^{\Delta n}$
Ion Product Constant for Water	$K_w = [OH^-][H^+] = K_a \times K_b$ = $1.0 \times 10^{-14}$ at $25^{\circ}C$
pH and pOH Relationship	14=pH+pOH
pH Defined	$pH = -\log\left[H^+\right]$
pK <sub>a</sub> Definition	$pK_a = -\log K_a$

pK $_{
m b}$  Definition  $pK_b = -\log K_b$  pOH and Base Ionization Equilibrium Constant Relationship  $pOH = pK_b + \log \frac{[HB^+]}{[B]}$ 

# Gases, Liquids, and Solutions

DESCRIPTION	EQUATION
Adibiatic change	PV=k
Boiling Point Elevation	$\Delta T_b = iK_b \times molality$
Charles' Law	$rac{V}{t}=k$
Combined Gas Law	$rac{P_1V_1}{n_1T_1} = rac{P_2V_2}{n_2T_2}$
Density of a Material	$D=rac{m}{V}$
Freezing Point Depression	$\Delta T_f = iK_f \times molality$
Graham's Law of Effusion	$rac{r_1}{r_2}=\sqrt{rac{M_2}{M_1}}$
Ideal gas equation	PV=nRT
Kinetic Energy per Mole	$rac{KE}{mole} = rac{3}{2}RTn$
Kinetic Energy per Mole	$rac{KE}{mole} = rac{3}{2}RTn$

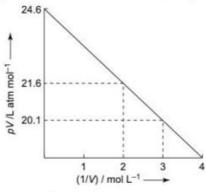
# Thermochemistry

DESCRIPTION	EQUATION
Acid Ionization Constant	$K_{m{a}} = rac{\left[H^{+} ight]\left[A^{-} ight]}{\left[HA ight]}$
Adibiatic change	PV=k
Base Ionization Constant	$K_b = rac{\left[OH^- ight]\left[HB^+ ight]}{\left[B ight]}$

Bohr Radius 
$$a_0 = \frac{\hbar^2}{m_e k e^2}$$
 Boiling Point Elevation 
$$\Delta T_b = i K_b \times molality$$
 Buffer Design Equation 
$$pH \approx p K_a - \log \frac{[HA]_0}{[A^-]_0}$$
 Cell Voltage 
$$E_{cell} = E_{cell}^\circ - \frac{RT}{n\Im} \ln Q = E_{cell}^\circ - \frac{0.0592}{n} \log Q$$
 Charles' Law 
$$\frac{V}{t} = k$$

Vander waal's force

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



The value of the van der Waals constant a is

(a)  $1.0 L^2 atm mol^{-2}$ 

(b)  $4.5 L^2$  atm mol<sup>-2</sup>

(c)  $1.5 L^2$  atm mol<sup>-2</sup> (d)  $3.0 L^2$  atm mol<sup>-2</sup>

Solution:

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

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

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

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

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

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

dilute solution containing 2.5 gm of nonvolatile

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

$$m = \frac{\Delta T_{\rm b}}{K_{\rm b}} = \frac{2 \text{ K}}{0.76 \text{ K kg mol}^{-1}} = \frac{2}{0.76} \text{ mol kg}^{-1}$$

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

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

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

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

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

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

Therefore, the choice (a) is correct.

shape of XeO2F2 molecule is seesaw

The shape of XeO<sub>2</sub>F<sub>2</sub> molecule is

(a) trigonal bipyramidal (b) square planar

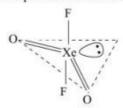
(c) tetrahedral

(d) see-saw

### Solution

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

There are five paires of electrons around Xe. To accommodate these, Xe undergoes dsp<sup>3</sup> hybridization leading to the trigonal bipyramidal arrangement of five paires of electrons. The structure of XeO<sub>2</sub>F<sub>2</sub> is



The shape of XeO<sub>2</sub>F<sub>2</sub> is sea-saw. Therefore, the **choice** (d) is correct.

Various increasing and Decreasing properties

Decreasing order of reactivity towards S<sub>N</sub>2 displacement:

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

Increasing order of reactivity towards S<sub>N</sub>1 displacement:

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

Increasing reactivity sequence of S<sub>N</sub>1 displacement of halogen: CH<sub>3</sub>X, 1° X, 2° X, 3° X, Inceasing reactivity sequence of S<sub>N</sub>2 displacement of halogen: CH<sub>3</sub>X, 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<sub>2</sub>C=CR<sub>2</sub>, R<sub>2</sub>C=CHR, R<sub>2</sub>C=CH<sub>2</sub>, RCH=CH<sub>2</sub>, CH<sub>2</sub>=CH<sub>2</sub> Increasing dehydration of alcohol in the presence of H<sub>2</sub>SO<sub>4</sub>:

ethyl alcohol, isopropyl alcohol, tert-butyl alcohol

Decreasing order of reactivity towards E2 dehydrohalogenation:

2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane, 3-bromopentane Increasing order of dehydrohalogenation

1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane calculate multiple bond energy of a C triple bond

Using the data provided, calculate the multiple bond energy of a C≡C bond in C<sub>2</sub>H<sub>2</sub>.

$$2C(s) + H_2(g) \rightarrow C_2H_2(g)$$
  $\Delta H_1 = 225 \text{ kJ mol}^{-1}$   
 $2C(s) \rightarrow 2C(g)$   $\Delta H_2 = 1410 \text{ kJ mol}^{-1}$   
 $H_2(g) \rightarrow 2H(g)$   $\Delta H_3 = 330 \text{ kJ mol}^{-1}$ 

Take the bond energy of C—H bond equal to 350 kJ mol<sup>-1</sup>.

## Solution:

Consider the following transformations.

$$2C(s) + H_{2}(g) \xrightarrow{\Delta H_{1}} H - C = C - H$$

$$\Delta H_{2} \qquad \Delta H_{3} \qquad -2 \varepsilon_{C-H} - \varepsilon_{C=C}$$

$$2C(g) + 2H(g) \xrightarrow{} H - -C = C - H$$

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

 $\varepsilon_{\text{C} = \text{C}} = \Delta H_2 + \Delta H_3 - \Delta H_1 - 2\varepsilon_{\text{C-H}} = (1410 + 330 - 225 - 2 \times 350) \text{ kJ mol}^{-1} = 815 \text{ kJ mol}^{-1}$ Therefore, the choice (d) is correct.

# Some facts student must know

Largest Anion - At

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

Most reactive solid element - Li

Most reactive liquid element - Cs

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

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

Liquid radioactive element - Francium

N.metal wid highest M.Pt - Carbon

Metal wid highest valency = Plutonium

highest tensile strength - Boron

Most ionic compound = CsF

Strongest base = Cs (OH)

Strongest basic oxide = Cs<sub>2</sub>O

Most conducting metal = Ag

-

# Topic wise grouping of information kind of Dictionary of Organic Chemistry

Compounds of carbon with other elements in the periodic table:



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.

Shared pair H 
$$\rightarrow$$
 No.  $\rightarrow$  H  $\rightarrow$  H  $\rightarrow$  No.  $\rightarrow$  No.

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

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

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

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

Further reaction of hemiactals with another molecule of alcohol leads to a full acetal. For example:  $CH(OH)(CH3)(OC_2H_5) + C_2H_5OH <==>CH(CH3)(OC_2H_5)_2$ 

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

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

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

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

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

# **Bond fission**

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

# Homolytic fission

## Homolysis

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

## **Heterolytic fission**

## Heterolysis

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

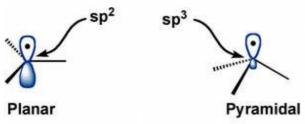
### Free radicals

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

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

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

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



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

So to summarize free radicals:

- Formed under activation by light or use of additional compounds called Radical Initiators.
- They are very reactive, because they have an unpaired electron which wants to get paired up.
- They are either pyramidal or planar with the lone electron in their sp<sup>3</sup> 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<sup>+</sup>, with alkyl halides as substrates.

$$(CH_3)_2CHF$$
 +  $Ag^+$  (AgNO<sub>3</sub> is used)  $\longrightarrow$  (CH<sub>3</sub>)<sub>2</sub>CH + AgF  $\downarrow$    
 $\downarrow$  = precipitate

Formation of carbocation

The precipitating out of the silver salt forces the equilibrium to shift towards the forwards reaction.

A Similar reaction is Finkelstein reaction is particularly useful for preparing iodoalkanes. The iodoalkanes are obtained by heating chloro or bromoalkanes with a concentrated solution of sodium iodide in dry acetone.

In Acetone after Reflux ( Heating in enclosed container ) for a long time [ Refluxing is a process of heating a liquid in a flask provided with a condenser. The vapours of the liquid which rise up get condensed back into the flask. ]

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

Sodium chloride and sodium bromide being less soluble in acetone get precipitated from the solution and can be removed by filtration. This also prevents the backward reaction to occur according to Le Chatelier's principle. The reaction gives the best results with primary halides.

With iodide, the solvate  $^{NaI} \cdot ^3 (^{CH}_3)_2 ^{CO}$  can be formed, in which each  $^{Na^+}$  is coordinated by 6 acetone ligands via oxygen lone pairs, and the I- ions fill in the gaps between these octahedral units, being surrounded by the methyl groups of the acetones. I- has a larger ionic radius compared to Cl- and Br- and thus fills the gap completely, thereby minimizing empty space in the lattice and its distance to Na+, which is, however, still larger than in solvent-free sodium iodide. This larger distance between the ions decreases the lattice energy, which in turn makes the compound readily soluble in acetone. Cl- and Br- are too small to fit in these gaps, and as the cation-anion distance becomes too large, the only way to minimize the lattice energy is the formation of a solvent-free structure NaX (X = Cl-, Br-). When the lattice energy is larger than the energy released by solvation of the ions, namely that of Na+ by complexation with acetone, the compound becomes insoluble and precipitates from the solution.

The positively charged carbon atom in carbocations is sp<sup>2</sup> 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<sup>2</sup> hybridized carbon), with empty p orbital perpendicular to the plane of the molecule.
- Reactive towards electron rich species.

# **Carbanions**

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

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

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

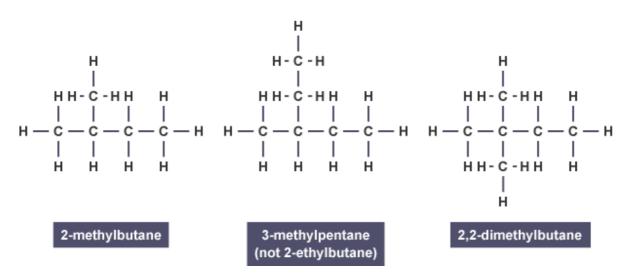
## To summarize carbanions:

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

#### Stability of intermediates

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

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



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

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 & \text{1} & \text{2} \\ \text{CH}_3 & \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \text{13} & \text{12-8} & \text{7} \\ \text{CH}_3 & \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 \\ \text{CH}_3 & \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3 \\ \text{CH}_4 & \text{CH}_5 - \text{CH}_5 \\ \end{array}$$

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

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

$${\overset{8}{\text{CH}_3}} - {\overset{7}{\text{CH}_2}} - {\overset{6}{\text{CH}_2}} - {\overset{5}{\text{CH}_2}} - {\overset{4}{\text{CH}}} - {\overset{3}{\text{CH}_2}} - {\overset{2}{\text{CH}_2}} - {\overset{1}{\text{CH}_3}} - {\overset{2}{\text{CH}_2}} - {\overset{1}{\text{CH}_3}} - {\overset{2}{\text{CH}_3}} - {\overset{2}{\text{CH}$$

4-Ethyl-5-methyloctane

$${\overset{8}{\text{CH}_3}} - {\overset{7}{\text{CH}_2}} - {\overset{6}{\text{CH}_2}} - {\overset{5}{\text{CH}_2}} - {\overset{4}{\text{CH}}} - {\overset{3}{\text{CH}_2}} - {\overset{2}{\text{CH}_2}} - {\overset{1}{\text{CH}_3}} - {\overset{1}{\text{CH}$$

4-Isopropyl-5-propyloctane

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

$$\overset{8}{\text{CH}_3} - \overset{7}{\text{CH}_2} - \overset{6}{\text{CH}_2} - \overset{5}{\text{CH}} - \overset{4}{\text{CH}} - \overset{3}{\text{CH}_2} - \overset{2}{\text{CH}_2} - \overset{1}{\text{CH}_3} \\ \overset{1}{\text{CH}_3} - \overset{2}{\text{CH}_2} - \overset{1}{\text{CH}_3}$$

4-Ethyl-5-methyloctane

$$\begin{array}{c} {}^{8} \text{CH}_{3} - {}^{7} \text{CH}_{2} - {}^{6} \text{CH}_{2} - {}^{5} \text{CH} - {}^{4} \text{CH} - {}^{3} \text{CH}_{2} - {}^{2} \text{CH}_{2} - {}^{1} \text{CH}_{3} \\ & {}^{C} \text{H}_{2} - {}^{C} \text{H} - {}^{C} \text{H}_{3} \\ & {}^{C} \text{H}_{3} - {}^{C} \text{H}_{2} - {}^{C} \text{H}_{3} \end{array}$$

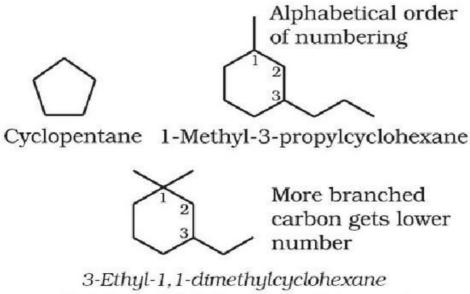
4-Isopropyl-5-propyloctane

The lowestsum rule.

$$\begin{array}{c} 7 \\ \text{CH}_3 - \overset{6}{\text{CH}}_2 - \overset{5}{\text{CH}} - \overset{4}{\text{CH}} - \overset{3}{\text{CH}} - \overset{2}{\text{CH}} - \overset{1}{\text{CH}}_3 \\ \text{CH}_3 - \overset{1}{\text{CH}}_2 - \overset{1}{\text{CH}}_3 - \overset{1}{\text{CH}}_3 \\ \text{CH}_4 - \overset{1}{\text{CH}}_4 - \overset{1}{\text{CH}}_5 \end{array}$$

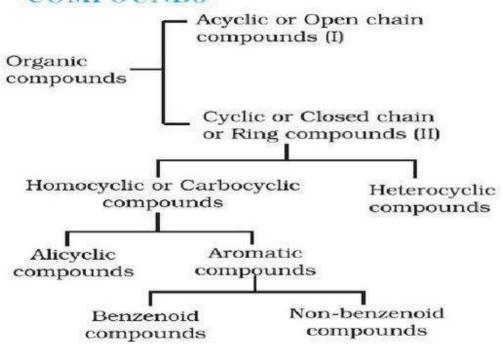
2,3,5-Trimethyl-4-propylheptane (not 3,5,6-Trimethyl-4-propylheptane)

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



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

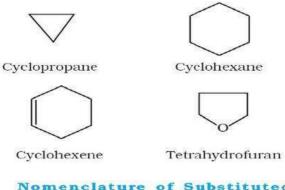
# CLASSIFICATION OF ORGANIC COMPOUNDS



# Alicyclic or closed chain or ring compounds

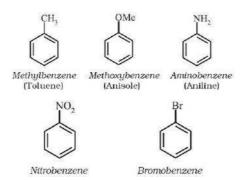
Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the form of a ring (homocyclic). Sometimes atoms other than carbon are also present in the ring (heterocylic).

#### Some examples are



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.



How Isomers are made?

(a) Normal to branched chain in alkane n-Alkane is heated with AlCl<sub>3</sub> at 570 K to give branched chain

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> 
$$\xrightarrow{AlCl_3}$$
 CH<sub>3</sub> CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>  $\xrightarrow{CH_3}$  CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub> CH<sub>3</sub>

(b) Shift of double bond

In the presence of catalyst like  $Al_2(SO_4)_3$ , alkene undergo isomerization at high temperature (770 – 970 K).  $CH_3CH_2CH=CH_2 \rightarrow CH_3CH_2CH=CHCH_3$ 

(c) Shift of triple bond

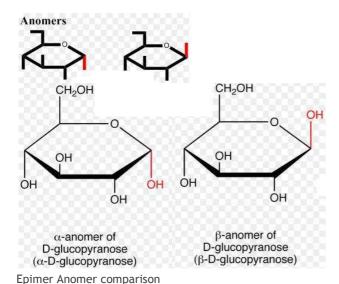
$$\begin{array}{c} \text{CH}_{3}\text{CH}_{2}\text{C} = \text{CH} \xrightarrow{\text{KOH}} \text{ [CH}_{3}\text{CH} = \text{C} = \text{CH}_{2}] \rightarrow \text{CH}_{3} - \text{C} = \text{C} - \text{CH}_{3} \\ & \text{2-butyne} \\ & \text{H}_{2}\text{O} \\ & \text{CH}_{3}\text{CH}_{2}\text{C} = \text{CNa} \xrightarrow{\text{NaNH}_{2} \text{ in}} \\ & \text{inert solvent} \end{array}$$

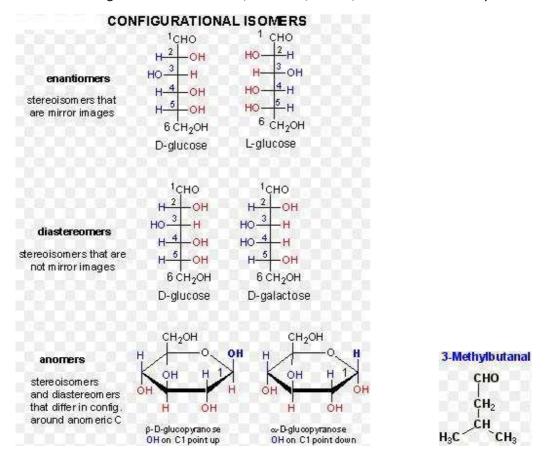
Heating with ethanolic potassium hydroxide shifts the triple bond towards the centre of the chain whereas heating with sodamide in an inert solvent shifts the bond towards the end of chain.

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

**Epimers** 

**Anomers** 





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

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

Various Methods of Reduction used in Organic Chemistry

(b) 
$$CH_3CH = CHCHO \xrightarrow{9-BBN} \xrightarrow{HOCH_2CH_2NH_2} CH_3CH = CHCH_2OH$$
; 9-BBN is 9-Borabicyclo[3.3.1]nonane

(c) 
$$CH_3CH_2CHO \xrightarrow{Z_1 + Conc.HCI} CH_3CH_2CH_3$$
 (d)  $CH_3COCH_3 \xrightarrow{LiAlH_4} CH_3CHCH_3$ 

$$\xrightarrow{NH_2NH_2 + KOH} CH_3CH_2CH_3$$
Wolff-Kishner reduction  $CH_3CH_2CH_3$ 

(e) RCOOH 
$$\xrightarrow{\text{1.LiAlH}_4}$$
 RCH<sub>2</sub>OH

(g) 
$$\begin{array}{c} \text{CH}_2\text{CN} & \text{CH}_2\text{CH}_2\text{NH}_2 \\ \hline & H_2, \text{Ni} \\ \hline & 140\,^{\circ}\text{C} \end{array}$$

(h) 
$$NO_2$$
  $NH_2$ 
 $NO_2$   $NO_2$   $NO_2$ 

Only one nitro group is reduced.

(i) 
$$RCI \xrightarrow{Mg} RMgCI \xrightarrow{H_2O} RH + Mg \xrightarrow{CI} OH$$

$$\downarrow LiAlH_4 \longrightarrow RH$$

(j) Rosenmund's reduction

$$RCOCI + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCI$$

Various methods of Oxidation

#### Oxidation

(a) RCH<sub>2</sub>OH 
$$\xrightarrow{\text{Pyridinium chlorochromate}}$$
 RCHO  $C_5H_5NH^+CrO_3Cl^-$ 

(b) 
$$R > CHOH \xrightarrow{K_2Cr_2O_7} R > C = O$$

(c) 
$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$

$$(d) \xrightarrow{CHO_3} \xrightarrow{CrO_3} \xrightarrow{H_2O} \xrightarrow{H^+}$$

(e) 
$$KMnO_4$$
  $COOH$ 

(f) RCH=CHCHO 
$$\frac{\text{Tollens}}{\text{reagent}}$$
 RCH=CHCOOH

Synthesis of p-bromonitrobenzene in 2 steps

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

Prepare m-bromoiodobenzene from benzene

OH

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

 $CH_3$ 

Alternatively, we may proceed as follows:

Secondary alcohol to Primary alcohol

$$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \xrightarrow{\quad \text{conc. H}_2\text{SO}_4 \quad} \text{CH}_3\text{CH} \xrightarrow{\quad \text{CH}_2 \quad} \frac{\text{HBr}}{\text{peroxide}} \text{ CH}_3\text{CH}_2\text{CH}_2\text{Br} \\ \text{OH} & \xrightarrow{\quad \text{aq. KOH} \quad} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \end{array}$$

To convert Ethylebenzene to Benzene and Ethylebenzene to phenylpropionic acid

Show the steps to carry out the following transformations.

(i) Ethylbenzene → benzene

Alcohol to alcohol with one carbon more

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

$$\begin{array}{c} O \\ \parallel \\ CH_{3}-CH_{2}-C \equiv C-H \longrightarrow CH_{3}-CH_{2}-CH_{2}-C-CH_{3} \\ \\ CH_{3}CH_{2}-C \equiv CH + Na^{+}NH_{2}^{-} \xrightarrow{-NH_{3}} CH_{3}CH_{2} - C \equiv C^{-} : Na^{+} \\ O \\ CH_{3}CH_{2} - C - CH_{3} \xrightarrow{H_{3}O^{+}, Hg^{2+}} CH_{3}CH_{2} - C \equiv C - CH_{3} \\ \end{array}$$

Alcohol to alcohol with one carbon less

$$\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{[O]}} \text{CH}_3\text{COOH} \xrightarrow{\quad \text{soda lime} \quad \text{CH}_4} \xrightarrow{\text{Cl}_2} \text{CH}_3\text{CI} \xrightarrow{\quad \text{aq. KOH} \quad \text{CH}_3\text{OH}} \text{CH}_3\text{OH}$$

Simple alcohol to complicated alcohol

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.

$$H \xrightarrow{C} O \longrightarrow H \xrightarrow{C} O$$
Formate ion
$$H \xrightarrow{C} O \longrightarrow H \longrightarrow H \xrightarrow{C} O \longrightarrow H$$
Formate acid

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

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

Amine to amine containing one carbon more

$$\text{RCH}_2\text{NH}_2 \xrightarrow[0 \text{ °C}]{\text{HNO}_2} \text{RCH}_2\text{OH} \xrightarrow{\text{PBr}_3} \text{RCH}_2\text{Br} \xrightarrow{\text{NaCN}} \text{RCH}_2\text{CN} \xrightarrow{\text{H}_2/\text{Ni}} \text{RCH}_2\text{CH}_2\text{NH}_2$$

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.

Br 
$$OCH_3$$
  $OCH_3$   $O$ 

The introduction of  $-NO_2$  group at para position in bromobenzene facilitates the nucleophilic replacement of -Br by  $-OCH_3$ .

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

## Write chemical tests to distinguish

#### between:

Solution. Formic acid 
$$\begin{pmatrix} O \\ || \\ H-C-OH \end{pmatrix}$$
 contains

both an aldehyde 
$$\begin{pmatrix} H \\ I \\ -C = O \end{pmatrix}$$
 as well as carboxyl

group 
$$\begin{pmatrix} -C - OH \\ \parallel \\ O \end{pmatrix}$$
 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.

$$HCOOH + 2[Ag(NH_3)_2]^+ + 2(OH)^-$$
  
Tollen's reagent

$$\longrightarrow$$
 2Ag  $\downarrow$  + CO<sub>2</sub>  $\uparrow$  + 2H<sub>2</sub>O + 4NH<sub>3</sub>

silver mirror

No silver mirror is formed with acetic acid.

(b) Formic acid reduced Fehling solution to red ppt. of Cu<sub>2</sub>O but acetic acid does not.

$$\begin{array}{c} HCOOH + 2Cu^{2+} + 4(OH)^{-} \longrightarrow Cu_{2}O \downarrow + CO_{2}\uparrow + 3H_{2}O \\ \hline Fehling solution & red ppt \\ (cuprous oxide) \end{array}$$

Amine to amine containing one carbon less

$$\mathsf{RCH_2NH_2} \xrightarrow[0]{\mathsf{HNO}_2} \mathsf{RCH_2OH} \xrightarrow[\mathsf{KMnO}_4]{\mathsf{[O]}} \mathsf{RCOOH} \xrightarrow{\mathsf{SOCl}_2} \mathsf{RCOCI} \xrightarrow{\mathsf{NH}_3} \mathsf{RCONH}_2 \xrightarrow{\mathsf{OBr}^-} \mathsf{RNH}_2$$

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

#### Convert

metafluoro benzoicacid

Aldehyde to aldehyde containing one carbon more

$$\begin{array}{c} H \\ C = O + CH_3MgBr \rightarrow H - C - OMgBr \xrightarrow{H_2O} CH_3CH_2OH \xrightarrow{C_5H_5NH^+CrO_3CI} CH_3CHO \\ H \end{array}$$

Convert Nitrobenzene to meta hydroxynitrobenzene ( or 4-nitrophenol )

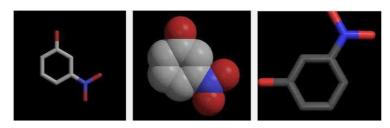
Convert 
$$OH$$
 in not more than 4 steps mentioning the reagents, reaction

conditions and intermediates in the above conversion.

The given conversion can be carried out as follows.

Nitrobenzene resonance structure

4 nitrophenol or metahydroxynitrobenzene



NO<sub>2</sub>

NO<sub>2</sub>

NO<sub>2</sub>

NO<sub>2</sub>

NaNO<sub>2</sub>/dil. H<sub>2</sub>SO<sub>4</sub>

$$0 \circ C - 5 \circ C$$

NH<sub>2</sub>

NO<sub>2</sub>

NH<sub>2</sub>

NO<sub>2</sub>

NH<sub>2</sub>

NO<sub>2</sub>

NH<sub>2</sub>

NH<sub>2</sub>

NO<sub>2</sub>

NH<sub>2</sub>

NH<sub>2</sub>

OH

NO<sub>2</sub>

NH<sub>2</sub>

NiHSO<sub>4</sub>

diazonium salt

(an intermediate compound)

Many conversions or preparations

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

- (i) Ethylbenzene from benzene [C2H5OH, PCI5, anhydrous AlCI3]
- (ii) Propanoic anhydride from propanol [AgNO<sub>3</sub>/NH<sub>4</sub>OH, P<sub>2</sub>O<sub>5</sub>]
- (iii) Acetoxime from acetaldehyde [K2Cr2O7/H+, Ca(OH)2 and NH2OH.HCl]

(i) 
$$C_2H_5OH + PCI_5 \longrightarrow C_2H_5CI + POCI_3 + HCI$$
  
 $C_6H_6 + C_2H_5CI \xrightarrow{AlCI_3} C_6H_5C_2H_5 + HCI$ 

$$\text{(ii)} \quad C_3H_7OH \xrightarrow{\quad AgNO_3/NH_4OH \quad} \quad C_2H_5COOH; \qquad 2C_2H_5COOH \xrightarrow{\quad P_2O_5 \quad} \quad (C_2H_5CO)_2O$$

(iii) 
$$CH_3CHO \xrightarrow{K_2Cr_2O_7/H^+} CH_3COOH$$
;  $CH_3COOH \xrightarrow{Ca(OH)_2} (CH_3COO)_2Ca$   
 $(CH_3COO)_2Ca \xrightarrow{heat} CH_3COCH_3 + CaCO_3$ ;  $CH_3COCH \xrightarrow{NH_2OH} CH_3$ 

Benzene to p-toluic acid

Benzene to p-toluic acid

Benzene to m-chlorobenzoic acid

Benzene to m-chlorobenzoic acid

$$\begin{array}{c|c} CH_3 & COOH & COOH \\ \hline \begin{array}{c} CH_3CI \\ \hline AlCl_3 \end{array} & \begin{array}{c} CH_3 \\ \hline \end{array} & \begin{array}{c} CH_2 \\ \hline \end{array} & \begin{array}{c} Cl_2 \\ \hline \end{array} & \begin{array}{c} Cl$$

Benzene to p-chlorobenzoic acid

Benzene to p-chlorobenzoic acid

$$\begin{array}{c|c} CH_3 & CH_3 & COOH \\ \hline \begin{array}{c} CH_3Cl \\ \hline AlCl_3 & \hline \end{array} & \begin{array}{c} CCl_2 \\ \hline Fe \end{array} & \begin{array}{c} \hline \\ \hline \\ \hline \end{array} & \begin{array}{c} CH_3Cl \\ \hline \end{array} & \begin{array}{c} \hline \\ \hline \\ \hline \end{array} & \begin{array}{c} CCOOH \\ \hline \end{array} & \begin{array}{c} \hline \\ \hline \\ \hline \end{array} & \begin{array}{c} CCOOH \\ \end{array} &$$

Acetic acid to Malonic acid

Acetic acid to malonic acid

$$CH_3COOH \xrightarrow{Br_2,\,P} BrCH_2COOH \xrightarrow{KCN} CNCH_2COOH \xrightarrow{H_2O} HOOCCH_2COOH$$

Ethyne to propanoic acid

Ethyne to propanoic acid

$$\text{HC} \! \equiv \! \text{CH} \xrightarrow{\text{Lindlar}} \text{H}_2\text{C} \! = \! \text{CH}_2 \xrightarrow{\text{HCI}} \text{CH}_3\text{CH}_2\text{CI} \xrightarrow{\text{KCN}} \text{C}_2\text{H}_5\text{CN} \xrightarrow{\text{H}_2\text{O}} \text{C}_2\text{H}_5\text{COOH}$$

Isopropyl alcohol to β-hydroxybutyric acid

Isopropyl alcohol to β-hydroxybutyric acid

$$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{Al}_2\text{O}_3} \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{HOCl}} \text{CH}_3\text{CHCH}_2\text{Cl} \xrightarrow{\text{KCN}} \text{CH}_3\text{CHCH}_2\text{CN} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHCH}_2\text{COOH} \\ \text{OH} & \text{OH} & \text{OH} & \text{OH} \end{array}$$

Acetic acid to Propanoic acid

Acetic acid to propanoic acid

$$\text{CH}_3\text{COOH} \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{PCl}_3} \text{CH}_3\text{CH}_2\text{CI} \xrightarrow{\text{KCN}} \text{CH}_3\text{CH}_2\text{CN} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{COOH}$$

Ethanoic acid to a mixture of methanoic acid and diphenyl ketone

Ethanoic acid to a mixture of methanoic acid and diphenyl ketone  $\begin{array}{c} \text{COCH}_3 \\ \text{CH}_3\text{COOH} \\ \text{(acetic acid)} \end{array} \xrightarrow{SOCl_2} \begin{array}{c} \text{CH}_3\text{COOI} \\ \text{AlCl}_3 \end{array} \xrightarrow{\text{(acetophenone)}} \\ \text{C}_6\text{H}_5\text{COC}_6\text{H}_5 + \text{HCOOH} \\ \text{(diphenyl} \\ \text{(formic acid)} \end{array} \xrightarrow{\text{[O]}} \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}} \begin{array}{c} \text{C}_6\text{H}_5 \end{array} \xrightarrow{\text{C}}$ 

Propanoic acid to acetic acid

Propanoic acid to acetic acid

$$\text{CH}_3\text{CH}_2\text{COOH} \xrightarrow[\text{heat}]{\text{NH}_3} \text{CH}_3\text{CH}_2\text{CONH}_2 \xrightarrow{\text{Br}_2/\text{KOH}} \text{CH}_3\text{CH}_2\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Cr}_2\text{O}^2_7} \text{CH}_3\text{COOH}$$

Aniline to 1, 2, 3-tribromobenzene

Ethanal to 2-hydroxy-3-butenoic acid

Ethanal to 2-hydroxy-3-butenoic acid

$$\begin{array}{c} \text{CH}_3\text{CHO} + \text{HCHO} & \xrightarrow{\text{H$^+$ or OH$^-$}} & \text{CH}_3\text{CHCHO} & \xrightarrow{\text{dil. HCl.}} & \text{CH}_2 = \text{CHCHO} \\ & \text{OH} & & \text{OH} & & \\ & & \text{OH} & & \text{CH}_2 = \text{CH} - \text{CH} - \text{COOH} \\ & & \text{OH} & & \text{OH} & & \\ \end{array}$$

Benzene to m-bromophenol

Benzene to m-bromophenol

Ethyl alcohol to Vinyl alcohol

Ethyl alcohol to vinyl acetate

Methylamine to ethylamine

$$\begin{array}{c} \text{Methylamine to ethylamine} \\ \text{CH}_3\text{NH}_2 \xrightarrow{\text{HNO}_2} \text{CH}_3\text{OH} \xrightarrow{\text{PCI}_3} \text{CH}_3\text{CI} \xrightarrow{\text{KCN}} \text{CH}_3\text{CN} \xrightarrow{\text{Sn/HCI}} \text{CH}_3\text{CH}_2\text{NH}_2 \end{array}$$

Benzene to m-bromotoluene

#### Benzene to m-bromotoluene

$$\begin{array}{c|c} CH_3 & CH_3 & CH_3 & CH_3 \\ \hline CH_3CI & HNO_3 & Fe \\ \hline NO_2 & NH_2 & NH_2 & NHCOCH_3 & NHCOCH_3 \\ \hline \\ CH_3 & CH_3 & CH_3 & CH_3 \\ \hline \\ NH_2 & NHCOCH_3 & NHCOCH_3 \\ \hline \\ CH_3 & CH_3 & CH_3 \\ \hline \\ NH_2 & NHCOCH_3 & NHCOCH_3 \\ \hline \\ NH_2 & NH_2 & NH_2 \\ \hline \\ NH_2 & NH_2 & NH_2 \\ \hline \end{array}$$

Benzaldehyde to cyanobenzene

## Benzaldehyde to cyanobenzene

Aniline to Chlorobenzene

#### Aniline to Chlorobenzene

$$\begin{array}{c|c} NH_2 & N_2CI & CI \\ \hline & NaNO_2/HCI & \hline & C\Gamma/CuCI & \\ \hline & 5^\circ C & \hline \end{array}$$

Ethylamine to Methylamine

$$CH_{3}CH_{2}NH_{2} \xrightarrow{HNO_{2}} CH_{3}CH_{2}OH \xrightarrow{Cr_{2}O_{7}^{2-}} CH_{3}COOH \xrightarrow{NH_{3}} CH_{3}CONH_{2} \xrightarrow{Br_{2}/KOH} CH_{3}NH_{2}$$

Benzene to m-dibromobenzene

#### Benzene to m-dibromobenzene

# Aniline to p-nitroaniline

# Aniline to p-nitroaniline

#### Toluene to m-nitrotoluene

Toluene to *m*-nitrotoluene
$$CH_3 \qquad CH_3 \qquad CH_3 \qquad CH_3$$

$$HNO_3 \qquad H_2SO_4 \qquad (CH_3CO)_2O \qquad HNO_3 \qquad H_2SO_4$$

$$NO_2 \qquad NHCOCH_3 \qquad NHCOCH_3$$

$$CH_3 \qquad CH_3 \qquad CH_3$$

$$CH_3 \qquad CH_3 \qquad H_2O \qquad H^2O \qquad H^2$$

$$NO_2 \qquad NO_2 \qquad NO_2 \qquad NH_2$$

Convert Benzene + Alcohol to  $\alpha$ -methylphenylacetic acid

## Benzene + alcohol to α-methylphenylacetic acid

Toluene to 3,5 dibromotoluene

# Toluene to 3, 5-dibromotoluene

Benzene to p-chloronitrobenzene

# Benzene to p-chloronitrobenzene

$$\begin{array}{c}
Cl \\
\hline
Fe
\end{array}$$

$$\begin{array}{c}
Cl \\
\hline
HNO_3 \\
\hline
H_2SO_4
\end{array}$$

$$\begin{array}{c}
Cl \\
\hline
NO_2
\end{array}$$

Toluene to 2,6 dibromotoluene

Benzene to 3,4-dibromonitrobenzene

Benzene to 3, 4-dibromonitrobenzene 
$$NO_2$$
  $NO_2$   $Br_2$   $HNO_3$   $H_2SO_4$   $Br$   $Br$   $Br$   $Br$   $Br$ 

Benzene to m-chloronitrobenzene

#### Benzene to m-chloronitrobenzene

$$\begin{array}{c|c}
 & \text{NO}_2 & \text{NO}_2 \\
\hline
 & HNO_3 \\
\hline
 & H_2SO_4
\end{array}$$

$$\begin{array}{c|c}
 & Cl_2 \\
\hline
 & Fe
\end{array}$$

$$\begin{array}{c}
 & Cl_2 \\
\hline
 & Cl
\end{array}$$

Nitrobenzene to benzamide

#### Nitrobenzene to benzamide

Benzene to 4-nitrobenzaldehyde

## Benzene to 4-nitrobenzaldehyde

Benzene to 4-amino-2-bromotoluene

## Benzene to 4-amino-2-bromotoluene

$$\begin{array}{c|c}
CH_3 & CH_3 & CH_3 \\
\hline
CH_3 & \hline
HNO_3 & \hline
H2SO_4 & \hline
NO_2 & \hline
Re & \hline
NO_2 & \hline
NO_2 & \hline
NH_2
\end{array}$$

$$\begin{array}{c}
CH_3 & CH_3 & CH_3 \\
\hline
Br & Fe,H^+ & \hline
NH_2
\end{array}$$

$$\begin{array}{c}
CH_3 & Fe,H^+ & \hline
NH_2
\end{array}$$

$$O_2N - O_H$$

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

$$CH_{3}CH = CHCH_{2}CH_{3} \xrightarrow{Br_{2}} CH_{3}CH - CHCH_{2}CH_{3}$$

$$Br Br$$

$$NaNH_{2}$$

$$H_{3}C = C \xrightarrow{CH_{2}CH_{3}} \xrightarrow{H_{2}/N_{1}} CH_{3}C = CCH_{2}CH_{3}$$

$$H_{3}C = C \xrightarrow{H} \xrightarrow{Na} NH_{3}$$

$$CH_{3}C = CCH_{2}CH_{3}$$

$$H_{4}C = CH_{2}CH_{3} \xrightarrow{NH_{3}} CH_{3}C = CCH_{2}CH_{3}$$

$$H_{5}C = CH_{2}CH_{3} \xrightarrow{NH_{3}} CH_{5}C = CH_{2}CH_{3}$$

$$H_{7}C = CH_{7}CH_{2}CH_{3} \xrightarrow{NH_{2}} CH_{7}C = CH_{7}CH_{2}CH_{3}$$

$$H_{7}C = CH_{7}CH_{7$$

Benzene to p-chlorobenzylalcohol

# Benzene to p-chlorobenzylalcohol

$$\begin{array}{c|c} CH_3 & CH_3 & CH_2CI & CH_2OH \\ \hline \\ CH_3CI & \hline \\ AlCl_3 & \hline \\ Cl_2 & \hline \\ Fe & \hline \\ Cl & Cl & Cl & Cl \\ \hline \end{array}$$

Convert Propanol to  $\alpha$ -hydroxypropanoic acid

# Propanol to $\alpha$ -hydroxypropionic acid

4-chloropentane-2-one

#### 3-Bromo-4-methylpentanoic acid

$$\begin{array}{ccc} \text{CHO} & \text{CHO} & \text{CH} = \text{CHCHO} \\ \\ \text{OH} & \text{OH} & \\ \\ \text{Vanillin} & \text{Salicylaldehyde} & \text{Cinnamaldehyde} \\ \end{array}$$

## p,p'- dihydroxybenzophenone

#### Hex-2-ene-4-ynoicacid

Heptan-2-one

Benzene to Mandelic Acid

Benzene to Mandelic acid 
$$\left(\begin{array}{c} -\text{CHCOOH} \\ \text{OH} \end{array}\right)$$

$$\left(\begin{array}{c} -\text{CH}_3\text{CI} \\ \text{AlCI}_3 \end{array}\right) \left(\begin{array}{c} -\text{CH}_3 \\ \text{Ac}_2\text{O} \end{array}\right) \left(\begin{array}{c} -\text{CHO} \\ \text{NaHSO}_3 \end{array}\right) \left(\begin{array}{c} -\text{CHCN} \\ \text{OH} \end{array}\right) \left(\begin{array}{c} -\text{CHCOOH} \\ \text{OH} \end{array}\right)$$

#### 4-Bromo-2-methylhexane

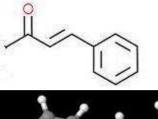
$$H^3C$$
 $CH^3$ 
 $CH^3$ 

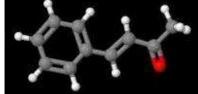
Heptanal

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

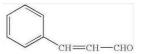
1-(4-Methoxyphenyl)-3-phenylprop-2-en-1-one

4-phenylprop-3-ene-2-one

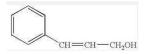




3-phenylprop-2-ene-1-al



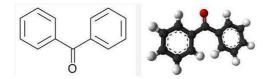
3-phenyl-prop-2-ene-1-ol



cyclopentancarbaldehyde



Benzophenone also diphenylmethanone



Tollen's Reagent

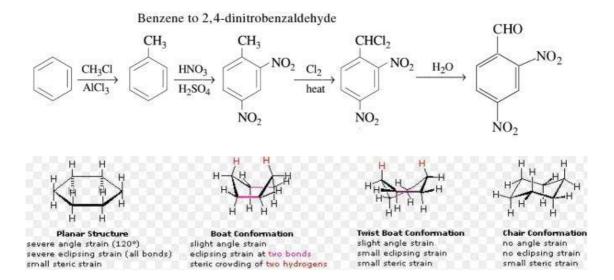
$$RCHO(aq) \ + \ 2Ag(NH_3)_2^{\ +}(aq) \ + \ 3OH^-(aq) \ \longrightarrow$$

An aldehyde

$$RCOO^{-}(aq) + 2Ag(s) + 4NH_{3}(aq) + 2H_{2}O$$

Free silver

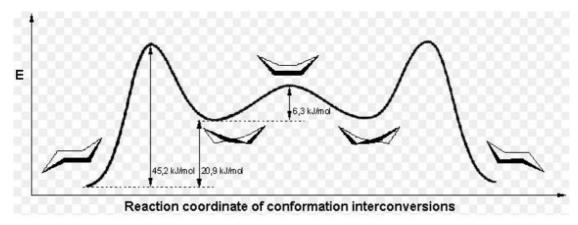
Benzene to 2,4-dinitrobenzaldehyde



Acetaldehyde to Acetylene

Acetaldehyde to acetylene

$$CH_{3}CHO \xrightarrow{Li AlH_{4}} CH_{3}CH_{2}OH \xrightarrow{alc. KOH} CH_{2} = CH_{2} \xrightarrow{Br_{2}} CH_{2} \xrightarrow{CH_{2} - CH_{2}} \underbrace{alc KOH}_{All M-All M-All$$

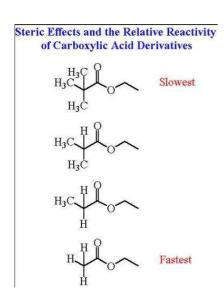


Identify the compounds

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

A compound (X) containing only C, H and O is unreactive towards sodium. It does not add bromine. It also does not react with Schiff's reagent. On refluxing with an excess of hydroiodic acid, X yields only one organic product Y. On hydrolysis Y yields a new compound Z which can be converted to Y by reaction with red phosphorus and iodine. The compound Z on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of this acid is 60. What are the compounds X, Y and Z? Write chemical equations leading to the conversion of X to Y. (1981) Solution Since the compound is unreactive towards sodium, it is neither alcohol (including phenol) nor carboxylic acid. It is also not an aldehyde. It may be a symmetrical ether because on refluxing with excess of HI, it gives only one product. Thus, we have

Now the equivalent weight of R'COOH is 60. From this, it follows that R' is —CH<sub>3</sub> group and hence R is —CH<sub>2</sub>CH<sub>3</sub> group. Thus, the compounds X, Y and Z are



Identify the compound

A hydrocarbon reacts with Bromine to give dibromo compound

One mole of a hydrocarbon A reacts with one mole of bromine giving a dibromo compound  $C_5H_{10}Br_2$ . Substance A on treatment with cold, dilute alkaline potassium permanganate solution forms a compound  $C_5H_{12}O_2$ . On ozonolysis, A gives equimolar quantities of propanone and ethanal. Deduce the structural formula of A.

Solution From the products of ozonolysis, we conclude that

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$$
  $\text{C=O} + \text{O=C} \\ \begin{array}{c} \text{H} \\ \text{CH}_3 \end{array}$   $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array}$   $\begin{array}{c} \text{C=C} \\ \text{CH}_3 \end{array}$   $\begin{array}{c} \text{C} \\ \text{C} \\ \text{C} \\ \text{C} \end{array}$ 

The compound A contains a double bond. This is also confirmed from the fact that the compound A reacts with one mole of bromine. Thus, the given reactions are

Identify the compound

An alkene A on ozonolysis yields acetone and an aldehyde

An alkene A on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidized to an acid B. When B is treated with bromine in presence of phosphorus, it yields a compound C which on hydrolysis gives a hydroxy acid D. This acid can also be obtained from acetone by the reaction with hydrogen cyanide followed by hydrolysis. Identify the compounds A, B, C and D.

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

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} = 0 \xrightarrow{\text{HCN}} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} \xrightarrow{\text{CN}} \begin{array}{c} \text{H}^+ \\ \text{OH} \end{array} \xrightarrow{\text{CH}_3} \begin{array}{c} \text{C} \xrightarrow{\text{COOH}} \\ \text{OH} \end{array}$$

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

$$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} \xrightarrow{\text{B}_{\text{F2/P}}} \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{C} \xrightarrow{\text{B}_{\text{F}}} \begin{array}{c} \text{Br} \\ \text{COOH} \\ \end{array} \xrightarrow{\text{H}_2\text{O}} \begin{array}{c} \text{CH}_3 \\ \text{COOH} \end{array} \xrightarrow{\text{COOH}} \begin{array}{c} \text{Br} \\ \text{COOH} \end{array}$$

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

2-methylpropanal

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

$$CH_3$$
  $C = O + OHC$   $CH$   $CH_3$   $CH_3$   $CH_3$   $C = CH$   $CH_3$   $CH_3$   $CH_3$   $CH_3$   $CH_3$ 

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

A: 
$$CH_3$$
— $C$ = $CH$ — $CH$ — $CH_3$ 
 $CH_3$ 
 $CH_3$ 

B:  $CH_3$ — $CH$ — $COOH$ 
 $CH_3$ 

2, 4-dimethylpent-2-ene

2-methylpropanoic acid

2, 4-dimethylpent-2-ene

2-methylpropanoic acid

2-hydroxy-2-methylpropanoic acid

Identify the compound

An aromatic comound contains 69.4% carbon, 5.8% hydrogen

An aromatic compound contains 69.4% carbon and 5.8% hydrogen. A sample of 0.303 g of this compound was analysed for nitrogen by Kjeldahl's method. The ammonia evolved was absorbed in 50 mL of 0.05 M sulphuric acid. The excess acid required 25 mL of 0.1 M sodium hydroxide for neutralization. Determine the molecular formula of the compound if its molar mass is 121 g mol-1. Draw two possible structures for this compound. Solution The reactions involved are

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$
  
 $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ 

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

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

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

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

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

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

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

Per cent of oxygen in the given aromatic compound = 100 - (69.4 + 5.8 + 11.6) = 13.2The ratios of atoms present in the given compound are

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

Hence, for the given compound, we have

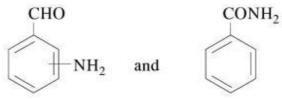
Empirical formula = C<sub>7</sub>H<sub>7</sub>NO

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

It is given that 121 g mol<sup>-1</sup> is also the molar mass. Hence,

Molecular formula =  $C_7H_7NO$ 

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



Identify the compound

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

An organic compound C, H<sub>2v</sub>O, was burnt with twice the amount of oxygen needed for complete combustion to CO<sub>2</sub> and H<sub>2</sub>O. The hot gases, when cooled to 0 °C and 1 atm pressure, measured 2.24 L. The water collected during cooling weighed 0.9 g. The vapour pressure of pure water at 20 °C is 17.5 mmHg and is lowered by 0.104 mmHg when 50 g of the organic compound is dissolved in 1000 g of water. Give the molecular formula of the organic compound.

Solution The combustion reaction is  $C_xH_{2x}O_x + xO_2 \rightarrow xCO_2 + yH_{2}O$ 

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

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

Thus, the empirical formula of the compound is  $C_{0.05}H_{2\times0.05}O_{0.05}$ , i.e.  $CH_2O$ . Now, according to Raoult's law  $-\frac{\Delta p}{p^*} = x_2 \text{ i.e. } \frac{0.104 \text{ mmHg}}{17.5 \text{ mmHg}} = \frac{(50 \text{ g/M})}{(50 \text{ g/M}) + (1000 \text{ g/18 g mol}^{-1})}$ 

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

Solving for M, we get  $M = 150.5 \text{ g mol}^{-1}$ 

Number of repeating units of CH<sub>2</sub>O in the molecular formula = 
$$\frac{150.5}{12 + 2 + 16} \approx 5$$

Hence, Molecular formula of the compound is C<sub>5</sub>H<sub>10</sub>O<sub>5</sub>.

Identify the Compound

Alcohol when heated with concentrated H2SO4

An alcohol A, when heated with concentrated H<sub>2</sub>SO<sub>4</sub> gives an alkene B. When B is bubbled through bromine water and the product obtained is dehydrohalogenated with excess of sodamide, a new compound C is obtained. The compound C gives D when treated with warm dilute H<sub>2</sub>SO<sub>4</sub> in presence of HgSO<sub>4</sub>. D can also be obtained either by oxidizing A with KMnO<sub>4</sub> or from acetic acid through its calcium salt. Identify A, B, C and D.

Solution The given reactions are as follows.

$$\begin{array}{c} A \xrightarrow{conc. H_2SO_4} & B \xrightarrow{1. Br_2} & C \xrightarrow{HgSO_4/H_2SO_4} & D \\ & \text{alkene} & O \end{array} \xrightarrow{alkene} C \xrightarrow{CH_3COO} Ca$$

The reaction of obtaining D from calcium acetate is

$$(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3$$
(D)

Hence, D is acetone. Since the latter is also obtained from the oxidation of alcohol A, compound A will be CH<sub>3</sub>CHCH<sub>3</sub>.

OH

Hence, the reactions depicted above are as follows

$$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \xrightarrow{\text{Conc.H}_2\text{SO}_4} \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{Br}_2} \text{CH}_3\text{CH} = \text{CH}_2 \\ \text{OH} & \text{oprpene} & \text{l} & \text{l} \\ \text{2-propanol} & \text{(B)} & \text{Br} & \text{Br} \end{array}$$

$$\begin{array}{c} \text{CH}_3\text{CCH}_3 \leftarrow \begin{bmatrix} \text{CH}_3\text{C} = \text{CH}_2 \\ \text{OH} \end{bmatrix} \xleftarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \\ \text{acetone} \\ \text{(D)} \end{array} \qquad \begin{array}{c} \text{CH}_3\text{C} \equiv \text{CH} \\ \text{propyne} \\ \text{(C)} \end{array}$$

Identify the compound

Certain hydrocarbon was found to contain 85.7% carbon

A certain hydrocarbon A was found to contain 85.7 per cent carbon and 14.3 per cent hydrogen. This compound consumes 1 molar equivalent of hydrogen to give a saturated hydrocarbon B. 1.0 g of hydrocarbon A just decolourized 38.05 g of a 5 per cent solution (by mass) of Br2 in CCl4. Compound A, on oxidation with concentrated KMnO4, gave compound C (molecular formula C4H8O) and compound C could easily be prepared by the action of acidic aqueous mercuric sulphate on 2-butyne. Determine the molecular formula of A and deduce the structures A, B and C.

Solution The ratio of atoms in the compound A is 
$$C: H: \frac{85.7}{12}: \frac{14.3}{1}: 7.14: 14.3: 1: 2$$

Thus, Empirical formula of A is CH2.

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

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

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<sub>2</sub> =  $\frac{1.0}{(5 \times 38.05/100)} \times 160$  g = 84.1 g.

Molar mass of A is 84.1 g mol-1.

The number of repeating CH<sub>2</sub> group in one molecule of A will be 6(= 84.1/14). Hence,

Molecular formula of A is C<sub>6</sub>H<sub>12</sub>. Now, it is given that

$$C_6H_{12} \xrightarrow{\text{conc. KMnO}_4} C_4H_8O + CH_3COOH$$
(C)

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

$$\begin{array}{c} \text{CH}_{3}\text{C} = \text{CCH}_{3} \xrightarrow{\text{H}_{2}\text{O}} & \begin{bmatrix} \text{CH}_{3}\text{C} = \text{CHCH}_{3} \\ \text{I} & \text{OH} \end{bmatrix} \rightarrow & \text{CH}_{3}\text{CCH}_{2}\text{CH}_{3} \\ \text{OH} & \end{bmatrix} \rightarrow & \text{CH}_{3}\text{CCH}_{2}\text{CH}_{3} \\ \text{OH} & \end{bmatrix}$$

Identify the compound

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

A liquid X, having a molecular formula C<sub>6</sub>H<sub>12</sub>O<sub>2</sub> is hydrolysed with water in the presence of an acid to give a carboxylic acid, Y, and an alcohol Z. Oxidation of Z with chromic acid gives Y. What are the structures of X, Y and Z?

Solution Since the hydrolysis of X gives a carboxylic acid (Y) and an alcohol (Z), the compound X must be an ester. Let it be RCOOR'. The compounds Y and Z will be RCOOH and R'OH, respectively, Since the oxidation of Z gives Y, we will have

$$R'OH \xrightarrow{[O]} RCOOH$$
 or  $RCH_2OH \xrightarrow{[O]} RCOOH$   
Hence, the given compound X may be written as  $RCOOCH_2R$ . From this it follows that  $2R = C_1H_2O_2 - C_2H_2O = C_2H_3$  or  $R = C_2H_3$ 

$$2R = C_6H_{12}O_2 - C_2H_2O = C_4H_{10}$$
 or  $R = C_2H_5$ 

X: CH3CH2COCH2CH2CH3 Propylpropanate Y: CH3CH2COOH Propanoic acid

Z: CH<sub>3</sub>CH<sub>5</sub>CH<sub>5</sub>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.

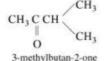
The ratios of atoms in the compound are

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

Hence Empirical formula is C<sub>5</sub>H<sub>10</sub>O.

Molar empirical mass = 86 g mol<sup>-1</sup>; same as the given molar mass

Thus, Molecular formula is C<sub>5</sub>H<sub>10</sub>O. The structure of the compound will be



Identify the compound

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

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

Solution The given reactions are

A + CH<sub>3</sub>COOH 
$$\xrightarrow{\text{H}_2\text{SO}_4}$$
 ester; A  $\xrightarrow{\text{mild}}$  C  $\xrightarrow{\text{50\% KOH}}$  A + D

(B)

D  $\xrightarrow{\text{PCl}_5}$   $\xrightarrow{\text{NH}_3}$  E  $\xrightarrow{\text{-H}_2\text{O}}$  HCN

C  $\xrightarrow{50\% \text{ KOH}}$  A + D is a Cannizzaro reaction and thus the compound C is an aldehyde with no The reaction α-hydrogen, C must be HCHO. From this it follows that A must be CH<sub>3</sub>OH as its mild oxidation gives HCHO. With this fact, we can write the given reactions as shown below.

$$\begin{array}{ccc} \text{CH}_3\text{OH} + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COOCH}_3; & \text{CH}_3\text{OH} & \underline{\text{[O]}} \rightarrow \text{HCHO} & \underline{50\% \text{ KOH}} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH} \\ \text{(A)} & \text{methyl acetate} & \text{[A]} & \text{(D)} \\ & \text{(B)} & & & & \end{array}$$

Hence

$$\begin{array}{c} \text{HCOOH} & \xrightarrow{\text{PCl}_5} & \text{HCOCI} & \xrightarrow{\text{NH}_3} & \text{HCONH}_2 & \xrightarrow{\text{-H}_2\text{O}} & \text{HCN} \end{array}$$

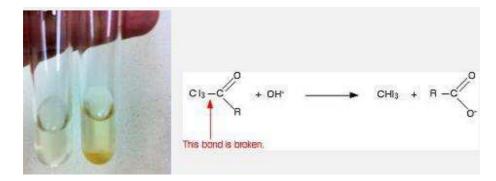
A: CH<sub>3</sub>OH methanol B: CH<sub>3</sub>COOCH<sub>3</sub> methylethonate D: HCOOH C: HCHO methanal methanoic acid

E: HCONH<sub>2</sub> methanamide

**lodoform Test** 

$$\begin{array}{c} O \\ II \\ R-C-CH_3 \end{array} \xrightarrow[NaOH]{} \begin{array}{c} O \\ II \\ R-C-O \end{array} Na^+ + CHI_3 \end{array}$$

OH R-CHCH<sub>3</sub> 
$$I_2$$
  $R$ -C-O  $I_1$   $I_2$   $R$ -C-O  $I_3$ 



Identify the compound

An organic compound X, on analysis gives 24.24 per cent carbon and 4.04 per cent hydrogen. Further, sodium extract of 1.0 g of X gives 2.90 g of silver chloride with acidified silver nitrate solution. The compound X may be represented by two isomeric structures, Y and Z. The compound Y on treatment with aqueous potassium hydroxide solution gives a dihydroxy compound, while Z on similar treatment gives ethanal. Find out the molecular formula of X and give the structures of Y and Z.

Solution Mass per cent of chlorine in the organic compound X

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

The ratios of atoms in the molecule of X are

$$C\!:\!H\!:\!C\!I\!::\frac{24.24}{12}\!:\!\frac{4.04}{1}\!:\!\frac{71.72}{35.5}\,::\,2\,:\,4\,:\,2\,::\,1\,:\,2\,:\,1$$

Empirical formula of X is CH2CI

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 C2H4Cl2.

The reaction are

$$\begin{array}{c} \operatorname{CH_3CHCl_2} & \xrightarrow{\operatorname{aq. KOH}} & [\operatorname{CH_3CH(OH)_2}] \to \operatorname{CH_3CHO} \\ \text{(Z)} & \operatorname{ethanal} \end{array}$$

$$ClCH_2CH_2Cl \xrightarrow{aq. KOH} HOCH_2CH_2OH$$
  
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:

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

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

- (a) Pyrolysis of alkanes
- (b) Benzene + Chloroethane (+ anhydrous AlCl<sub>3</sub>)
- (c) CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> + NaOH
- (d) Preparation of alkanes
- (e) Phenol + CHCl<sub>3</sub> (NaOH)
- (f) C2H5Br + alcKOH

- (p) Elimination reaction
- (q) Saponification
- (r) Wurtz reaction
- (s) Friedel-craft reaction
- (t) Reimer-Tiemann reaction
- (u) Cracking

Ans:

$$(a) - (u);$$

$$(b) - (s)$$

$$(c) - (q)$$

$$(d) - (r)$$

$$(e) - (t)$$
:

$$(f) - (p)$$

Identify the compound

A mixture of two aromatic compounds A and B was separated by dissolving in chloroform followed by extraction with aqueous KOH solution. The organic layer containing compound A, when heated with alcoholic solution of KOH produced a compound C  $(C_7H_5N)$  associated with an unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform and then acidified gave a mixture of two isomeric compounds D and E of molecular formula  $C_7H_6O_2$ . Identify the compounds A, B, C, D, and E and write their structures. Solution We have

# $\begin{array}{c|c} \text{Mixture of A and B} \\ \hline & \text{CHCl}_3 + \text{KOH} \\ \hline \\ \text{organic layer} \\ \text{(A)} \\ \text{alc. KOH} \\ \hline \\ \text{C}_7\text{H}_5\text{N} \\ \text{(C)} \\ \text{unpleasant odour} \\ \hline \\ \text{C}_7\text{H}_6\text{O}_2 \\ \text{(D)} \\ \text{(E)} \\ \hline \end{array}$

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

$$N \equiv C$$
 $NH_2$ 
 $C$ 
 $C$ 
 $C$ 
 $C$ 

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

Rearrangement by migration of Bromine

Rearrangement, by migration of Br, of initially formed 1° radical into more stable  $2^{\circ}$  or  $3^{\circ}$  radical. Chlorination of either *n*-propyl or isopropyl bromide gives 1-bromo-2-chloropropane.

$$CI \xrightarrow{CH_3CH_2CH_2Br} CH_3CHCH_2Br \xrightarrow{CH_3CHBrCH_2} CH_3CHBrCH_2 \xrightarrow{rearr.} CH_3CHCH_2Br \xrightarrow{Cl_2} CH_3C CH_2Br$$

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

$$\begin{array}{c} \text{Cl} & \xrightarrow{\text{(CH_3)_2CHCH_2Br}} \text{(CH_3)_2CCH_2Br} \\ & \xrightarrow{\text{(CH_3)_3CBr}} \text{(CH_3)_2C} \xrightarrow{\text{CH}_2} \xrightarrow{\text{rearr.}} \text{(CH_3)_2CCH_2Br} \\ & & \text{Br} \end{array}$$

Identify the Compound

An organic compound containing C, H and O exists in two isomeric forms A and B. A mass of 0.108 g of one of the isomers gives on combustion 0.308 g of  $CO_2$  and 0.072 g of  $H_2O$ . A is insoluble NaOH and NaHCO<sub>3</sub> while B is soluble in NaOH. A reacts with concentrated HI to give compounds C and D. C can be separated from D by the ethanolic  $AgNO_3$  solution and D is soluble in NaOH. B reacts readily with bromine to give compound E of molecular formula,  $C_7H_5OBr_3$ . Identify A, B, C, D and E with justification and give their structures.

Solution We have

Per cent of carbon in the compound = 
$$\frac{M_C}{M_{CO_2}} \frac{m_{CO_2}}{m_{compound}} \times 100 = \left(\frac{12}{44}\right) \left(\frac{0.308}{0.108}\right) (100) = 77.78$$

Per cent of hydrogen in the compound = 
$$\frac{2\,M_{\rm H}}{M_{\rm H_2O}} \frac{m_{\rm H_2O}}{m_{\rm compound}} \times 100 = \left(\frac{2}{18}\right) \left(\frac{0.072}{0.108}\right) (100) = 7.41$$

Per cent of oxygen in the compound = 100 - (77.78 + 7.41) = 14.81.

The ratios of atoms in the compound are

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

Hence, Empirical formula of the compound is C7H8O.

Since the isomer B on reacting with bromine water gives compound E (C<sub>7</sub>H<sub>5</sub>OBr<sub>3</sub>), the molecular formula of A and B will be the same as the empirical formula derived above, since both contain the same number of carbon atoms. As E is obtained from B by the substitution of hydrogen with bromine and since there is high carbon content in B, the compounds A and B must be aromatic. Now, since compound A is insoluble in NaOH and NaHCO<sub>3</sub> 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

The bromination of B gives

$$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 \end{array} \xrightarrow{\text{bromination}} \begin{array}{c} \text{OH} \\ \\ \text{Br} \end{array}$$

The reaction of compound A with HI is

$$\begin{array}{cccc}
OCH_3 & OH \\
& & & \\
& & & \\
\hline
(A) & & (D) & (C)
\end{array}$$

The compound C can be separated from D by use of ethanolic AgNO<sub>3</sub> solution as it is soluble in it whereas D will remain insoluble. The compound D will be soluble in NaOH as it is phenol. Hence, the structures of A, B, C, D and E are

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

- (a) Decarboxylation
- (b) Ozonolysis
- (c) Williamson's synthesis
- (d) Dichloroethylene

- (p) Addition reaction
- (q) Sodalime
- (r) Structure of alkene
- (s) Ether

Ans:

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

Identify the compound

Basic volatile Nitrogen compound

A basic volatile nitrogen compound gave a foul smelling gas when treated with chloroform and alcoholic potash. A 0.295 g sample of the substance, dissolved in aqueous HCl, and treated with  $\mathrm{NaNO}_2$  solution at  $0\,^{\circ}\mathrm{C}$  liberated a colourless, odourless gas whose volume corresponded to  $112\,$  mL at STP. After the evolution of the gas was complete, the aqueous solution was distilled to give an organic liquid which did not contain nitrogen and which on warming with alkali and iodine gave a yellow precipitate. Identify the original substance. Assume that it contains one N atom per molecule.

Solution Since the compound gives a foul smelling gas on treating with CHCl<sub>3</sub> and alcoholic KOH, the compound must be a primary amine.

$$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCI + 3H_2O$$
 (1)  
alkyl isocyanide  
(foul smelling gas)

Since the compound on treating with NaNO<sub>2</sub>/HCl at 0 °C produces a colourless gas, the compound must be an aliphatic primary amine.

$$RNH_2 + HNO_2 \rightarrow ROH + N_2 + \frac{H_2O}{}$$
(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

Amount of compound RNH<sub>2</sub> = 
$$\frac{1}{200}$$
 mol

If M is the molar mass of RNH<sub>2</sub>, then

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

Thus, the molar mass of alkyl group R is (59 - 16) g mol<sup>-1</sup>, i.e. 43 g mol<sup>-1</sup>. Hence, R must be C<sub>3</sub>H<sub>7</sub>.

From Eq. (2), it is obvious that the liquid obtained after distillation is ROH. Since this gives yellow precipitate with

alkali and iodine (iodoform test), it must contain  $CH_3$ —C— group. Hence, it is concluded that ROH is OH

CH
$$_3$$
—CH—CH $_3$ . Thus, the original compound is CH $_3$ —CH—CH $_3$  OH NH $_2$  isopropylamine

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

- (a) Lucas test
- (b) Neutral FeCl<sub>3</sub>
- (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,  $C_8H_6$ , on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A. Solution The given reactions are

$$\begin{array}{c} C_8H_6 \xrightarrow{\text{dil. } H_2SO_4} B \xleftarrow{\text{AlCl}_3} C_6H_6 + \text{acid chloride} \\ (A) & \downarrow I_2/KOH \end{array}$$

The reaction of B with  $I_2$  in KOH is iodoform reaction. The compound D is iodoform,  $CHI_3$ . The compound B must contain —COCH $_3$  group so as to exhibit iodoform reaction. Since D is obtained from benzene by Friedel-Crafts reaction, it is an aromatic ketone ( $C_6H_5COCH_3$ ). The compound C must be an acid.

The compound A may be represented as  $C_6H_5C_2H$ . Since it gives  $C_6H_5COCH_3$  on treating with dilute  $H_2SO_4$  and  $HgSO_4$ , it must contain a triple bond (—C=CH) in the side chain. Hence, the given reactions may be represented as

$$C \equiv CH$$

$$COCH_3$$

$$HgSO_4$$

$$HgSO_4$$

$$COCH_3$$

$$COCH_3$$

$$COOH$$

$$COOH$$

$$COOH$$

$$I_2/KOH$$

$$COOH$$

Identify the compound

An organic compound  $E(C_5H_8)$  on hydrogenation gives compound  $F(C_5H_{12})$ . Compound E on ozonolysis gives formaldehyde and 2-keto-propanal. Deduce the structure of compound E. Solution Since there are four hydrogen atoms added in the reaction

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

2-ketopropana

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

reaction can be explained as follows.

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

Friedel Crafts Reaction

$$C_{6}H_{6} + CH_{3}CH_{2}CH_{2}CI \xrightarrow{AlCl_{3}} C_{6}H_{5}CH_{2}CH_{2}CH_{3} + C_{6}H_{5}CHCH_{3} \atop major \ product}$$

$$C_{6}H_{6} + CH_{3}CHCH_{2}CI \xrightarrow{AlCl_{3}} C_{6}H_{5} - C - CH_{3} \atop CH_{3} (only \ product)$$

$$CH_{3} CH_{3} CH_{3}$$

Identify the compound

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

An organic compound A has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with FeCl<sub>3</sub> solution. The compound A when treated with CO<sub>2</sub> and NaOH at 140 °C under pressure gives B which on being acidified gives C. The compound C reacts with acetyl chloride to give D which is a well known pain killer. Identify A, B, C and D and explain the reactions involved.

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

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

 $C: H: O :: \frac{76.6}{12}: \frac{6.38}{1}: \frac{17.02}{16}:: 6.38: 6.38: 1.064:: \frac{6:6}{6}: 1$  Empirical formula of A is  $C_6H_6O$ . Molar empirical formula mass of A = 94 g mol<sup>-1</sup> Hence, This tallies with the given molar mass (=  $2 \times 47 \text{ g mol}^{-1}$ ). Thus Molecular formula of A is  $C_6H_6O$ . Since, the compound A gives characteristic colour with FeCl3, it must be a phenol. The given reactions are

OH OH OH OH COOH
$$(A) + CO_2 \xrightarrow{\text{NaOH} \atop \text{140 °C, high} \atop \text{pressure}} (B) COONa  $\xrightarrow{\text{H}^+} (C)$  COOH
$$(C) \xrightarrow{\text{NaOH} \atop \text{OH}} (C) COOH$$

$$(D) \xrightarrow{\text{Aspirin (pain killer)}} (C)$$$$

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

Friedel-Crafts oil alkenes Fermentation Lewis acid soap

Dehydrohalogenation cuprous chloride anhydrous AlCl<sub>3</sub> Sandmeyer yeast chlorobenzene

Saponification alcoholic alkali ethanol

Ans:

Friedel-Crafts; Lewis acid; anhydrous AlCl<sub>3</sub>

Fermentation; yeast; ethanol Dehydrohalogenation; alcoholic alkali; alkenes

Sandmeyer; cuprous chloride; chlorobenzene

Saponification; oil; soap

Identify the compound

An organic compound A of molar mass 140.5 gm per mole has 68.32% Hydrogen

An organic compound A of molar mass  $140.5~{\rm g}~{\rm mol}^{-1}$  has 68.32% C, 6.4% H and 25.26% Cl. Hydrolysis of A with dilute acid gives compound B,  $C_8H_{10}O$ . Compound B can be oxidized under mild conditions to compound C,  $C_8H_8O$ . Compound C forms a phenylhydrazone D with PhNHNH $_2$  and gives a positive iodoform test. Deduce the structures of compounds A to D with proper reasoning.

Solution The ratios of atoms in a molecule of A are

$$C: H: C1: : \frac{68.32}{12} : \frac{6.4}{1} : \frac{25.26}{35.5} : : 5.69 : 6.4 : 0.71 : : 8 : 9 : 1$$

Hence, Empirical formula of A is  $C_8H_9Cl$ . Molar empirical formula mass of A = 140.5 g mol<sup>-1</sup>

This tallies with the given molar mass. Thus Molecular formula of A is C<sub>8</sub>H<sub>0</sub>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—COCH3 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.

$$CI \qquad OH \qquad O \\ H-C-CH_3 \qquad H-C-CH_3 \qquad C-CH_3 \qquad CH_3-C=NNHPh$$

$$(A) \qquad (B) \qquad (C) \qquad PhNHNH_2 \qquad (D)$$

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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was used to reach the end point. The molarity of the household bleach solution is

Bleaching powder contains a salt of an oxoacid as one of its components. The anhydride of that oxoacid is

Solutions:

For Q.11, we may write

Household bleach + 2 KI → I<sub>2</sub> + products

$$I_2 + 2Na_2S_2O_3 \rightarrow Na_2S_4O_6 + 2NaI$$

Amount of 
$$Na_2S_2O_3$$
 used =  $VM = (48 \times 10^{-3} \text{ L}) (0.25 \text{ mol L}^{-1}) = 12 \times 10^{-3} \text{ mol}$ 

Amount of 
$$I_2$$
 generated =  $\frac{1}{2}$  (12 × 10<sup>-3</sup> mol) =  $\frac{6}{6}$  × 10<sup>-3</sup> mol

Assuming 1 mol of household bleach produces 1 mol I2, we will have

Amount of household bleach in 25 mL solution =  $6 \times 10^{-3}$  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 Cl<sub>2</sub>O + H<sub>2</sub>O → 2HOCl

Hence, we have

The choice (c) is correct

The choice (a) is correct.

Match the compounds/ions in Column I with their properties/reactions in Column II.

# Column I

- (a) C<sub>6</sub>H<sub>5</sub>CHO
- (b) CH<sub>3</sub>C ≡ CH
- (c) CN
- (d) I

#### Column II

- (p) gives precipitate with 2,4-dinitrophenylhydrazine
- (q) gives precipitate with AgNO<sub>3</sub>
- (r) is a nucleophile
- (s) is involved in cyanohydrin formation

Ans:

$$(a) - (p), (q), (s);$$
  $(b) - (q);$ 

$$(b) = (a)$$

(c) 
$$-(q)$$
, (r), (s); (d)  $-(q)$ 

$$(d) = (a)$$

In decreasing order of Oxidation state of Nitrogen

Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen ?

(a) HNO3, NO, NH4Cl, N2

(b) HNO<sub>3</sub>, NO, N<sub>2</sub>, NH<sub>4</sub>Cl

(c) HNO3, NH4Cl, NO, N2

(d) NO, HNO<sub>3</sub>, NH<sub>4</sub>Cl, N<sub>2</sub>

#### Solution:

The oxidation states of nitrogen in the given compounds are as follows.

$$HNO_3: +1 + x + 3(-2) = 0$$

$$\Rightarrow x = +5$$

NO: 
$$x + (-2)$$

$$\Rightarrow x = +2$$

$$NH_4C1: x + 4 (+1) + (-1) = 0$$

$$\Rightarrow x = -3$$

$$N_2$$
:  $2(x) = 0$ 

$$\Rightarrow x = 0$$

 $\text{HNO}_3: +1 + x + 3 \ (-2) = 0 \implies x = +5 \qquad \text{NO}: \quad x + (-2) = 0 \implies x = +2$   $\text{NH}_4\text{Cl}: x + 4 \ (+1) + (-1) = 0 \implies x = -3 \qquad \text{N}_2: \quad 2(x) = 0 \implies x = 0$ 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) 
$$h^2/(4\pi^2 ma_0^2)$$

(a) 
$$h^2/(4\pi^2 m a_0^2)$$
 (b)  $h^2/(16\pi^2 m a_0^2)$  (c)  $h^2/(32\pi^2 m a_0^2)$  (d)  $h^2/(64\pi^2 m a_0^2)$ 

(c) 
$$h^2/(32\pi^2 ma_0^2)$$

(d) 
$$h^2/(64\pi^2 ma_0^2)$$

# Solution:

Bohr model of an atom satisfies the following two requirements.

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

$$\frac{(Ze)(e)}{(4\pi\varepsilon_0)r^2} = \frac{mv^2}{r}$$

$$mvr = n\left(\frac{h}{2\pi}\right)$$

Eliminating v in these two expressions, we get

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

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

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

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

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

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

Question on Aldol reaction

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

is
(a) 1

$$CH_3CHO + 4HCHO \xrightarrow{conc. aq. NaOH} HO OH$$
 $OH$ 
 $OH$ 
 $OH$ 
 $OH$ 

# Solution:

The given reaction may be formulated as follows.

There are three aldol condensations and one Cannizzaro reaction.

Therefore, the choice (c) is correct

An organic compound undergoes first order decomposition

An organic compound undergoes first-order decomposition. The time taken for its decomposition to 1/8 and 1/10 of its initial concentration are  $t_{1/8}$  and  $t_{1/10}$ , respectively. What is the value of  $(t_{1/8}/t_{1/10})*10?$  (log 2 = 0.3.)

For first-order decomposition of A, the rate law is

 $ln(1/8) = -k t_{1/8}$  and  $ln(1/10) = -k t_{1/10}$ Hence

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

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

Therefore, the answer is 9.

Allene has sp hybridization

In allene (C<sub>3</sub>H<sub>4</sub>), the type(s) of hybridization of the carbon atom is (are)

Solution:

The structure of allene is 
$${}^{H}_{C} = {}^{2}_{C} = {}^{3}_{C} + {}^{H}_{U}$$

In this molecule, carbon atoms 1 and 3 are sp2 hybridized while the carbon atom 2 is sp hybridized. Therefore, the choice (b) is correct.

Number of chiral carbon and optically active products

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

$$CH_{3}-CH=CH - \begin{matrix} CH_{3} & H \\ CH_{-}CH=CH-CH=CH-CH_{3} & is \end{matrix}$$
(a) 0 (b) 1 (c) 2 (d) 4
$$Solution: \\ CH_{3}-CH_{2}=CH - \begin{matrix} CH_{3} & H \\ CH_{3}-CH_{2}=CH - \begin{matrix} CH_{2}-CH_{2}-CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{3}-CH_{4}-CH_{4}-CH_{5}$$

None of the products will be optically active.

Therefore, the choice (a) is correct.

Carboxylic functional group is present in aspirin

The carboxylic functional group (-COOH) is present in

(a) picric acid

(b) barbituric acid

(c) ascorbic acid

(d) aspirin

## Solution:

The structures of the given compounds are as follows.

Therefore, the choice (d) is correct.

Identify the compound

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

$$I \xrightarrow{\text{(CH}_3\text{COONa)}} J \xrightarrow{\text{(i) H}_2,\text{Pd/C}} K$$

$$\xrightarrow{\text{(iii) SOCl}_2} \text{(iii) anhyd. AlCl}_1$$

J(C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>) gives effervescence on treatment with NaHCO<sub>3</sub> and positive Baeyer's test.

# Q-The compound K is

# Q-The compound I is

Perkin Condensation

#### Solutions:

The compound J must contain a —COOH group as it gives effervescence with NaHCO<sub>3</sub>. Also, it is an unsaturated compound as it gives positive Baeyer's test (decolourization of pink colour of alkaline KMnO<sub>4</sub>). Since the compound J is obtained by treating the compound I with (CH<sub>3</sub>CO)<sub>2</sub>O and CH<sub>3</sub>COONa, and more over the compound J seems to be aromatic (high carbon content), the compound I amongst the choices given in Q.14 seems to be benzaldehyde as it shows Perkin condensation shown in the following

The conversion J to K is as follows.

Hence, we have

The choice (c) is correct.

The choice (a) is correct.

#### Question on isomers

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

- (a) M and N are non-mirror image stereoisomers. (b) M and O are identical
- (c) M and P are enantiomers (d) M a

# (d) M and Q are identical

#### Solution

First of all, we may draw Fischer projections of the given compounds

$$M \longrightarrow HO \longrightarrow H$$

$$HO \longrightarrow H$$

M and N are non-mirror images.

M and P are enantiomers.

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

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

Aldohexose exists in D configuration

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

#### Solution:

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

$$\begin{array}{c} \text{CHO} \\ \text{CH}_2 \\ \text{H} \longrightarrow \text{OH} \\ \text{H} \longrightarrow \text{OH} \\ \text{CH}_2\text{OH} \end{array} \longrightarrow \begin{array}{c} \text{HO} \longrightarrow \text{C} \\ \text{CH}_2 \\ \text{H} \longrightarrow \text{OH} \\ \text{H} \longrightarrow \text{OH} \\ \text{OH} \end{array} \longrightarrow \begin{array}{c} \text{CH}_2\text{OH} \\ \text{H} \longrightarrow \text{OH} \\ \text{OH} \end{array}$$

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<sub>2</sub>OH group above the ring) and 8 are of L-configurations (CH<sub>2</sub>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 ?

Solution

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

Acidic side chain < neutral chain < basic side chain

$$(pH = 3)$$
  $(pH = 5.5 - 6.0)$   $(pH = 9 - 10)$ 

This pH is known as isoelectric point.

At pH = 7, the acidic side chain (for which isoelectric point < 7) exists as a negatively-charged species (e.g. —COO $^-$ ) and the basic side chain (for which isoelectric point > 7) exists as a positively charged species (e.g. —NH $_3^+$ ). Since peptides IV, VI, VIII and IX contain —NH $_2$  group in R $_1$  or/and R $_2$  group(s), these are expected to exist as positively-charged species.

Therefore, the correct answer is 4.

Try to figure out what sequence is depicted

neopentane < isopentane < n-pentane. A branched chain isomer has a lower boiling point than a straight chain isomer. The more numerous the branches, the lower the boiling point. The branching lowers the boiling point for all families of organic compounds. Branching causes the shape of molecule to approach towards a sphere and thus surface area decreases, with the result that the intermolecular forces become weaker and are overcome at a lower temperature.

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

(CH<sub>3</sub>)<sub>3</sub>CCOOH < (CH<sub>3</sub>)<sub>2</sub>CHCOOH < CH<sub>3</sub>CH<sub>2</sub>COOH < CH<sub>3</sub>COOH < 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).

$$H_3C$$
  $COOH$   $COOH$ 

 $(CH_3)_3CCOOCH_3 < (CH_3)_2CHCOOCH_3 < CH_3COOCH_3 < HCOOCH_3$  $CH_3COOC(CH_3)_3 < CH_3COOCH(CH_3)_2 < CH_3COOC_2H_5 < CH_3COOCH_3$ 

Try to figure out the sequences

adipic acid < succinic acid < malonic acid < oxalic acid Acidity decreases with increase in the intervening CH<sub>2</sub> groups. isobutane < n-butane < n-butyl chloride < n-butanol chlorobenzene < benzene < toluene < methoxybenzene

Decreasing order of reactivity towards alcoholic silver nitrate:

2-bromo-1-phenylethene, α-phenylethyl bromide, β-phenylethyl bromide

Increasing order of reactivity towards aqueous NaOH:

chlorobenzene, m-chloronitrobenzene, o-chloronitrobenzene, 2,4-dinitrochlorobenzene,

2,4,6-trinitrochlorobenzene

Increasing reactivity towards HCN: CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub>, HCHO, C<sub>2</sub>H<sub>5</sub>COCH<sub>3</sub>
Increasing basicity: *p*-toluidine, *N*, *N*-dimethyl-*p*-toluidine, *p*-nitroaniline, aniline.
Increasing ease of hydrolysis: CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>COCl, (CH<sub>3</sub>CO)<sub>2</sub>O, CH<sub>3</sub>CONH<sub>2</sub>
Increasing order of acid strength:

CICH<sub>2</sub>COOH, CH<sub>3</sub>CH<sub>2</sub>COOH, CICH<sub>2</sub>CH<sub>2</sub>COOH, (CH<sub>3</sub>)<sub>2</sub>CHCOOH, CH<sub>3</sub>COOH Increasing reactivity in nucleophilic substitution reactions: CH<sub>3</sub>F, CH<sub>3</sub>I, CH<sub>3</sub>Br, CH<sub>3</sub>Cl

major product H in the given reaction sequence

The major product H in the given reaction sequence

$$CH_3-CH_2-CO-CH_3 \xrightarrow{CN^-} G \xrightarrow{95\% H_2SO_4} H$$

#### 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:

 $\alpha$ -chlorophenylacetic acid, p-chlorophenylacetic acid, phenylacetic acid,  $\alpha$ -phenylpropionic acid Decreasing order of acidity of carboxylic acids:

p-nitrobenzoic acid, p-nitrophenylacetic acid, β-(p-nitrophenyl) propionic acid

Increasing order of basicity: ammonia, aniline, cyclohexylamine

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

Decreasing order of basicity: aniline, p-methoxyaniline, p-nitroaniline

Increasing order of acidity: benzene sulphonic acid, benzoic acid, benzyl alcohol, phenol

Decreasing order of acidity: m-bromophenol, m-cresol, m-nitrophenol, phenol

Decreasing order of acidity of substituted phenol:

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

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

Increasing order of nitration: benzene, chlorobenzene, nitrobenzene, toluene

Increasing order of reactivity towards alcoholic silver nitrate:

1-bromo-1-butene, 3-bromo-1-butene, 4-bromo-1-butene

Explain these by solving in right order -

Increasing reactivity towards S<sub>N</sub>1 solvolysis:

benzyl chloride, p-chlorobenzyl chloride, p-methoxybenzyl chloride, p-methylbenzyl chloride,

p-nitrobenzyl chloride

Increasing order of reactivity towards elimination by alcoholic KOH:

1-phenyl-2-bromopropane, 1-phenyl-3-bromopropane

Decreasing order of reactivity towards aqueous HBr: Isomeric pentyl alcohols

Increasing order of reactivity towards aqueous HBr:

1-phenyl-1-propanol, 3-phenyl-1-propanol, 1-phenyl-2-propanol

Decreasing order of reactivity towards aqueous HBr:

benzyl alcohol, p-cyanobenzyl alcohol, p-hydroxybenzyl alcohol

Increasing order of reactivity towards aqueous HBr:

benzyl alcohol, diphenylmethanol, methanol and triphenylmethanol

Decreasing order of reactivity towards bromination:

anisole, benzene, toluene, chlorobenzene, nitrobenzene, phenol

Increasing order of reactivity towards bromination:

hydroquinone, p-methoxyphenol, p-methylphenol, p-chlorophenol, p-nitrophenol, sym-trihydroxybenzene

Decreasing order of acidity of carboxylic acids:

butanoic acid, 2-bromobutanoic acid, 3-bromobutanoic acid, 4-bromobutanoic acid

Decreasing reactivity towards S<sub>N</sub>1 substitution: 1-chloropropene 3-chloropropene, n-propylchloride

Decreasing acidity: H<sub>2</sub>O, HC≡CH, NH<sub>3</sub>, RH, ROH

Decreasing basicity: R<sup>-</sup>, HC≡C<sup>-</sup>, NH<sub>2</sub>, OH<sup>-</sup>, OR<sup>-</sup> Decreasing order of reactivity towards the addition of HCl:

styrene, p-chlorostyrene, p-methylstyrene, p-nitrostyrene

Decreasing order of reactivity towards dehydration:

 $\alpha$ -phenyl ethyl alcohol,  $\alpha$ -(p-nitrophenyl) ethyl alcohol,  $\alpha$ -(p-aminophenyl) ethyl alcohol

Various Increasing Properties

Increasing stability of free radicals: <sup>o</sup>CH<sub>3</sub>, 1°, 2°, 3°, allyl, vinyl CH<sup>+</sup><sub>3</sub>, 1°, 2°, 3° Increasing stability of carbocation: Increasing enthalpy of reaction:

$$CH_3Br \rightarrow CH_3^+ + Br^ \Delta H_1$$
  
 $CH_3CH_2Br \rightarrow CH_3CH_2^+ + Br^ \Delta H_2$ 

$$\text{CH}_3\text{CHCH}_3 \rightarrow \text{CH}_3\overset{+}{\text{C}}\text{HCH}_3 + \text{Br}^ \Delta H_3$$

Br

Increasing order of reactivity towards S<sub>N</sub>2 displacement:

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

compound undergoes decarboxylation most readily

The compound that undergoes decarboxylation most readily under mild condition is

$$(a) \begin{array}{c|cccc} COOH & COOH & COOH & CH_2COOH \\ \hline \\ (b) & (c) & (d) & (d$$

#### Solution:

β-Ketocarboxylic acid is unstable acid. It readily undergoes decarboxylation through a cyclic transition state.

Therefore, the choice (b) is correct.

A compound contains 88.89%C and 11.1%H. It gives white precipitate with ammoniacal silver nitrate. The compound is

(a) 
$$C_5H_7C = CH$$

(b) 
$$C_8H_0C = CH$$
 (c)  $C_6H_{11}C = CH$  (d)  $C_4H_7C = CH$ 

(c) 
$$C_6H_{11}C = CH$$

(d) 
$$C_4H_7C = CH$$

Ans:

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

Only the compound C<sub>6</sub>H<sub>11</sub>C = CH has composition 4 times the composition of empirical formula.

More the number of electron withdrawing group stronger is the acid

# Cl<sub>3</sub>CCOOH > Cl<sub>2</sub>CHCOOH > ClCH<sub>2</sub>COOH > CH<sub>3</sub>COOH

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

Try to figure out what sequence is depicted

FCH,COOH > CICH,COOH > BrCH,COOH > ICH,COOH

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

CH3COOH < CICH2CH2COOH < CICH2COOH

$$HO \stackrel{\frown}{\bigcirc} COOH < H_3C \stackrel{\frown}{\bigcirc} COOH < \stackrel{\frown}{\bigcirc} COOH < Br \stackrel{\frown}{\bigcirc} COOH$$

H<sub>2</sub>O < C<sub>2</sub>H<sub>5</sub>OH < C<sub>6</sub>H<sub>5</sub>COOH < HCOOH < HCI

phenol < p-nitrophenol < H2CO3 < C6H5COOH

 $C_6H_5NH_2 < C_6H_5NHCH_3 < NH_3 < CH_3NH_2 < (CH_3)_2NH$ 

(CH<sub>3</sub>)<sub>3</sub>N < CH<sub>3</sub>NH<sub>2</sub> < (CH<sub>3</sub>)<sub>2</sub>NH. (CH<sub>3</sub>)<sub>3</sub>N is the weakest because of steric factors.

1-butanol < 2-butanol < 2-methyl-2-propanol. A tertiary alcohol reacts immediately, a secondary alcohol reacts within five minutes and a primary alcohol does not.

2-methyl-2-propanol < 2-butanol < 1-butanol. Reactivity of ROH is  $CH_3OH > 1^{\circ} > 2^{\circ} > 3^{\circ}$ .

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

(a) CH<sub>3</sub>CONH<sub>2</sub>

(b)  $C_2H_5CONH_2$  (c)  $C_3H_7CONH_2$ 

(d) C<sub>3</sub>H<sub>5</sub>CONH<sub>2</sub>

Ans:

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

(a) CH<sub>3</sub>CONH<sub>2</sub>

(b)  $C_2H_5CONH_2$  (c)  $C_3H_7CONH_2$  (d)  $C_3H_5CONH_2$ 

Hence

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

Hence, the compound is C<sub>2</sub>H<sub>5</sub>CONH<sub>2</sub>.

Try to figure out what sequence is depicted

$$CH_3CHO < CH_3COCH_3 < CH_3COCH_2CHO < CH_3COCH_2COCH_3$$
  
 $NO_2 > F > CI > OCH_3 > C_6H_5 > CH_3 > C_2H_5 > (CH_3)_2CH > (CH_3)_3C$ .

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

$$CH_2 = CH_2 < CH_3CH = CHCH_3 < (CH_3)_2C = CH_2$$

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

$$CH_2 = CHC_2H_5 < CH_3CH = CHCH_3 < CH_2 = CH = CH = CH_2 < CH_3 = CH = CH = CH_2$$

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

$$C_6H_5CH_3 < C_6H_5CH_2CI < C_6H_5CHCI_2 < C_6H_5CCI_3$$

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

An aromatic compound contains 69.4% C and 5.8% H

An aromatic compound contains 69.4%C and 5.8%H. A sample of 0.3 g of this compound give ammonia which neutralizes 25 mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. The empirical formula of the compound is

Ans:

Amount of  $H_2SO_4$  neutralized =  $(25 \times 10^{-3} \text{ L})(0.05 \text{ M}) = 1.25 \times 10^{-3} \text{ mol}$ 

The neutralization reaction is 2NH<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.

Amount of NH<sub>3</sub> evolved =  $2 \times 1.25 \times 10^{-3}$  mol =  $2.5 \times 10^{-3}$  mol Mass of N in the compound =  $(2.5 \times 10^{-3} \text{ mol})$  (14 g mol<sup>-1</sup>) = 0.035 g

Per cent of N in the compound = 
$$\frac{0.035}{0.3} \times 100 = 11.67$$

Per cent of O in the compound = 100 - (69.4 + 5.8 + 11.67) = 13.13

Ratio of atoms in the compound is

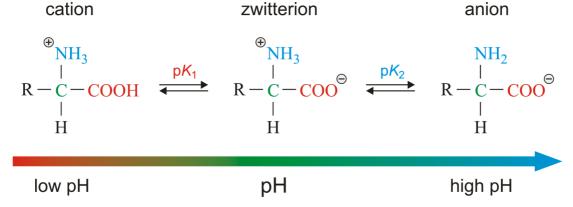
$$C:H:N:O::\frac{69.4}{12}:\frac{5.8}{1}:\frac{11.67}{14}:\frac{13.13}{16}::5.78:5.8:0.83:0.82::7:7:1:1$$

Hence, empirical formula: C7H7NO

Alternatively, calculate per cent of C in the given choices which comes out to be (a) 0.55, (b) 0.69, (c) 0.58 and (d) 0.65 only for choice (b), the answer tallies.

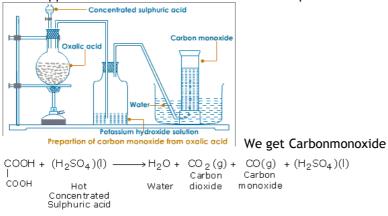
Zwitter lons - The Hydrogen atom ( rather ion ) moves to different positions depending on the PH ( So can have a positive charge at some position, or a negative charge at some other position, depending on the pH )

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?



# IMPORTANT ORDER AND FACTS OF ORGANIC CHEMISTRY

- 1. RCOCl > RCOOCOR > RCOOR > RCONH<sub>2</sub> Nucleophilic substitution reaction.
- 2. HI > HBr > HCl > RCOOH >  $C_6H_5OH > H_2O > CH \equiv CH > NH_3$  (Acidic nature).

- 3. CCl<sub>3</sub>CHO > HCHO > CH<sub>3</sub>CHO > CH<sub>3</sub>COCH<sub>3</sub> Nucleophilic addition reaction.
- 4.  $CH_2 = CH_2 > CH \equiv CH > C_6H_6$  Electrophilic addition reaction.

5. 
$$\bigcirc$$
 OH >  $\bigcirc$  OR >  $\bigcirc$  OR >  $\bigcirc$  Plectrophilic

Substitution Reaction

6. 
$$CH_2CI > CI - CH_2 - CH = CH_2 > C_2H_5CI > CH_2 = CH - CI$$
Nucleophilic Substitution Reaction

7. 
$$(\Box)_3C - CI > (C_6H_5)_3C - CI > \Box$$
  $-CH_2CI > C_2H_5CI$   
Nucleophilic Substitution Reaction

10. 
$$(CH_3)_2C = C(CH_3)_2 > CH_3 - CH = C - (CH_3)_2 > CH_3 - CH = CH - CH_3 > CH_3 - CH = CH_2 (Stability)$$

11. 
$$CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH = CH - CH_3 > CH_3 - CH_3 = CH_3 (Heat of Hydration)$$

- 13.  $NI_3 > NBr_3 > NCl_3 > NF_3$  (Basic strength)
- 14.  $Br_2 > Cl_2 > l_2$  (Selectivity for halogenation)
- 15. Halogenation of alkenes by cyclic halonium state, so anti attack takes place.
- 16. Hydroboration followed by oxidation is always anti markownikoff's addition due to steric effect.
- 17. Oximercuration demercuration is markownikoff's addition of water because some carbocation character in cyclic mercurium state.
- 18.  $CHCl_3$  in the presence of strong bases forms biradical :  $CCl_2$  which undergo addition with double or triple bonds.
- 19. When conjugated diene reacts with alkene or alkyne it is known as diel's elder synthesis.
- 20. Ozonolysis of cyclo alkadiene forms one mole dialdehyde while ozonolysis of cyclo alkadiene forms two moles of dialdehyde.
- 21. Ozonolysis with (CH<sub>3</sub>)<sub>2</sub>S is known as reductive ozonolysis.
- 22. Hydration of alkyne occur's in HgSO<sub>4</sub> and dil H<sub>2</sub>SO<sub>4</sub>.

- 23.1-alkynes forms ppt with Ag(NH<sub>3</sub>)<sub>2</sub><sup>®</sup> and Cu(NH<sub>3</sub>)<sub>4</sub><sup>+</sup>.
- 24. Cis-2-butene reacts with Br2 to forms dl(±) pair of enantiomers of 2,3-dibromobutane while in case of trans-2-butene forms meso-2,3-dibromo butane due to anti addition always.
- 25. Haloform test given by species with CH<sub>3</sub>CO-group but not in case of A.A.E. and tert. Butyl alcohol.
- 26. Chloral reacts with chloro benzene in con. H<sub>2</sub>SO<sub>4</sub> to form insectiside DDT.
- 27. NBS is used for free radical allylation.
- 28. Rate for  $S_N^{-1}$  reaction is  $3^{\circ} > 2^{\circ} > 1^{\circ}$  in protic polar solvent.
- 29. Rate for  $S_N^2$  reaction is 1° > 2° > 3° in polar aprotic solvent like DMSO, DMF, HMPT.
- 30. Chemical reactions like Hoffmann carbylamine and Reimer Tiemann's reaction active species is biradical CCl<sub>2</sub>.
- 31. If cyclo 1,3-penta diene reacts with CHCl<sub>3</sub> and potassium tert. butoxide to form chlorobenzene.
- 32. Alkyl halides reacts with AgCN to form isocyanides due to ambident nature of nucleophile, other ambident nucleophiles are  $\overset{\Theta}{\text{NO}_2}$  and  $\text{SO}_3^{-2}$ .
- 33. In dehydration of alcohols active species is carbocation so rearrangement occurs like hydride shift or alkyl shift.
- 34. Dehydration of cyclobutyl methyl alcohol ring expansion takes place, formation of cyclo pentene occurs.
- 35. In esterification where acid reacts with alcohol to form ester, OH given by acid while H by alcohol

- 36. Ether's reacts with HI to form alcohol and halide where fission of lower ether by  $S_N^2$  mechanism while higher ethers like ter. butyl methyl ether or alkyl methyl ether by  $S_N^1$  mechanism.
- 37. Quantitative estimation of ethers is done by ziesal's method.
- 38. If unsym. cyclic ether undergo fission it depends upon medium weather it is acid or basic like in acidic medium some character of carbocation so nucleophile goes to carbon where more alkyl groups are there while reverse in basic medium due to steric factor.
- 39. Aldehydes are reducing agent while ketones are not.
- 40. Aldehydes and ketones are separated by tollen's reagent.
- 41. Carbonyl and noncarbonyl are seprated by sodium bi sulphite and bradye's reagent.
- 42. As the size of alkyl group increases steric hindrance comes into play, reactivity towards nucleophilic addition decreases.
- 43. Aldehydes with hydrogen atom in the presence of dil base undergo enolization and form  $\stackrel{\circ}{\sim}$

- 44. If there is two-CHO group with <sup>∞</sup>hydrogen atom to form cyclic intra aldol product.
- 45. Aldehydes without -hydrogen atom in the presence of con. alkali to form each molecule of acid and alcohol by hydride active species.
- 46. Glyoxal reacts with con. KOH to form glycolate ion by Intra Cannizaro's.
- 47. Pinacol pinacolone type reactions involve protonation, deprotonation and alkyl shift.
- 48. Aldol, Perkin, reformatsky and knovengel's reactions are classified as carbanian active reaction.
- 49. In Beckmann's rearrangement migration of group which is anti to-OH group takes place.
- 50. Beckmann's rearrangent is a reaction of oximes in the presence of  $H_2SO_4$  or  $PCl_5$  to produce N-alkyl amide derivatives.
- 51. Migratory attitude of alkyl group in Pinacol-pinacolone, beckmann's and bayer villegar oxidation is  $-C_6H_5 > (CH_3)_3C > (CH_3)_2CH > C_2H_5 > CH_3$
- 52. Cyclo hexanoneoxime on beckmann's reaction gives caprolectum which on reaction with  $\overset{\text{th}}{\text{H}}$  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 redusing power of aromatic aldehyde.
- 59. HCOOH respond to oxidising agent due to presence of CHO group.
- 60. HI >  $H_2SO_4$  >  $HNO_3$  > RCOOH >  $H_2CO_3$  >  $C_6H_5OH$  >  $H_2O$  > CH  $\equiv CH$  >  $NH_3$  >  $CH_3$  C  $\equiv CH$  >  $CH_2$  =  $CH_2$  >  $H_2$  this is decreasing acidic nature.
- 61. Acids with  $\infty$ -hydrogen atom when reacts with halogen in the presence of P to form  $\infty$ -haloacid (HVZ).
- 62. Carboxyllic acid on reaction with  $PCl_5$ ,  $CH_2N_2$  and  $H_2O$  to form higher acid or next homologue.
- 63. For reactivity of acid derivatives use funda weaker the base better the leaving group.
- 64. Acid amide on reaction with PCl<sub>5</sub> to form alkane nitrile.
- 65. Anhydride on reaction with carbonyl compound in the presence of base (carbanian) forms  $\infty$ ,  $\beta$  unsaturated carboxyllic acid (perkin reaction)

- 66. Amide on reaction with Br<sub>2</sub> and alkali to form primary amine of lower homologue. Intermediate species is nitrene which undergo intra rearrangement to form RNH<sub>2</sub>.
- 67. Ester's with  $^{\infty}$ -hydrogen atom in the presence of strong base to form carbanian undergo nucleophilic substitution reaction forms  $^{\beta}$ -keto ester for example ethyl acetate in the presence of pot. ter. Butoxide form aceto acetic ester (AAE). reaction is known as clesen's ester condensation of four types
- (a) Simple clesen's ester condensation.
- (b) CROSS clesen's ester condensation.
- (c) Intra CEC (Dieckmann's condensation).
- (d) mixed clesen ester condensation.
- 68. For a compound to be aromatic it must be cyclic, planar and obey  $(4n + 2)^{\pi}$  electron rule.
- 69. Cyclooctatetraene is non aromatic compound while pyrrole, pyredene, furan, cyclopentadieneylanion all are aromatic.
- 70. In aromatic electrophilic substitution reaction there is no hydrogen isotopic effect except sulphonation and iodination.
- 71. m- directing groups like nitrobenzene and benzaldehyde cannot undergo fridal craft reaction.
- 72. Phenol is less acidic than general carboxylic acid, cannot react with NaHCO<sub>3</sub>.
- 73. Anilene is more reactive than phenol towards electrophilic substitution reaction because less energy difference between nitrogen and carbon.
- 74. Benzene diazonium chloride reacts with phenol or anilene to form azo compounds.
- 75.  $C_6H_5NH_2 > C_6H_5OH > C_6H_5OR > C_6H_5Br > C_6H_5NO_2$  (Reactivity towards electrophilic substitution reaction

#### General Series - Chemistry Fact Sheet - 3

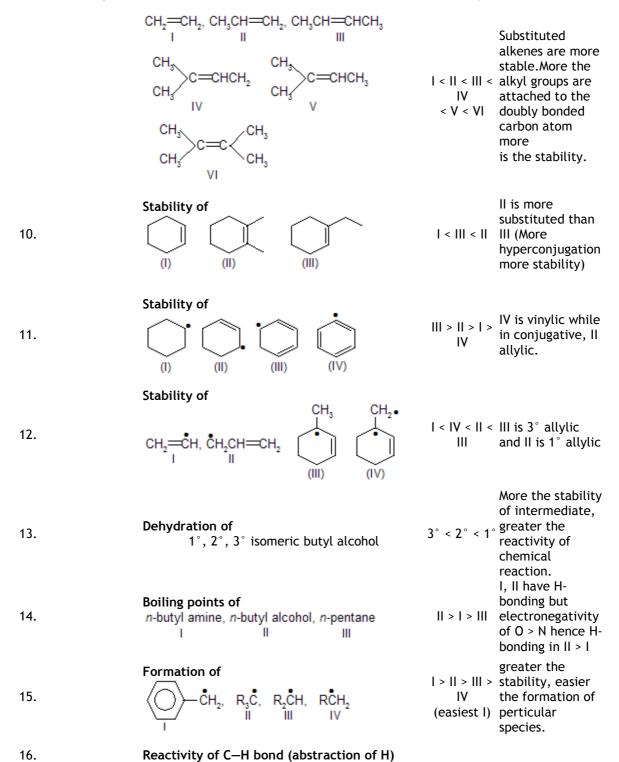
General series	Order	Why?	
1.	B.P. of  CH <sub>3</sub> CH <sub>2</sub> OH, CH <sub>3</sub> OCH <sub>3</sub> , CH <sub>3</sub> CH <sub>3</sub>	>    >	There is intermolecular H-bonding I. III has weak force of attraction and is most volatile. Intramolecular H-bonding in o-isomer makes it more volatile.
2.	B.P. of o, m, p-nitro phenol	o < m < p	

# Reactivity of ... with Tollen's reagent

- 3. HCHO, CH<sub>3</sub>CHO, CH<sub>3</sub>COCH<sub>3</sub> C<sub>6</sub>H<sub>5</sub>CHO
- -CHO group is
  easily oxidised
  I > II > IV > compared to keto
  III group due to
  redusing
  hydrogen.
- 4. Reactivity of ... with Fehling's solution I > II > IV > -do-IIII III = III = IV (above) IIII = -do-IIII
- 5. Extent of hydration of

  O O CHO CHO

  I < II < III < III < Halide makes C of carbonyl group more electropositive.
- 7. Reactivity of isomeric 1°, 2°, 3° butyl halide towards elimination (E1 or E2) due to stability of  $3^{\circ} < 2^{\circ} < 1^{\circ}$  intermediate carbocation
- 8. Dehydration of OH OH OH OH to dehydration is more easily dehydrated. IV is vinylic, hence least.
- 9. Stability of



Leaving nature (tendency) of  $\dots$  in  $S_N$  reaction.

18.

20.

I < II < III ~ If acid is strong, its conjugate 

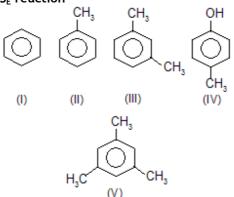
< V < VI < VII base is weak and greater the leaving tendency.

Rate of esterification of the following acids with MeOH

the  $\alpha-C$  increases, the tetrahedrally bonded interme. diate becomes more crowded and these slower the rate.

As the size of the substituents on

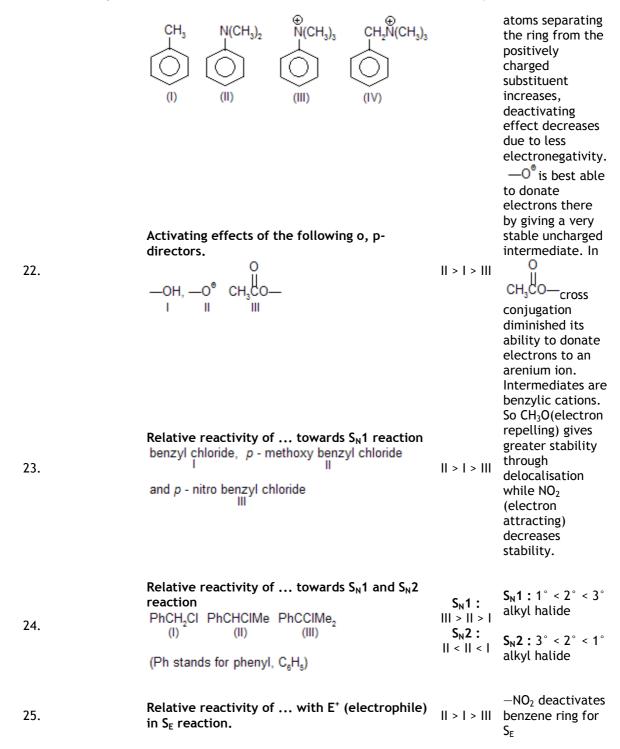
19. Relative reactivity of ... with electrophile in  $S_E$  reaction



 $\begin{array}{c} -\mathsf{CH}_3 \text{ is } o\text{-, } p\text{-} \\ \mathsf{I} > \mathsf{II} > \mathsf{IV} \quad \text{directing and} \\ > \mathsf{III} > \mathsf{V} \quad \text{responsible for activation.} \end{array}$ 

Relative reactivity of these compunds with electrophile in  $S_E$  reaction

21. Relative reactivity of ... with electrophile in II > I > IV > II As the number of  $S_E$  reaction.



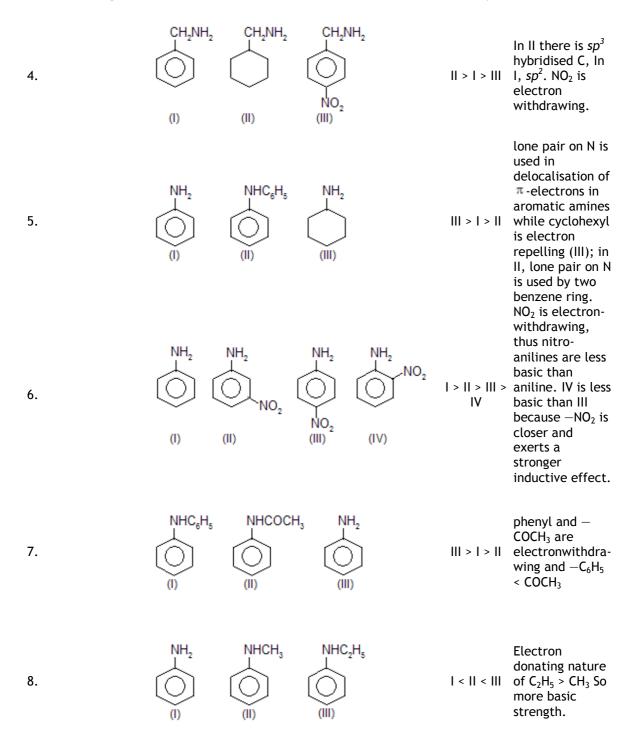
$$NO_2$$
 $CI$ 
 $NO_2$ 
 $NO_2$ 

26. Order of  $S_N 2$  reactivity of alkoxide nucleophiles

 $I < IV < V < \\ III \\ < II \\ < II \\$ 

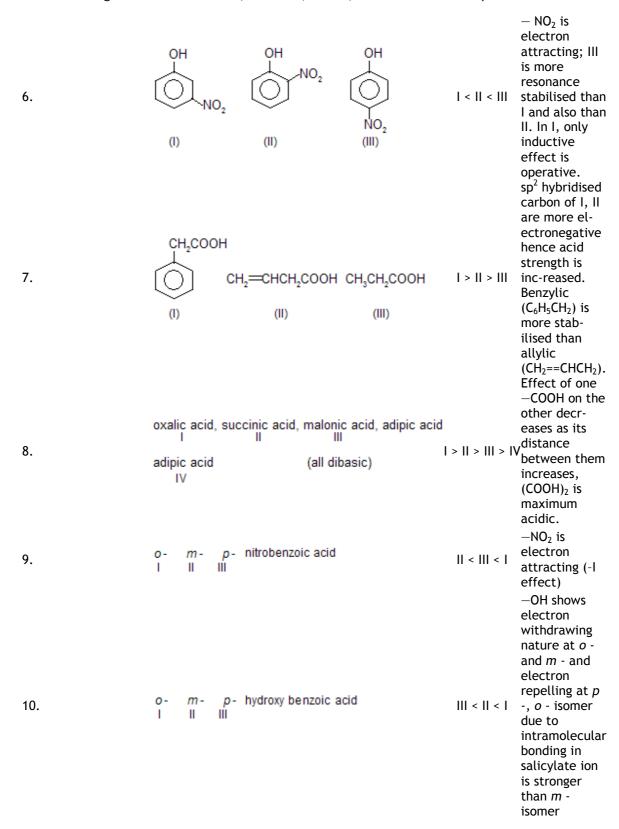
Basic power - Chemistry Fact Sheet - 2

Why? Basic power Order lone pair on N is not used in resonance of  $\pi$ electrons in I. In II lone pair of 1. | > ||| > || the ring is itself used in delocalisation (II) (III) while that of outside ring in III. −OCH<sub>3</sub> is strong electron donating group. OCH, This is due to ortho effect, all | > || > ||| > 2. the aniline are less basic than *p*-substituted (II) (III) (IV) aniline due to steric hindrance. I (hyper conugation and NH<sub>2</sub> NH<sub>2</sub> NH, induction) II (induction) IV | > || > ||| > 3. (ortho effect), I۷ ortho effect normally (II)(III)(IV) decreases basic nature.



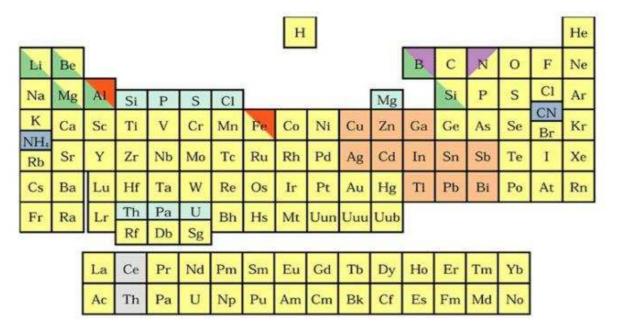
# Acidic Powers & Their Orders - Chemistry Fact Sheet

	Acidic power	Order	Why?	
1.		1- , 2- , 3- chlorobutanoic acid	<    <	Farther the (- l) group (Cl), lesser the acidic strength
2.		1-, 2-, 3- methyl pentanoic acid	<    <	Farther the (+I) group, greater the acidic power
3.		OH OH CH <sub>3</sub> OH NO <sub>2</sub>	<   <	-CH <sub>3</sub> is electron donating and - NO <sub>2</sub> is electron attracting
4.		OH OH CH <sub>3</sub> OH CH <sub>3</sub>	<   <	-CH <sub>3</sub> is electron repelling; decreases acidic strength of phenol
5.		OH OCH3 OH OH OCH3	<   <	<ul> <li>OCH<sub>3</sub> group contains +M effect and decreases acidic poer.</li> </ul>



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



## Given two Equations

$$(1) B_2O_3 + 6NaOH -> (X) + 3H_2O$$

$$(2) B_2O_3 + 2NaOH -> (Y) + H_2O$$

What are (X) and (Y)?

Ans: X is Sodium Borate and Y is Sodium meta borate

$$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3$$
 (Sodium Borate) +  $3H_2O$ 

$$B_2O_3 + 2NaOH \rightarrow 2NaBO_2$$
 (Sodium metaborate) +  $H_2O$ 

-

Silica is soluble in which of the following acids?

(1) HF (2) HCl (3) HBr (4) HI

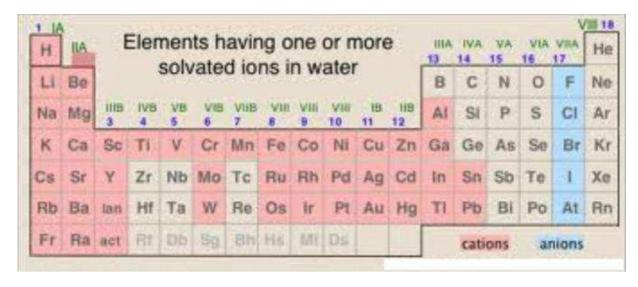
Solution:  $SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$  and again  $SiF_4 + 2HF \rightarrow H_2SiF_6$  (Hydroflurosilicic acid)

-

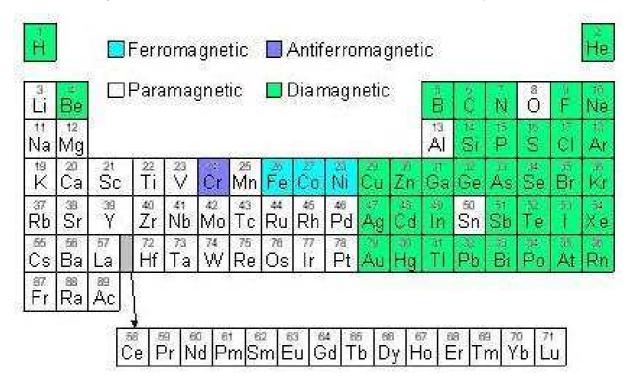
K<sub>3</sub>Co(NO<sub>2</sub>)<sub>6</sub> is Fischer's Salt

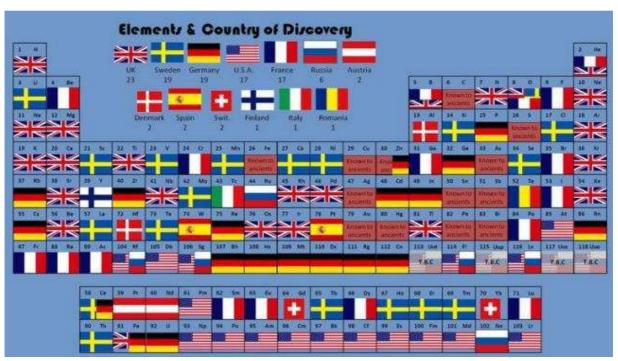
The brown ring test for  $NO_3^-$  is due to formation of the complex  $[Fe(H_2O)_5NO]^{2+}$ 

Merck's perhydrol is 30.4% H<sub>2</sub>O<sub>2</sub>



H<sub>2</sub>SO<sub>5</sub>, H<sub>2</sub>S<sub>2</sub>O<sub>8</sub> have peroxide linkages





Bromine reacting with NaOH in cold and hot give different mix of products. Specify

 $Br_2 + 2NaOH (cold) -> NaBr + NaOBr + H_2O$ 

 $3Br_2 + 6 NaOH (Hot) \rightarrow 5NaBr + NaBrO_3 + 3H_2O$ 

Malachite decomposes to give A +  $CO_2$  +  $H_2O$  and compound A on reduction with Carbon gives CO + B

# Identify A and B

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

CuO + C -> Cu ( B ) + CO

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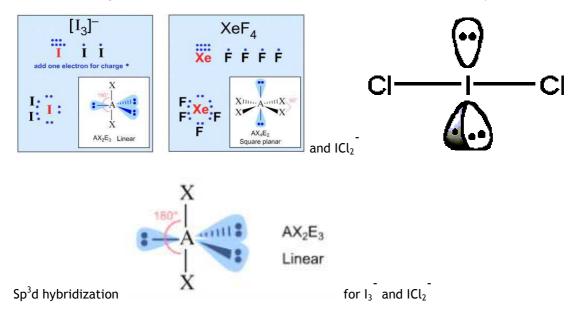
Some examples of Complex Anions

$$K_2PtCl_6 < == > 2K^+ + [PtCl_6]^{2-}$$

$$Na_3AlF_6 < == > 3Na^+ + AlF_6^{-3}$$

$$K_2SiF_6 < == > 2K^+ + SiF6^{-2}$$

Н	ton B											FI PA		- E			2 He
3	4											5	6	7	8	9	10
Li	Be											В	C	N	0	F	Ne
11	12											13	14	15	16	17	18
Na	Mg				- (13	9_3		10			63	Al	Si	Р	5	CI	Ar
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
K	Ca	Sc	Ti	٧	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Υ	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1	Xe
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	-71	Hf	Ta	W	Re	Os	.lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	-103	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuc
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	00
	W)	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
		89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	123
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	
	ilso kno kw Mer	n antiqu wn whe ndeleev ning pu	n (akw) publish	ed his	periodic	ished h table (	1869)	elemer	nts (178)		also	57 . 7 48 48 7		hed his to 2000	0	ic table	(1945

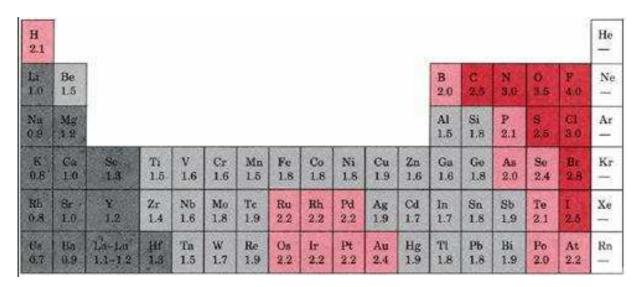


The ionization potential of Pb is higher than Sn due to poor shielding by 14f electrons present in Pb

Selenous acid H<sub>2</sub>SeO<sub>3</sub> (Oxidation Number of Se is +4)

Telluric acid  $H_6TeO_6$  (Oxidation Number of Te is +6)

#### Electronegativity Values (in Pauling Scale)



Microcosmic Salt is Na(NH<sub>4</sub>)HPO<sub>4</sub> Sodium ammonium hydrogen phosphate

Which of the following electrolyte will be most effective in coagulation of gold sol?

(1) 
$$NaNO_3$$
 (2)  $K_4Fe(CN)_6$  (3)  $Na_3PO_4$  (4)  $MgCl_2$ 

Gold sol is a negatively charged coagulation which is carried out by positively charged ion furnished by electrolyte

Coagulating power depends on the valency of cation of electrolyte. (Schulze Hardy Law )  $Mg^{2+}$  ion has highest valency so  $MgCl_2$  is most effective.

Organometallic compounds are Metal atoms directly linked with Carbon. So  $\text{Ti}(OC_3H_7)_4$  is not an organometallic compound.

V-T-E				Peri	odic 1	table	of ele	ectro	nega	tivity	usin	g the	Paul	ing s	cale			
-	• Atom	ic rad	ius d	ecrea	ses -	Ioniz	ation	ener	gy inc	rease	s → E	lectr	onega	tivity	incre	ases		
Group →	1	2	3	4	5	6	7	8	9	10	11.	12	13	14	15	16	17	18
1 Period																		
1	H 2.20																	He
2	Li	Be											8	C	-N	-0	- TE	Ne
97	0.98	1.57											2.04	2.55	3.04	3.44	3.98	
3	Na	Mg											Al	Si	P	S	O.	Ar
	0.93	1.31									LOS OF		1.61	1.90	2.19	2.58	3.16	
4	K	Св	Sc	Ti	٧	Gr	Min	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	W
377	0.82	1.00	1.36	1.54	1.63	1.66	1.55	1.83	1.88	1.91	1.90	1.65	1.81	2.01	2.18	2.55	2.96	3100
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pa	Ag	Cd	In	Sn	Sb	Te	-	Χe
18	0.82	0.95	1.22	1.33	1.6	2.16	1.9	2.2	2.28	2.20	1.93	1.69	1.78	1.96	2.05	2.1	2.66	2.6
6	Cs	Ba	*	Hf	Ta	W	Re	Os	- Ir	Pt	Au	Hg	TI.	Pb	81	Po	At	Bn
	0.79	0.89		1.3	1.5	2.36	1.9	2.2	2.20	2.28	2.54	2.00	1.62	1.87	2.02	2.0	2.2	2.2
7	Fr 0.7	Ra 0.9	27/2	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	FI	Uup	Lv	Uus	Uuc
-22	210000000000000000000000000000000000000		La	Ce	Pr	No	Pm	Sm	Eu	Gd	Tb	Dv	Ho	Er	Tm	Yb	Lu	
	Lantha	noids	1.1	1.12	1.13	1.14	1.13	1.17	1.2	1.2	1.1	1.22	1.23	1.24	1,25	1.1	1,27	
			Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr.	
	** Acti	noids	1.1	1.3	1.5	1.38	1.36	1.28	1.13	1.28	1.3	1.3	1.3	1.3	1.3	1.3	1.3	

IUPAC name of Diamminetetraaquacobalt III chloride

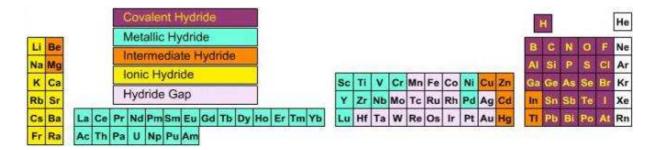
As per IUPAC nomenclature, the name of the complex [Co(H<sub>2</sub>O)<sub>4</sub>(NH<sub>3</sub>)<sub>2</sub>] Cl<sub>3</sub> is

- (a) Tetraaquadiaminecobalt(III) chloride
- (b) Tetraaquadiamminecobalt(III) chloride
- (c) Diaminetetraaquacobalt(III) chloride
- (d) Diamminetetraaquacobalt(III) chloride

#### Solution:

While naming a complex, the ligands are quoted in alphabetical order, regardless of their charges (followed by the metal). The oxidation state of the central metal is shown by a Roman numeral in brackets immediately following the metal name without any intervening blank. NH<sub>3</sub> is named as ammine and not as amine. Hence, the IUPAC name of the given compound is Diamminetetraaquacobalt(III) chloride.

Therefore, the choice (d) is correct.



Color of light absorbed by aqueous solution of CuSO4

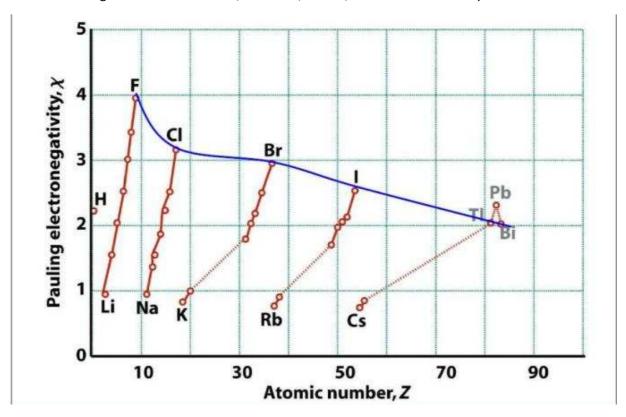
The colour of light absorbed by an aqueous solution of CuSO4 is

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

# Solution :

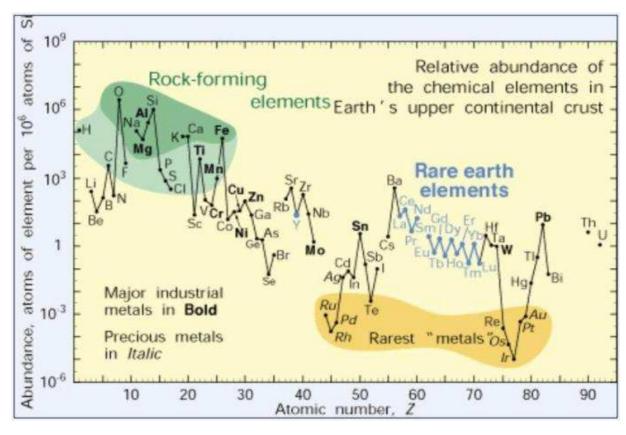
An aqueous solution of CuSO<sub>4</sub> is blue. The colour of light absorbed by this solution is that of complimentary colour which is orange-red.

Therefore, the choice (a) is correct



#### Periodic Table of the Elements Abundance of Elements in Seawater near the Surface all values are in mg/L He Ne 0 17 CI Al Mg Ar Ca ñ Cr Mn Fe Co Cu Zn Ge Zr Nb Tc Rh Pd Ag Cd 85 At Pt TI Hf W Os lr Ta 81 Rm Cs Bis Re Au Hig Pb Ra Db Bh Mt Rg Uut FI Uup Uuo Lanthanides Nd Pm Eu Gd Tb Dy Yb Sm Ho Tm Lu Actinides Cf 10° - 10° 10" - 10" 10

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





#### Half-life of Most Stable Isotope h<sub>10</sub> > 10<sup>8</sup> years 10<sup>5</sup> yrs < h<sub>va</sub> < 10<sup>6</sup> yrs He 1 yr < h<sub>10</sub> < 10<sup>3</sup> yrs 24 Symbol 1 day < h<sub>10</sub> < 10<sup>3</sup> yrs B Li Be C N 0 F Ne Al SI P s CI Ar Na Mg ٧ K Ca Sc Ti Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr Nb Mo Pd Cd Sh Rb Sr Zr Tc Ru Rh Ag In Sn Te 1 Xe Hf W Re Pt Ba Ir Hg TI Pb Bi Cs Ta Os Au Po At Rn Hs Fr Ra Rf Db Bh Mt Ds Rg Cn Uut FI Uup Lv Uuo Sg Lanthanides La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu U Bk Cf Actinides Ac Th Pa Np Pu Am Cm Es Fm Md

#### Periodic Table of the Radioactive Elements

Temperature dependent Magnetic behaviour

 $NiCl_2\{P(C_2H_5)_2(C_6H_5)\}_2$  exhibits temperature dependent magnetic behaviour (paramagnetic/diamagnetic). The coordination geometries of  $Ni^{2+}$  in the paramagnetic and diamagnetic states are respectively

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

#### Solution .

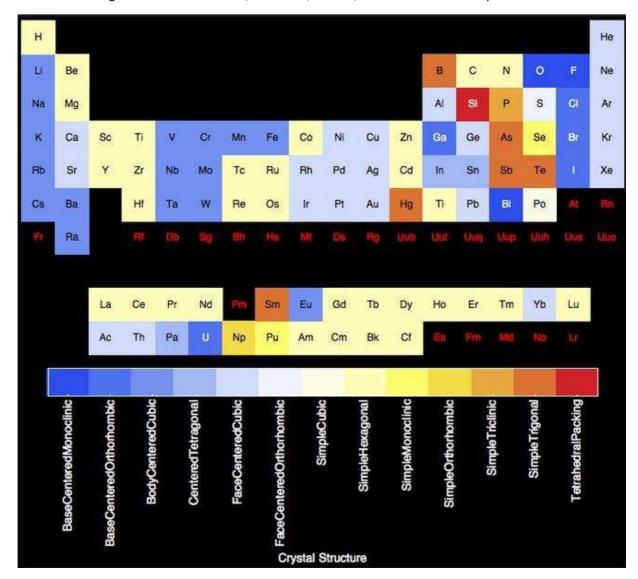
In the paramagnetic state, the complex will have unpaired 3d electrons in Ni<sup>2+</sup> ion, whereas no such electrons (i.e. all the 3d electrons will be paired) are present in the diamagnetic state.

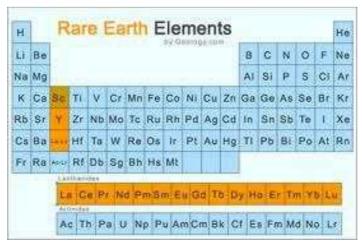
The electronic configuration of  ${}_{28}\text{Ni}^{2+}$  is  $\boxed{\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow\uparrow}$ 

If the two unpaired electrons remain present in the ion, it will undergo sp<sup>3</sup> hybridization to accommodate ligands and the geometry of the complex ion will be tetrahedral.

If the two unpaired electrons are coupled, the ion will be diamagnetic and it can undergo dsp<sup>2</sup> hybridization to accommodate ligands leading to the square planar geometry to the complex ion.

Therefore, the choice (c) is correct.





Reaction of white phosphorus with aqueous NaOH

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

(a) redox reaction, -3 and -5

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

#### Solution:

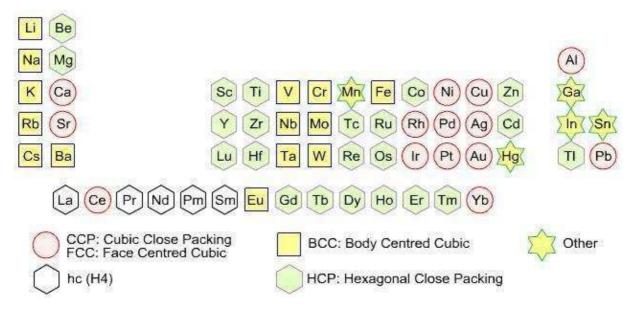
The reaction is 
$$\stackrel{0}{P_4}$$
 + 3NaOH + 3H<sub>2</sub>O  $\rightarrow$  PH<sub>3</sub> + 3NaH<sub>2</sub> PO<sub>2</sub>

The salt NaH2PO2 undergoes the following changes on heating.

$$^{+1}_{4\text{NaH}_{2}\text{PO}_{2}} \rightarrow \text{Na}_{4} + ^{5}_{2}\text{O}_{7} + ^{2}_{2}\text{PH}_{3} + ^{4}_{2}\text{O}_{0}$$

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

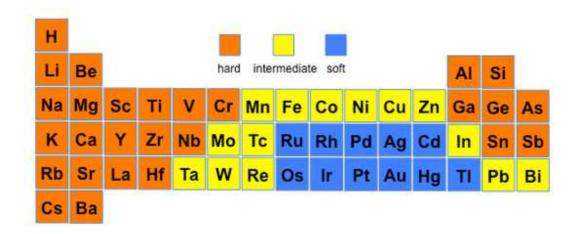
Therefore, the choice (c) is correct.



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

- (a) For electropositive metals (hard acids) the order of stabilities of the Halide complexes F > Cl > Br > I but for highly polarizing soft acid metal ions such as  $Hg^{+2}$ , we see the reverse order.
- (b) The most electropositive metals (hardest acids) show a greater tendency of forming complexes, with hard ligands such as F or Oxygen containing ligands.

Class A

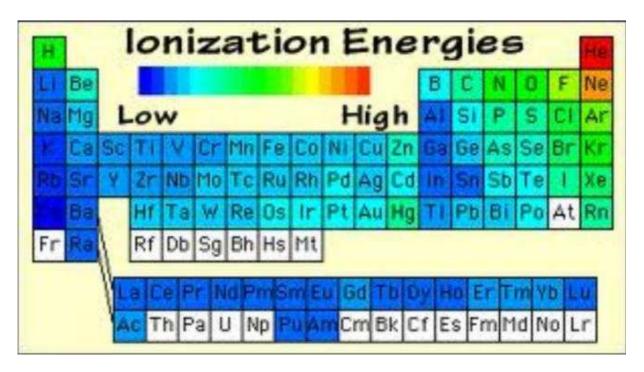


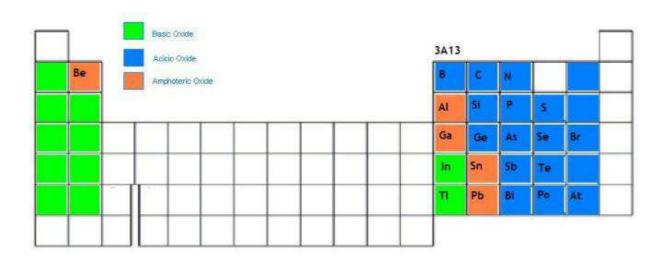
Class A Class C (Yellow ) Class B Class C (Yellow )

Metals are classified according to their acceptor properties.

- Class A Hard Acids. Show affinities to ligands whose basicity is proportional to protons.
- Class B Soft acids form stable olefin complexes.

Class C - Borderline metals





1 <b>H</b>		L	est	iits (	וו וכ	ег	lame	e ie	SUIC	or Va	ano	us C	all	nis			2 He
Li	4 Be											5 B	6 <b>C</b>	7 <b>N</b>	8 <b>O</b>	9 <b>F</b>	10 Ne
11 Na	12 Mg (White)											13 Al	l4 Si	15 <b>P</b>	16 S	17 <b>CI</b>	18 <b>Ar</b>
<u></u>	20 €a	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 <b>Co</b>	28 Ni	N 12	30 <b>Zn</b>	31 Ga	32 Ge	- As	Se	35 Br	36 Kr
Rb	Si	39 <b>Y</b>	40 <b>Zr</b>	41 Nb	42 <b>Mo</b>	43 Te	44 Ru	45 Rh	46 Pd	47 <b>Ag</b>	48 Cd	-	50 Sn	51 <b>Sb</b>	52 Te	53 1	54 Xe
III Car	56 <b>Ba</b>	57 La	72 <b>Hf</b>	73 <b>Ta</b>	74 W	75 <b>Re</b>	76 Os	77 Ir	78 Pt	79 <b>Au</b>	80 <b>Hg</b>	81 T1	The Park	83 Bi	84 <b>Po</b>	85 At	86 Rn
87 <b>Fr</b>	88 Ra	89 <b>Ac</b>	104 <b>Rf</b>	105 <b>Db</b>	106 <b>Sg</b>	107 <b>Bh</b>	108 Hs	109 <b>Mt</b>	110	111	112	113	114				1.
,		-		58 Ce	59 <b>Pr</b>	60 Nd	61 <b>Pm</b>	62 Sm	63 <b>Eu</b>	64 <b>Gd</b>	65 <b>Tb</b>	66 <b>Dy</b>	67 <b>Ho</b>	68 Er	69 <b>Tm</b>	70 <b>Yb</b>	71 Lu
				90 <b>Th</b>	91 <b>Pa</b>	92 U	93 <b>Np</b>	94 <b>Pu</b>	95 <b>Am</b>	96 Cm	97 Bk	98 <b>Cf</b>	99 Es	100 Fm	101 <b>Md</b>	102 <b>No</b>	103 Lr

						Electi	ron affir	nities in	the pe	riodic t	able						{hide
1	2	3	14	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 73																	He
EI 80	Be											B 27	C 122	N	0 141	F 328	Ne •
Na 53	Mg											Al 42	Si 134	P 72	S 200	CI 349	Ar
K 48	Ca 2	Sc 18	Ti 8	V 51	Cr 65	Mn	Fe 15	Co 64	Ni 112	Cu 119	Zn	Ga 41	Ge 119	As 79	Se 195	Br 324	Kr •
Hb 47	Sr 5	Y 30	Zr 41	Nb 86	Mo 72	To	Ru 101	Rh 110	Pd 54	Ag 126	Cq	In 39	Sn 107	Sb 101	Te 190	l 295	Xe
Co 46	Ba 14		HE	Ta 31	W 79	Re	Os 104	lr 150	Pt 205	Au 223	Hg	TI 36	Рb 35	Bi 91	Po	At	- Fin
FF	Ra	**	RI	Db	Sg	Bh			Ds	Pig	Cn	1111/11/20		Uup	Lv		Uuo
			To.	Co	Dr	Net										2	Lu
	* Lanth	anides	45	92				-				- 50	1,0		99		33
	** Ac	tinides	Ac	Th	Pa	U	Np	Po	Am	Cm	Bk	CI	Es	Fm	Md	No	U
	73 Li 80 Na 53 K 48 Hb 47 Cs 48	H 773  U Be 60 .  Na Mg 53 .  K Ca 48 2  Rb Sr 47 5  Cs Ba 46 14  Fr Ra 1	H 773  U Be 600 .  Na Mg 53 .  K Ca Sc 18  Hb Sr Y 7 5 30  Ca Bu .  46 14	H: 773  Li Be . 600 . Na Mg . 53 . K Ca Sc Ti 18 8  Rb Sr Y Zr 47 5 30 41  Fr Ra . Ri . Ri .	H-73  UI Be . 80 . Na Mg . 53 . K Ca Sc Ti V 48 2 18 8 51  Hb Sr Y Zr Nb 47 5 30 41 86  Ca Ba . Hf Ta . 48 14  Fr Ra . Rf Db . *Lanthanides La Ce . 45 92	H- 73  LI Be	1 2 3 4 5 6 7  H; 773  Li Be 60 .  Na Mg 53 .  K Ca Sc Ti V Cr Mn 48 2 18 8 51 65 .  Hb Sr Y Zr Nb Mo Tc 47 5 30 41 86 72 .  Ca Ba . Hf Ta W Re 48 14 . Hf Ta W Re 66 14 . Hf Ta W Re 77	1 2 3 4 5 6 7 8  H 773  UI Be .  N8 Mg .  K Ca Sc Ti V Cr Mn Fe .  48 2 18 8 51 65 . 15  Hb Sr Y Zr Nb Mo Tc Ru .  47 5 30 41 86 72 . 101  Cp Ba . HI Ta W Re Os .  48 14	1 2 3 4 5 6 7 8 9  H; 73  UI Be 60 .  Na Mg 53 .  K Ca Sc Ti V Cr Mn Fe Co 48 2 18 8 51 65 . 15 64  Hb Sr Y Zr Nb Mo Tc Ru Rh 47 5 30 41 86 72 . 101 110  Cs Ba . Hf Ta W Re Os Ir 48 14 . Hf Ta W Re Os Ir 48 14 . Hf Ta W Re Os Ir 48 14 . Hf Ta W Re Mo Iso Fr Ra . Rf Db Sg Bh Hs Mt	1 2 3 4 5 6 7 8 9 10  H' 73  UI Be . N8 Mg . S3 . K Ca Sc Ti V Cr Mn Fe Co Ni 48 2 18 8 51 65 . 15 64 112  Hb Sr Y Zr Nb Mo Tc Ru Hh Pd 47 5 30 41 86 72 . 101 110 54  Cs Ba . Hf Ta W Re Os Ir Pt 48 14 . Re Re 104 150 205  Fr Ra . Rf Db Sg Bh Hs Mt Ds  *Lanthanides 45 92 Pr Nd Pm Sm Eu	1 2 3 4 5 6 7 8 9 10 11  H; 73  UI Be 60 .  Na Mg 53 .  K Ca Sc Ti V Cr Mn Fe Co Ni Cu 48 2 18 8 51 65 . 15 64 112 119  Hb Sr Y Zr Nb Mo Tc Ru Hh Pd Ag 47 5 30 41 86 72 . 101 110 54 126  Ca Ba . Hf Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 14 . Ri Ta W Re Os Ir Pt Au 48 16 17 . Ri Ta W Re Os Ir Pt Au 48 17 . Ri Ta W Re Os Ir Pt Au 48 19 . Ri Ta W Re Os Ir Pt	H: 73  UI Be	1 2 3 4 5 6 7 8 9 10 11 12 13  HT 773  UI Be	1 2 3 4 5 6 7 8 9 10 11 12 13 14  H 73  UI Be 60  1	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15  H; 73  UI Be 0	1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16  H 73  UI Be 80 .	H

	Gro 1	up										nents (		960				18
1	H 1310	2											13	14	15	16	17	He 2370
100	Li 520	<b>Be</b> 900											<b>B</b> 800	C 1090	N 1400	0 1310	F 1680	Ne 2080
200	Na 490	Mg 730	3	4	5	6	7	8	9	10	11	12	AI 580	Si 780	P 1060	S 1000	CI 1250	Ar 1520
	<b>K</b> 420	<b>Ca</b> 590	<b>Sc</b> 630	Ti 660	V 650	Cr 660	Mn 710	Fe 760	<b>Co</b> 760	Ni 730	<b>Cu</b> 740	<b>Zn</b> 910	<b>Ga</b> 580	Ge 780	As 960	<b>Se</b> 950	Br 1140	Kr 1350
	<b>Rb</b> 400	<b>Sr</b> 550	<b>Y</b> 620	Zr 660	<b>Nb</b> 670	Mo 680	Tc 700	<b>Ru</b> 710	Rh 720	Pd 800	<b>Ag</b> 730	<b>Cd</b> 870	In 560	Sn 700	<b>Sb</b> 830	<b>Te</b> 870	1010	Xe 1170
	<b>Cs</b> 380	<b>Ba</b> 500	<b>La</b> 540	Hf 700	<b>Ta</b> 760	<b>W</b> 770	Re 760	Os 840	Ir 890	Pt 870	Au 890	Hg 1000	TI 590	<b>Pb</b> 710	Bi 800	Po 810	At	Rn 1030
-	Fr	Ra 510																

cyanide extraction process of silver from argentite ore

In the cyanide extraction process of silver from argentite ore, the oxidizing and reducing agents used are

(a) O2 and CO, respectively

(b) O2 and Zn dust, respectively

(c) HNO<sub>3</sub> and Zn, respectively

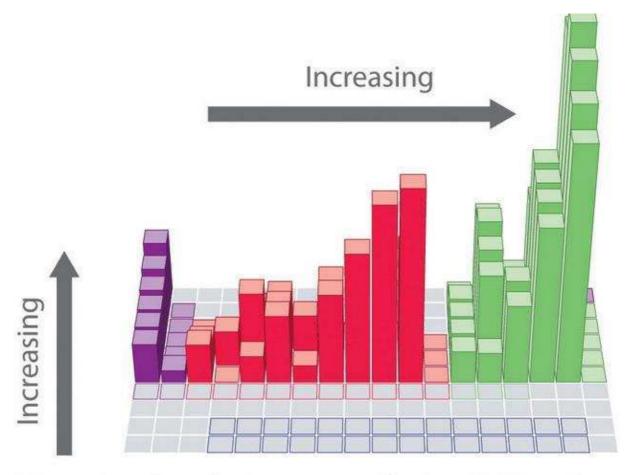
(d) HNO3 and CO, respectively

#### Solution:

The argentite ore contains  $Ag_2S$ . After crushing and concentration by froth flotation process, the ore is leached with 0.4 - 7% solution of sodium cyanide kept agitated with a current of air.

Silver passes into the solution as argentocyanide.  $Ag_2S + 4NaCN \rightleftharpoons 2Na [Ag(CN)_2] + Na_2S$ The air blown removes  $Na_2S$  as  $Na_2S_2O_3$  and  $Na_2SO_4$  causing the above reaction to proceed to completion. Silver

is recovered by adding zinc into argentocyanide.  $2Ag(CN)_2^- + Zn \rightarrow [Zn(CN)_4]^{2^-} + 2Ag$ Thus, oxidizing agent is  $O_2$  (from air) and the reducing agent is Zn. Therefore, the **choice (b)** is correct.



Magnitude of electron affinity (kJ/mol), s-, p-, and d-block elements



Common Name Chemical Name

acetone dimethyl ketone; 2-propanone (usually known as acetone)

acid potassium sulfate potassium bisulfate

acid of sugar oxalic acid ackey nitric acid

alcali volatil ammonium hydroxide

alcohol, grain ethyl alcohol
alcohol sulfuris carbon disulfide
alcohol, wood methyl alcohol

alum aluminum potassium sulfate

alumina aluminum oxide
antichlor sodium thiosulfate
antimony black antimony trisulfide
antimony bloom antimony trioxide
antimony glance antimony trisulfide
antimony red (vermillion) antimony oxysulfide

aqua ammonia aqueous solution of ammonium hydroxide

aqua fortis nitric acid

aqua regia nitrohydrochloric acid aromatic spirit of ammonia ammonia in alcohol arsenic glass arsenic trioxide

azurite mineral form of basic copper carbonate

asbestos magnesium silicate
aspirin acetylsalicylic acid
baking soda sodium bicarbonate
banana oil (artificial) isoamyl acetate
barium white barium sulfate

benzol benzene

bicarbonate of soda sodium hydrogen carbonate or sodium bicarbonate

bichloride of mercury mercuric chloride

bichrome potassium dichromate
bitter salt magnesium sulfate

black ash crude form of sodium carbonate

black copper oxide cupric oxide

black lead graphite (carbon)
blanc-fixe barium sulfate

bleaching powder chlorinated lime; calcium hypochlorite

blue copperas copper sulfate (crystals)

blue lead lead sulfate
blue salts nickel sulfate

blue stone copper sulfate (crystals)

blue vitriol copper sulfate bluestone copper sulfate

bone ash crude calcium phosphate

bone black crude animal charcoal

boracic acid boric acid

borax sodium borate; sodium tetraborate

bremen blue basic copper carbonate

brimstone sulfur

burnt alum anhydrous potassium aluminum sulfate

burnt lime calcium oxide
burnt ochre ferric oxide
burnt ore ferric oxide

brine aqueous sodium chloride solution

butter of antimony antimony trichloride

butter of tin anhydrous stannic chloride

butter of zinc zinc chloride

calomel mercury chloride; mercurous chloride

carbolic acid phenol

carbonic acid gas carbon dioxide
caustic lime calcium hydroxide
caustic potash potassium hydroxide
caustic soda sodium hydroxide
chalk calcium carbonate

Chile saltpeter sodium nitrate
Chile nitre sodium nitrate

Chinese red basic lead chromate

Chinese white zinc oxide

chloride of soda sodium hypochlorite chloride of lime calcium hypochlorite

chrome alum chromic potassium sulfate

chrome green chromium oxide
chrome yellow lead (VI) chromate
chromic acid chromium trioxide
copperas ferrous sulfate

corrosive sublimate mercury (II) chloride corundum (ruby, sapphire) chiefly aluminum oxide cream of tartar potassium bitartrate

crocus powder ferric oxide

crystal carbonate sodium carbonate

dechlor sodium thiophosphate

diamond carbon crystal

emery powder impure aluminum oxide

epsom salts magnesium sulfate

ethanol ethyl alcohol

farina starch

ferro prussiate potassium ferricyanide

ferrum iron

flores martis anhydride iron (III) chloride fluorspar natural calcium fluoride

fixed white barium sulfate

flowers of sulfur sulfur

'flowers of' any metal oxide of the metal

formalin aqueous formaldehyde solution

French chalk natural magnesium silicate

French vergidris basic copper acetate galena natural lead sulfide

Glauber's salt sodium sulfate

green verditer basic copper carbonate

green vitriol ferrous sulfate crystals gypsum natural calcium sulfate

hard oil boiled linseed oil heavy spar barium sulfate

hydrocyanic acid hydrogen cynanide

hypo (photography) sodium thiosulfate solution

Indian red ferric oxide

Isinglass agar-agar gelatin

jeweler's rouge ferric oxide killed spirits zinc chloride

lampblack crude form of carbon; charcoal

laughing gas nitrous oxide
lead peroxide lead dioxide
lead protoxide lead oxide
lime calcium oxide

lime, slaked calcium hydroxide

limewater aqueous solution of calcium hydroxide

liquor ammonia ammonium hydroxide solution

litharge lead monoxide
lunar caustic silver nitrate
liver of sulfur sufurated potash
lye or soda lye sodium hydroxide
magnesia magnesium oxide
manganese black manganese dioxide

marble mainly calcium carbonate

mercury oxide, black mercurous oxide methyl alcohol methanol methylated spirits methyl alcohol milk of lime calcium hydroxide milk of magnesium magnesium hydroxide milk of sulfur precipitated sulfur "muriate" of a metal chloride of the metal muriatic acid hydrochloric acid

natron sodium carbonate
nitre potassium nitrate
nordhausen acid fuming sulfuric acid

oil of mars deliquescent anhydrous iron (III) chloride

oil of vitriol sulfuric acid

oil of wintergreen (artificial) methyl salicylate
orthophosphoric acid phosphoric acid
Paris blue ferric ferrocyanide
Paris green copper acetoarsenite

Paris white powdered calcium carbonate

pear oil (artificial) isoamyl acetate

pearl ash potassium carbonate

permanent white barium sulfate plaster of Paris calcium sulfate

plumbago graphite

potash potassium carbonate
potassa potassium hydroxide
precipitated chalk calcium carbonate
Prussic acid hydrogen cyanide

pyro tetrasodium pyrophosphate

quicklime calcium oxide

quicksilver mercury

red lead lead tetraoxide

red liquor aluminum acetate solution red prussiate of potash potassium ferrocyanide red prussiate of soda sodium ferrocyanide

Rochelle salt potassium sodium tartrate

rock salt sodium chloride rouge, jeweler's ferric oxide

rubbing alcohol isopropyl alcohol
sal ammoniac ammonium chloride
sal soda sodium carbonate
salt, table sodium chloride

salt of lemon potassium binoxalate salt of tartar potassium carbonate saltpeter potassium nitrate silicon dioxide silica slaked lime calcium hydroxide soda ash sodium carbonate soda nitre sodium nitrate soda lye sodium hydroxide soluble glass sodium silicate dilute sulfuric acid

spirit of hartshorn ammonium hydroxide solution

hydrochloric acid spirit of salt spirit of wine ethyl alcohol spirits of nitrous ether ethyl nitrate

sugar, table sucrose

sour water

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 sulfuric acid vitriol

washing soda sodium carbonate sodium silicate water glass white caustic sodium hydroxide white lead basic lead carbonate white vitriol zinc sulfate crystals yellow prussiate of potash potassium ferrocyanide

yellow prussiate of soda sodium ferrocyanide

zinc vitriol zinc sulfate zinc white zinc oxide

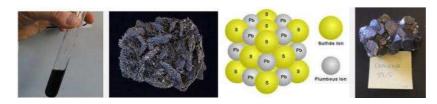
Westron - A refrigerant.  $C_1$   $C_2H_2Cl_4$ 

Colours of Compounds

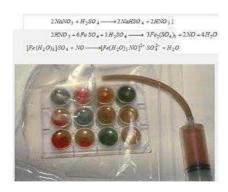
# Cr2(SO4)3 - green



PbS - Black



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



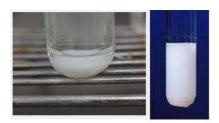
(CH3COO)3Fe - blood red



NH4Cl - white fumes

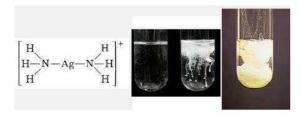


AgCl - curdy white precipitate



AgCl - curdy white precipitate

AgCl + NH4OH -> Ag(NH3)2Cl +H2O



AgCl + NH40H --> Ag(NH3)2Cl +H20

CrO3 + HCl -> CrO2Cl2 (deep red fumes) + H2O



CrO2Cl2 (deep red fumes)

#### NaOH + CrO2Cl2 -> Na2CrO4 (yellow) + NaCl + H2O

# Na2CrO4 (yellow)

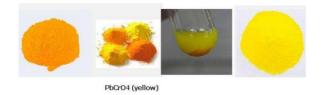


#### **Sodium Chromate**

Sodium chromate is used in the industry to manufacture chromium compounds. Sodium chromate (Na2CrO4) is a yellow solid chemical compound. It is used in many industries like petroleum industry, textile industry. Sodium chromate is used in the industry as an important source for manufacture of chromium compounds. Sodium Chromate makes a protective film on metal surfaces and is used is corrosion control applications such as coolants containing alcohols and water cooling systems.



Na2CrO4 + Pb(CH3COO)2 -> PbCrO4 (yellow) + CH3COONa

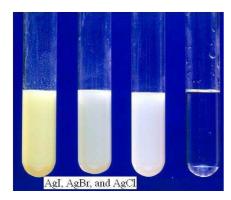


NaBr + AgNO3 -> AgBr (pale yellow) + NaNO3





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



NO<sub>2</sub>



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)



Mo308.xH2O - molybdenum blue



SiF4 + H2O -> H4SiO4 (silicic acid - white) + H2SiO4



Na2S + Na2[Fe(CN)5NO] -> Na4[Fe(CN)5NOS) - violet colour



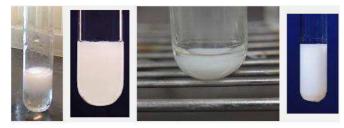
Na2S + CdCO3 -> CdS (yellow) + Na2CO3



Na3[Co(NO2)6] + KCl -> K3[Co(NO2)6] (potassium cobaltnitrate - yellow ppt) + NaCl



AgCl, PbCl2, Hg2Cl2 - white

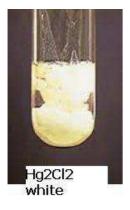


AgCl White

#### PbCl2 is white



Hg2Cl2 is white



H2S, PbS, Bi2S3, CuS - black

**H2S** is Black



# PbS is Black



Bi2S3 is Black

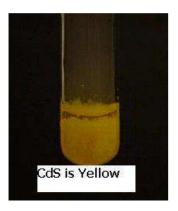


CuS - black



CdS, As2S3, SnS2 - Yellow

CdS is Yellow



As 2S3 is Yellow





SnS2 is Yellow





Sb2S3 is orange



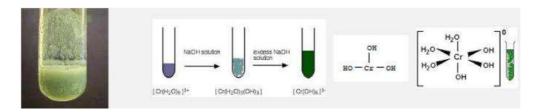
Sb2S3 is Orange

# SnS is Brown



SnS is Brown is your teacher says so. SnS is Yellow if your teacher says so :-)

# Cr(OH)3 is green



# Chromium (III) Oxide is Green

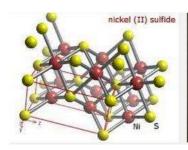


CoS, NiS - black

# CoS is black



NiS is Black Mineral Millerite







**Cobalt Oxide is Black** 



Cobalt Sulphate is deep red brown



# Cobalt Nitrate is deep red brown



# Cobalt Chloride is deep Brown red



# Cobalt Acetate is deep Brown



Azulene - Deep Bue

 $Iodoform - CHI_3 \ {\begin{tabular}{c} Yellow \\ \hline \end{tabular}}$ 

Iron Phenol complex - Violet - [ Fe (  $OC_6H_5$ )<sub>6</sub> ]<sup>-3</sup>

 $6 C_6 H_5 OH + FeCl_3 - -> [Fe (OC_6 H_5)_6]^{-3} + 3 H^+ + Cl^-$ 

Ammonium Phosphomolybdate - Yellow -  $(NH_4)_3PO_4.12MoO_3$  ( Yellow )

Prusian Blue - Fe<sub>4</sub> [Fe(CN)<sub>6</sub>]<sub>3</sub>.xH<sub>2</sub>O

[Fe(CN)<sub>3</sub> NOS ]<sup>-4</sup> - Violet

[Fe(SCN)]<sup>2+</sup> Blood Red

 $[Co(NH_3\ )_5\ Br]^{+2}\ SO_4^{-2}$  - Violet - Pentaaminebromocobalt(III)sulphate

$$[Co(NH_3)_5SO_4]^+Br^- \rightarrow Red$$

#### Test for Halogen:

Halogens present in an organic compound forms sodium halide on fusion with sodium metal. Sodium halide extracted with water can be easily identified by adding silver nitrate solution after acidifying with dil.  $HNO_3$ .

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

$$Na + Cl \rightarrow NaCl$$

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

$$Na + Br \rightarrow NaBr$$

$$NaBr + AgNO_3 \rightarrow AgBr + NaNO_3$$

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

$$Na + I \rightarrow NaI$$

#### Test for Nitrogen:

The carbon and nitrogen present in the organic compound on fusion with sodium metal gives sodium cyanide (NaCN) soluble in water. This is converted in to sodium ferrocyanide by the addition of sufficient quantity of ferrous sulphate. Ferric ions generated during the process react with ferrocyanide to form prussian blue precipitate of ferric ferrocyanide.

$$Na + C + N \rightarrow NaCN$$

$$6NaCN + FeSO_4 \rightarrow Na_4[Fe(CN)_6] + Na_2SO_4$$

Sodium ferrocyanide

$$Na_4[Fe(CN)_6] + Fe^{3+} \rightarrow Fe_4[Fe(CN)_6]_3$$

Ferric ferrocyanide

FeCl3 + K4[Fe(CN)6] -> Fe4[Fe(CN)6]3 (prussian blue) + KCl



#### Test for Sulphur:

If sulphur is present in the organic compound, sodium fusion will convert it into sodium sulphide. Sulphide ions are readily identified using sodium nitroprusside.

$$Na + S \rightarrow Na_2S$$

$$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$$

Sodium nitroprusside violet colour

#### Test for both Nitrogen and Sulphur:

If both nitrogen and sulphur are present in an organic compound, sodium fusion will convert it into sodium thiocyanate which then react with  $Fe^{3+}$  to form blood colour complex  $[Fe(SCN)]^{2+}$ 

$$Na + C + N + S \rightarrow NaSCN$$

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

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

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



BaCO3 powder

# SrCO3 is white



CaCO3 powder is white



CaCO3 Calcium Carbonate Powder

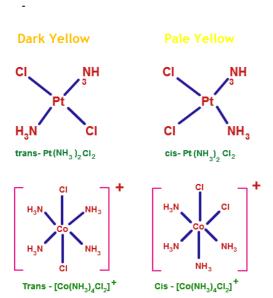
## Mg(NH4)PO4 is white



Pentaamminechlorocobalt(III)Bromide

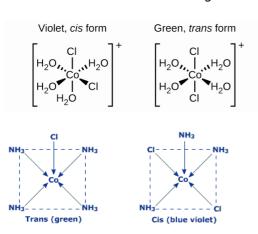
# $[\ Co(NH_3)_5CI\ ]\ CI_2\ _{Pentaamminechlorocobalt(III)chloride}$





Cis is Blue Violet

trans is green



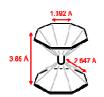
Eta bonds - Also known as Hapticity - Hapticity is the coordination of a ligand to a metal center via an uninterrupted and contiguous series of atoms.

The hapticity of a ligand is described with the Greek letter  $\eta$  ('eta'). For example,  $\eta 2$  describes a ligand that coordinates through 2 contiguous atoms. In general the  $\eta$ -notation only applies when multiple atoms are coordinated (otherwise the  $\kappa$ -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  $\kappa$ -notation is used once again. Lastly, bridging ligands are described with the  $\mu$  ('mu') notation.

Ferrocene - bis(η5-cyclopentadienyl)iron



Uranocene - bis $(\eta 8-1,3,5,7$ -cyclooctatetraene)uranium



 $W(CO)3(PPri3)2(\eta 2\text{-H2}\ )$  - the first compound to be synthesized with a dihydrogen ligand ( also known as Dihydrogen Complexes )

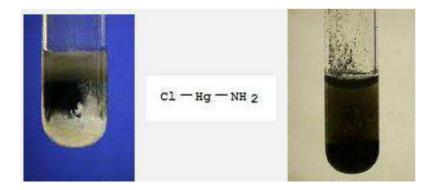
 $IrCl(CO)[P(C6H5)3]2(\eta 2-O2)$  - the dioxygen derivative which forms reversibly upon oxygenation of Vaska's complex.

\_

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

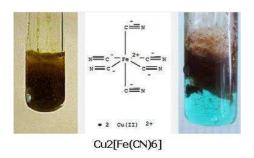


#### Oxidation of Phenol

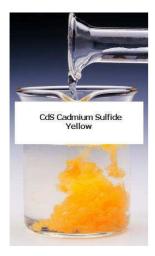
#### **Test of Phenol**

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

## Cu(NO3)2 + K4[Fe(CN)6] -> Cu2[Fe(CN)6] (Chocolate brown) +KNO3



## Cd(NH3)4(NO3)2 + H2S -> CdS (yellow) + NH4NO3 + NH3



HgCl2 + SnCl2 -> Hg2Cl2 (white) + SnCl4



## Liebermann's Nitroso Reaction

SbCl3 + H2O -> SbOCl (white) + HCl

## **SbOCI Antimony oxychloride**



## **Antimony Trioxide is white**



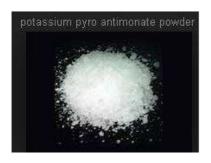
**Antimony Pentoxide is gray** 



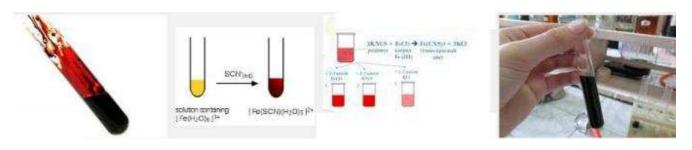
**Antimony Trichloride is white** 



#### Potassium antimonate white



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



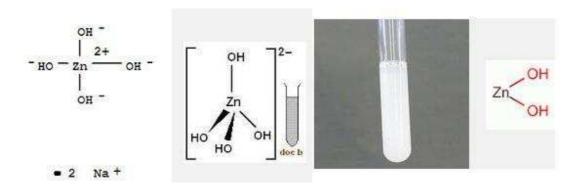
## **Can Test**

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.

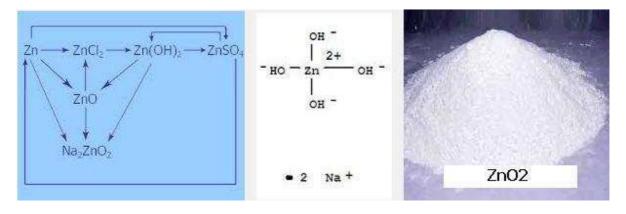
$$(NH_4)_2[Ce(NO_3)_6] + 2C_6H_5OH \rightarrow [Ce(NO_3)_4 (C_6H_5OH)_2] + 2NH_4NO_3$$
  
CAN Phenol green or brown ppt.

Phenol gives blue colour with ammonia and sodium hypo chlorite.

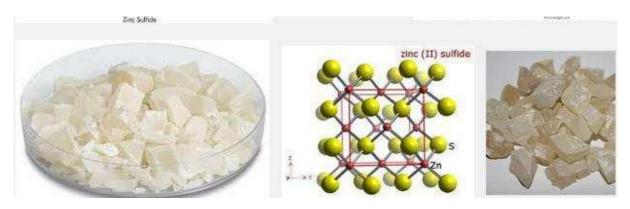
ZnCl2 + 2NaOH -> Zn(OH)2 (white ppt) + 2NaCl



Zn(OH)2 + NaOH -> Na2ZnO2 (soluble) + H2O

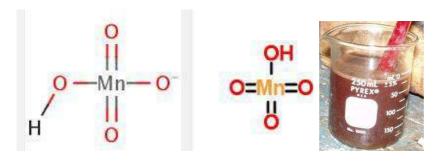


Na2ZnO2 + H2S -> ZnS (white) + NaOH



$$\begin{array}{cccc} 2KI + H_2O + O_3 & \longrightarrow 2KOH + O_2 + I_2 \\ \text{Potassium Ozone} & \text{Potassium Iodine} \\ \text{iodide} & \text{hydroxide} & \text{(Violet vapours)} \end{array}$$

Mn(NO3)2 + Pb3O4 + HNO3 -> HMnO4 (pink) + Pb(NO3)2 + H2O





Co(NO2)3 + KNO2 -> K3[Co(NO2)6] (yellow)



Na4Co(CO3)2 + H2O + [O] -> Na3Co(CO3)2 (green coloration) + NaOH

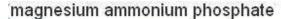




NiCO3 + [O] -> Ni2O3 (black) + CO2



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





K2HgI4 + NH4CI + KOH -> NH2HgOHgI (lodide of millon's base, brown ppt) + KCI + H2O



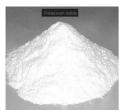
## Chromium oxide powder is green



#### Bismuth oxide is Yellow



#### KI Potassium lodide is white



Tin reacts with conc. HNO<sub>3</sub> forming metastannic acid (H<sub>2</sub>SnO<sub>3</sub>).

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

SnO<sub>2</sub> is an amphoteric oxide.

Stannous chloride (SnCl<sub>2</sub>) acts as a good reducing agent. It reduces HgCl<sub>2</sub> to first Hg<sub>2</sub>Cl<sub>2</sub> and then to Hg. It also reduces FeCl<sub>3</sub> to FeCl<sub>2</sub>.

Stannic chloride (SnCl<sub>4</sub>) is a liquid and fumes in air due to hydrolysis. It acts as a Lewis acid and dissolves in concentrated HCl forming H<sub>2</sub>SnCl<sub>6</sub>.

SnCl<sub>4</sub>.5H<sub>2</sub>O is called butter of tin.

SnS dissolves in yellow ammonium sulphide.

#### Aluminum Oxide is white

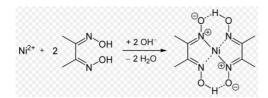


Mercuric iodide Hgl<sub>2</sub>: It is a yellow solid below 400K but changes to red solid above 400K.

It dissolves in excess of KI forming K2HgI4;

Alkaline solution of K<sub>2</sub>Hgl<sub>4</sub> is called Nessler's reagent.

Add NH4OH excess and dimethylglyoxime to NiCl2 then a rosy red ppt of nickel appears





A sample of Ni(dmgH)<sub>2</sub>

CuO + B2O3 (Glassy bead) -> Cu(BO2)2 (Copper metabolite - blue)



## Compounds of zinc

Zinc oxide ZnO: Zincite (ZnO) is also called Philospher's wool. It is a white powder, becomes yellow on heating and again white on cooling. It is amphoteric in nature. It is used as a white pigment under the name Zinc white or Chinese white.

Zinc Sulphate (white vitriol), ZnSO<sub>4</sub>. 7H<sub>2</sub>O: It is a colourless transparent crystal highly soluble in water. It is used as an eye-lotion and for preparing double salts. On heating it loses its molecules of water as,

ting it loses its molecules of water as,
$$ZnSO_4.7H_2O \xrightarrow{375K} ZnSO_4. H_2O \xrightarrow{725K} ZnSO_4$$

$$\xrightarrow{1075K} ZnO + SO_2 + O_2$$

Verdigris - basic copper acetate



This pigment was used to the Middle Ages in paints. Until the nineteenth century this was the most vibrant shade of green available and it was used by artists widely. The color comes from copper acetate and you should know that it is highly toxic to humans.

## **Compounds of Mercury**

(1) Mercuric oxide, HgO: It is obtained as a red solid by heating mercury in air or oxygen for a long time at 673 K



 $2Hg + O_2 \rightarrow 2 HgO$  ( red ) or by heating mercuric nitrate alone or in the presence of Hg

Heat

2Hg ( 
$$NO_3$$
 )<sub>2</sub>  $\rightarrow$  2HgO + 4NO<sub>2</sub> + O<sub>2</sub>

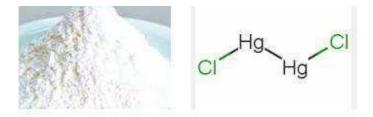
red



When NaOH is added to a solution of HgCl<sub>2</sub>, yellow precipitate of HgO are obtained.

$$Hg_2 CI_2 + 2NaOH \rightarrow HgO \downarrow + H_2O + 2NaCl$$

(yellow)



Red and yellow forms of *HgO* differ only in their particle size. On heating to 673 K, yellow form changes to red form.



It is used in oil paints or as a mild antiseptic in ointments.

(2) Mercuric chloride,  $HgCl_2$ : It is obtained by treating Hg with  $Cl_2$  or by heating a mixture of NaCl and  $HgSO_4$  in presence of small amount of  $MnO_2$  (which oxidizes any Hg(I) salts formed during the reaction).

#### Heat

## $MnO_2$





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).

$$\label{eq:2dgCl2} \begin{array}{l} 2 \text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_4 \\ \\ \text{white ppt.} \\ \\ \text{Hg}_2 \text{Cl}_2 + \text{SnCl}_2 \rightarrow 2 \text{Hg} + \text{SnCl}_4 \\ \\ \\ \text{grey} \end{array}$$

With ammonia it gives a white ppt. known as infusible white ppt.

 $\begin{array}{l} \operatorname{HgCl_2} + 2\operatorname{NH_3} \to \operatorname{Hg} \left( \ \operatorname{NH_2} \right) \operatorname{CI} + \operatorname{NH_4} \operatorname{CIA} \ \text{dilute solution of HgCl_2} \ \text{is used as an antiseptic.(3)} \ \text{Mercuric iodide,} \ Hgl_2 : \ \text{It is obtained when a required amount of} \ KI \ \text{solution is added to a solution} \ \text{of} \ \cdot \operatorname{HgCl_2} \operatorname{HgCl_2} + 2\operatorname{KI} \to \operatorname{Hgl_2} + 2\operatorname{KCl}^{(\text{red})} \operatorname{Below} \ 400 \ K, \ \operatorname{Hgl_2} \ \text{is red but above} \ 400 \ K, \ \text{it turns yellow} \ \\ HgI_2 \ \text{below} \ 400 \ K \ \text{hgl_2} \ \text{is red but above} \ 400 \ K, \ \text{it turns yellow} \ \\ HgI_2 \ \text{below} \ 400 \ K \ \text{hgl_2} \ \text{readily dissolves in excess of} \ KI \ \text{solution to form the} \ \left( \ \operatorname{Hgl_4} \right)^2 \ \text{complex ion.} \ \operatorname{Hgl_2} + 2\operatorname{KI} \to \ K_2\operatorname{Hgl_4} \ \text{Red ppt.} \ \text{soluble colourless solution} \ \end{array}$ 

An alkaline solution of  $K_2$  [Hgl<sub>4</sub>] is called Nessler's reagent and is used to test NH<sup>+</sup><sub>4</sub> ions.

It gives a brown ppt. of NH<sub>2</sub> - Hg - O Hg - I (lodide of Millon's base) with NH<sup>+</sup><sub>4</sub> ions.

$$2K_2$$
 [  $HgI_4$  ] +  $NH_3$  +  $3KOH \rightarrow NH_2$ .  $HgO$ .  $HgI$  +  $7KI$  +  $2H_2$  O

It is used in ointments for treating skin infections.

(4) Mercurous chloride,  $Hg_2Cl_2$ : It is obtained as under:

(a) 
$$Hg_2$$
 (  $NO_3$  ) +  $2NaCl \rightarrow Hg_2 Cl_2 + 2NaNo_3$ 

white ppt.

#### Heat in an iron retort

(b)  $HgCl_2 + Hg \rightarrow Hg_2 Cl_2$  (condenses on cooling)

It is purified by sublimation.

Mercurous chloride is also called calomel. It is a white powder insoluble in  $H_2O$ . On heating, it decomposes to give  $HgCl_2$  and Hg.

Heat
$$_{Hg2} Cl_2 \rightarrow Hgcl_2 + Hg$$

It dissolves in chlorine water forming mercuric chloride.

With ammonia, it turns black due to the formation of a mixture of finely divided black Hg and mercuric amino chloride.

$$Hg_2Cl_2 + 2NH_3 \rightarrow Hg + NH_2 HgCl + NH_4Cl$$

It is used to prepare standard calomel electrode and as a purgative in medicine.

(5) Mercuric sulphide, HgS: The solubility product of HgS is lower than that of ZnS and hence it gets precipitated as black solid when  $H_2S$  is passed through an acidic solution of any mercury (II) salt.

$$HgCl_2 + H_2S \rightarrow HgS + 2HCl$$

It is insoluble in water and HCl but dissolves in aqua regia (1 part conc. HNO<sub>3</sub> + 3 parts conc. HCl)

3HCl + HNO
$$_3 \rightarrow$$
 NOCl + 2H $_2$ O + 2 [ Cl ]   
Aqua regia Nitrosyl chloride Nacent chlorine HgS + 2 | Cl |  $\rightarrow$  HgCl $_2$  + S  $\downarrow$ 

(Soluble)

(black)

On sublimation, its colour changes to red and hence it is used as a red pigment.

(6) Mercuric sulphate,  $HgSO_4$ : It is obtained when HgS is treated with conc.  $H_2SO_4$ .

$$Hg + 2H_2 SO_4 \rightarrow HgSo_4 + SO_2 + 2H_2O$$

It is a white solid which decomposes on heating to give mercurous sulphate.

$$\Delta$$

$$3HgSo_4 \rightarrow Hg_2 SO_4 + Hg + 2SO_2 + 2O_2$$

It is used as a catalyst in the hydration of alkynes to give aldehydes or ketones. It is also used as a cosmetic under the name Vermillon and in ayurvedic medicine as makardhwaj.

- (7) Amalgams: Mercury forms alloys commonly known as amalgams, with all metals except iron and platinum. Hence it is transported in iron containers.
- (8) Alloy of transition metal: See in table discuss earlier in metallurgy.

#### **XXXXXXXXXXXXXXXXXXXXX**

The common Anions are divided into 3 groups for the purpose of identification:

```
Those which evolve gases with dilute hydrochloric acid:
Carbonate (CO<sub>3</sub><sup>2</sup>-)
bicarbonate(HCO<sub>3</sub><sup>-</sup>)
Nitrite(NO<sub>2</sub>)
Sulphide (S<sup>2</sup>-)
Sulphite(SO<sub>3</sub><sup>2</sup>-)
Thiosulphate(S<sub>2</sub>O<sub>3</sub><sup>2</sup>-)
Those which do not react with dilute HCl, but which do evolve gases or volatile liquids with
concentrated sulphuric acid:
Chloride (Cl<sup>-</sup>)
Bromide (Br<sup>-</sup>)
lodide ( l⁻)
Nitrate (NO<sub>3</sub><sup>-</sup>)
Those which do not react with either dilute hydrochloric acid or concentrated sulphuric acid:
Phosphate (PO<sub>4</sub><sup>3</sup>-)
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Borate (B_4O_7^{2-})
Sulphate (SO<sub>4</sub> <sup>2-</sup>)
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A Radical is an atom, or group of atoms that behaves like a single atom. Examples: H, K, Na, Cu, Pb, simple radicals; NH 4, SO 2, NO 2, compound

A Basic Radical is a metal, or any radical behaving like a metal. Examples: Ag, Cu, Ca, Na, and NH 4 the last

so classified because it behaves like such simple radicals as Na, K, and Li.

An Acid Radical is a nonmetal, or any radical behaving like a nonmetal. Examples : Cl, Br, I, SO 2, NO2

An Acid is a substance containing H that may be replaced by a basic radical. When a nonmetal is combined with H only, as in HC1, HBr, H 2 S, the compound is said to be a binary (i.e. composed of two elements) acid, or an hydracid. When the nonmetal is combined with H and O, the compound is called a ternary (i.e. composed of three or more elements) acid, or an oxyacid; and the characteristic name of the acid is formed by adding the termination -ic to the name of the nonmetal to denote more oxygen, or the termination -ous to denote less. Examples:  $H_2SO_4$  sulphuric, and  $H_2SO_3$  sulphurous acid.

These are classified in six different groups in accordance with certain properties which permit a group precipitation by a single reagent. A reagent used for precipitation of a whole group is called a general reagent.

A reagent used as a test for a single substance is known as a special reagent.

**Experiments showing Method of Classification** 

Use the following solutions: AgNO<sub>3</sub>, Cu(NO3)<sub>2</sub>, AsCl<sub>3</sub>, Fe<sub>2</sub>Cl<sub>6</sub>, Co(NO3)<sub>2</sub>, Ba(NO3)<sub>2</sub>, NaCl.

Take about 2 c.c. of each solution, and add HC1.\*

Points to be Observed Whether a precipitate is formed.

Whether the precipitate is soluble in an excess of the reagent.

\* Always use dilute acids unless otherwise directed.

**GROUPING THE BASES** 

The color of each precipitate.

Whether there is change in color of the precipitate.

Change in color of solutions.

Chemical equations.

Tabulate all results carefully in your notebook, according to the following scheme:

HC1 was added to the seven solutions with the following results:

```
Typical of Gr. I AgNO 3 + HC1 = AgCl w. pp. + I IN () 8. Typical of Gr. II A Cu(NO_3)_2 + II Cl = No change. Typical of Gr. II B AsCl 3 + HC1 = No change. Typical of Gr. III Fe _2 Cl _6 + HC1 = No change. Typical of Gr. IV Co(NO _3) _2 + IIC1 = No change. Typical of Gr. V Ba(NO _3) _2 + HC1 = No change. Typical of Gr. VI NaCl + HC1 = No change.
```

#### 1) Anions which react with dilute hydrochloric acid

	Carbonates (CO <sub>3</sub> <sup>2</sup> ·)	Bicarbonates (HCO <sub>2</sub> ·)	Nitrites (NO <sub>2</sub> ·)
	All carbonates except those of alkali metals, and ammonium are very slightly or difficulty soluble in water. Accordingly reactions in solution are only carried out in case of the soluble salts.	All bicarbonates are water soluble.	Most nitrites are water soluble except that of silver.
Solid salt + dil. HCl	Effervescence and a colourless odourless gas is evolved, Carbon dioxide(CO <sub>2</sub> ), Na;CO <sub>2</sub> +2HCl →2NaCl+H <sub>2</sub> O+CO <sub>2</sub>	Effervescence and a colourless odourless gas is evolved. Carbon dioxide(CO <sub>2</sub> ), NaHCO <sub>2</sub> +HCl → NaCl+H <sub>2</sub> O+CO <sub>2</sub>	Pungent brown fumes are evolved consisting mainly of nitrogen dioxide (NO <sub>2</sub> ), which is produced by the combination of nitric oxide (NO) with the oxygen of the air.  NaNO <sub>2</sub> + HCl → NaCl+ HNO <sub>2</sub> 3HNO <sub>2</sub> → HNO <sub>2</sub> + H <sub>2</sub> O + 2NO  2NO + O <sub>2</sub> → 2 NO <sub>2</sub>

	Carbonate	Bicarbonate	Nitrites
To	differentiate between CO22 and	HCO <sub>3</sub> :	Confirmatory tests of nitrites:
1 )Salt solution + magnesium sulphate solution	White precipitate of magnesium carbonate  Na <sub>2</sub> CO <sub>3</sub> +MgSO <sub>4</sub> → MgCO <sub>3</sub> ↓+ Na <sub>2</sub> SO <sub>4</sub>	No ppt. in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained:  2NaHCO <sub>3</sub> + MgSO <sub>4</sub> → Na <sub>2</sub> SO <sub>4</sub> + Mg(HCO <sub>3</sub> ) <sub>2</sub>	1) The brown ring test: To a dilute solution of the nitrite, add two drops of freshly prepared ferrous sulphate solution (FeSO <sub>4</sub> ), and then add dil. H <sub>2</sub> SO <sub>4</sub> very carefully drop by drop down the inside of the test tube: a brown ring forms due to the formation of (Fe.NO)SO <sub>4</sub> .  Note:
2) Salt solution + mercuric chloride solution	Reddish brown precipitate of mercuric carbonate Na <sub>2</sub> CO <sub>3</sub> + HgCl <sub>2</sub> → HgCO <sub>3</sub> ↓+2NaCl	soluble in water  Mg(HCO <sub>5</sub> ) <sub>2</sub> → MgCO <sub>5</sub> ↓+CO <sub>2</sub> ppt +H <sub>2</sub> O  No ppt. in the cold, but on heating a reddish-brown ppt. of mercuric carbonate is obtained:  2 NaHCO <sub>5</sub> + HgCl <sub>2</sub> → 2 NaCl + Hg(HCO <sub>3</sub> ) <sub>2</sub>	If the addition of dil H <sub>2</sub> SO <sub>4</sub> is not down the inside of the test tube, the solution becomes brown color (we can not notes the ring).  2) solution of nitrite + potassium iodide
	3	soluble in water $Hg(HCO_3)_2 \xrightarrow{\blacktriangle} HgCO_3 \downarrow +CO_2$ $ppt + H_2O$	3) Solution of nitrite. + acidified solution o potassium permanganate KMnO <sub>4</sub> (i.e. KMnO <sub>4</sub> + dil H <sub>2</sub> SO <sub>4</sub> ): the purple colour of the permanganate disappears. (the nitrite solution is an reducing agent.  5KNO <sub>2</sub> + 2KMnO <sub>4</sub> + 3H <sub>2</sub> SO <sub>4</sub> →  5KNO <sub>3</sub> + K <sub>2</sub> SO <sub>4</sub> + 2MnSO <sub>4</sub> + 3H <sub>2</sub> O





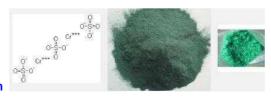




	Sulphites (SO <sub>3</sub> <sup>2</sup> ·)	Thiosulphates (S2O32)	Sulphides (S2·)
	All sulphites are slightly soluble in water except the alkali metal sulphites and the ammonium salt.	Sodium thiosulphate is readily soluble in water, other thiosulphates are slightly soluble.	All sulphides, except those of alkali, alkali earth metals and the ammonium ion are slightly soluble in water.
Solid salt ÷ dilute HCl	Sulphur dioxide gas (SO <sub>2</sub> ), is evolved, which is recognizable by its pungent smell:  Na <sub>2</sub> SO <sub>3</sub> + 2HCl → 2NaCl +H <sub>2</sub> O + SO <sub>2</sub> Test for sulphur dioxide:  Dip a small piece of paper into an acidic solution of potassium dichromate, and hold it over the mouth of the test tube. The paper will turn green, because the sulphur dioxide reduces the dichromate to a chromic sulphate:  3SO <sub>2</sub> + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> SO <sub>4</sub> → K <sub>2</sub> SO <sub>4</sub> + Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + H <sub>2</sub> O Orange Green colour colour	Colourless gas with pungent odour, which turns an acidified potassium dichreomate paper green, is evolved (SO <sub>2</sub> ), and a yellow precipitate of sulphur (S) appears:  Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> +2 HCl →2 NaCl + H <sub>2</sub> O+SO <sub>2</sub> + S↓  3SO <sub>2</sub> + K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> SO <sub>4</sub> → K <sub>2</sub> SO <sub>4</sub> + Cr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + H <sub>2</sub> O  Orange Green colour	Colourless gas, hydrogen sulphide (H <sub>2</sub> S) <sub>∞</sub> is evolved which is recognizable by its bad smell.  Na <sub>2</sub> S + 2HCl → 2 NaCl + H <sub>2</sub> S  Test for hydrogen sulphide: Dip a piece of paper in a solution of lead acetate, and hold it over the mouth of the test tube in which the H <sub>2</sub> S is being generated. The paper will turn black due to the formation of lead sulphide.  H <sub>2</sub> S + Pb(CH <sub>3</sub> COO) <sub>2</sub> → PbS + 2 CH <sub>3</sub> COOH



K2SO4 is white



Cr2(SO4)3 is green

	Sulphites	Thiosulphates	Sulphides
Confirmatory tests: 1) Salt solution + silver nitrate solution (AgNO <sub>3</sub> )	A white precipitate forms (silver sulphite Ag <sub>2</sub> SO <sub>3</sub> ), which dissolves in excess of sulphite, due to the formation of soluble complex.  Na <sub>2</sub> SO <sub>3</sub> + 2 AgNO <sub>3</sub> → Ag <sub>2</sub> SO <sub>3</sub> ↓ +2 NaNO <sub>3</sub> ppt  Ag <sub>2</sub> SO <sub>3</sub> + Na <sub>2</sub> SO <sub>3</sub> → 2 Na[AgSO <sub>3</sub> ]  Soluble complex	A white precipitate forms (silver thiosulphate Ag <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ), which is soluble in excess of the thiosulphate due to the formation of complex, which is unstable( it changes to yellow, brown and finally to black Ag <sub>2</sub> S).  Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> +2 AgNO <sub>3</sub> → Ag <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ↓ +2 NaNO <sub>3</sub> White pot	A black precipitate of silver sulphide. (Ag <sub>2</sub> S) is formed. Na <sub>2</sub> S+2AgNO <sub>3</sub> → Ag <sub>2</sub> S↓+2NaNO <sub>3</sub> ppt
2) Salt solution + lead acetate solution Ph(CH <sub>3</sub> COO) <sub>2</sub>	A white ppt. of lead sulphite (PbSO <sub>3</sub> ) is formed.  Na <sub>2</sub> SO <sub>3</sub> + Pb(CH <sub>3</sub> COO) <sub>2</sub> →  PbSO <sub>3</sub> 1+2 CH <sub>3</sub> COONa  ppt	A white ppt of lead thiosulphate (PbS <sub>2</sub> O <sub>3</sub> ) is formed, the ppt turns black (PbS) on boiling.  Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> +Pb(CH <sub>3</sub> COO) <sub>2</sub> → PbS <sub>2</sub> O <sub>3</sub> ↓ + 2CH <sub>3</sub> COONa  White ppt PbS <sub>2</sub> O <sub>3</sub> + H <sub>2</sub> O → PbS↓ + H <sub>2</sub> SO <sub>4</sub> Black ppt	A black ppt. of lead sulphide (PbS) is formed.  Na <sub>2</sub> S +Pb(CH <sub>3</sub> COO) <sub>2</sub> → PbS <sub>1</sub> + 2CH <sub>3</sub> COONa  Black ppt
	* Salt solution + drops of acidified solution of KMnO4: The purple colour of the permanganate will disappear. The sulphite reduces the permanganate ion_to (Mn²*) which is almost colourless.  5Na₂SO₃ +2KMnO₄+3H₂SO₄ →5Na₂SO₄+K₂SO₄+2MnSO₄+3H₂O		* Salt solution + Sodium mitroprosside solution : A violet colour is formed.

Sulphites	Thiosulphates
Salt solution + 2 drop	s of dil. H <sub>2</sub> SO <sub>4</sub> + Iodine solution(I <sub>2</sub> )
The brown colour of the iodine solution di $Na_2SO_3 + I_2 + H_2O \rightarrow Na_2SO_4 + 2HI$	The brown colour of the iodine solution disappears, because the iodine is reduced to the iodide ion, which is colourless.  At the same time, the thiosulphate is oxidized to tetrathionate:  2Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> + I <sub>2</sub> → Na <sub>2</sub> S <sub>4</sub> O <sub>6</sub> + 2 NaI

## 2) Anions which react with concentrated sulphuric acid

Note: Do these tests in fuming cuper because, the gases which are given off in these tests are extremely irritating, and can cause damage to the sensitive mucous membranes of nose and throat.

	Chlorides (Ct)	Bromides (Br)	Iodides (1')	Nitrates (NO <sub>3</sub> )
	All chlorides are water soluble except the chlorides of silver, mercurous and cuprous.	Bromides resemble chlorides in their solubility.	Iodides resemble chlorides and bromides in their solubility. However, bismuth iodide is insoluble.	All nitrates are soluble in water except some basic nitrates.
Solid salt + conc.H <sub>2</sub> SO <sub>4</sub> :	Effervescence with evolution of colourless gas, Hydrogen chloride (HCi).  2NaCi + H <sub>2</sub> SO <sub>4</sub> → Na <sub>2</sub> SO <sub>4</sub> +2 HCi  Test for HCl gas. Dip a clean glass rod into a bottle of conc. ammonia solution, and hold it close to the mouth of the test tube in which the HCl is being produced. Dense white fumes of ammonium chloride will be formed: HCl +NH <sub>3</sub> → NH <sub>4</sub> Cl	Raddish fumes evolve and the solution turns orange due to libertion of bromine (Br <sub>2</sub> )  2NaBr + H <sub>2</sub> SO <sub>4</sub> → 2HBr + Na <sub>2</sub> SO <sub>4</sub> 2HBr + H <sub>2</sub> SO <sub>4</sub> → 2H <sub>2</sub> O + SO <sub>2</sub> + Br <sub>2</sub>	Violet fumes are evolved, (Iodine gas I <sub>2</sub> ) and a brown or black precipitate is formed in the test tube.  2KI + 2 H <sub>2</sub> SO <sub>4</sub> → K <sub>2</sub> SO <sub>4</sub> +2H <sub>2</sub> O+ SO <sub>2</sub> +I <sub>2</sub>	Fig. 1 a small piece of copper metal and drops of water are added, dense brown fumes of nitrogen dioxide (NO <sub>2</sub> ) will be given off.  If no results, heat carefully.  2KNO <sub>3</sub> + H <sub>2</sub> SO <sub>4</sub> → K <sub>2</sub> SO <sub>4</sub> + 2HNO <sub>3</sub> 4HNO <sub>3</sub> + Cu → Cu(NO <sub>3</sub> ) <sub>2</sub> + 2H <sub>2</sub> O+2NO <sub>2</sub>

	Chlorides	Bromides	Iodides	Nitrates
Confirmatory tests: 1) Salt solution + silver nitrate (AgNO <sub>3</sub> )	A dense white ppt of silver chloride (AgCl) slowly turns a violet colour when exposed to bright sunligt. NaCl +AgNO <sub>3</sub> → AgCl + NaNO <sub>3</sub> ppt	A yellowish white precipitate of silver bromide(AgBr) is formed.  NaBr + AgNO₃ → AgBr↓ + NaNO₃  ppt	A yellow precipitate of silver iodide (AgI) is formed.  KI +AgNO₃ → AgI↓ + KNO₃  gpt	-3/8
2) Salt solution + lead acetate Pb(CH <sub>3</sub> COO) <sub>2</sub>	A white precipitate of lead chloride (PbCl <sub>2</sub> ) is formed which is soluble in hot water, and reprecipitates on cooling 2NaCl + Pb(CH <sub>3</sub> COO) <sub>2</sub> →PbCl <sub>2</sub> ↓+ 2CH <sub>3</sub> COONa	A white precipitate of lead bromide (PbBr <sub>2</sub> ) appears which is soluble in boiling water and reprecipitates on cooling. 2NaBr + Pb(CH <sub>3</sub> COO) <sub>2</sub> → PbBr <sub>2</sub> ↓ + 2CH <sub>3</sub> COONa	A yellow precipitate of lead iodide (PbI <sub>2</sub> ) is formed which dissolves in boiling water and recrystallises on cooling.  2KI + Pb(CH <sub>3</sub> COO) <sub>2</sub> → PbI <sub>2</sub> ↓ + 2CH <sub>3</sub> COOK	
			*Salt solution + Mercuric chloride (HgCh):  A reddish precipitate of mercuric iodide is formed which dissolves in excess of KI.  HgCl <sub>2</sub> + 2KI → HgI <sub>2</sub> ↓ + 2KCl ppl HgI <sub>2</sub> + 2KI → K <sub>2</sub> [HgI <sub>4</sub> ] soluble	Brown ring test The nitrate solution is mixed with freshly prepared FeSO <sub>4</sub> solution, then conc. H <sub>2</sub> SO <sub>4</sub> is added and allowed to flow causiously on the side of the test tube. A brown ring (Fe.NO)SO <sub>4</sub> is formed at the interface of the two layers. The brown ring disappears on shaking the solution.
			+ Salt solution. + copper substate CuSO <sub>4</sub> : A brown ppt. of couprous iodide CuI and iodine I <sub>2</sub> . 4KI+2 CuSO <sub>4</sub> → 2CuI↓+2K <sub>2</sub> SO <sub>4</sub> +I <sub>2</sub>	

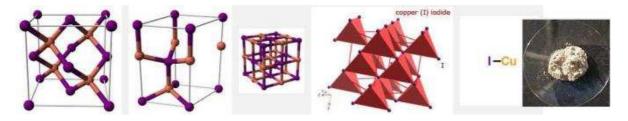


AgCl is white

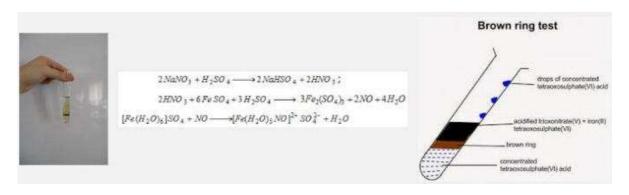




## **Cul Cuprous lodide**



## **Brown Ring Test**



## 3)Anions which do not react with acids:

	Phosphates (H <sub>2</sub> PO <sub>4</sub> °, HPO <sub>4</sub> <sup>2</sup> °, PO <sub>4</sub> <sup>3</sup> °)	Borates (BO <sub>2</sub> ··BO <sub>3</sub> ····, B <sub>4</sub> O <sub>2</sub> ···)	Sulphates (SO <sub>4</sub> 2-)
	Most phosphates are insoluble in water except those of ammonium and alkali metals.	Ammonium and alkali metal borates are water soluble while other borates are slightly soluble in water.	All sulphates are soluble in water except those of some divalent metals e.g. calcium, strontium, barium and lead.
Salt solution + Barium chloride solution (BaCl <sub>2</sub> )	A white precipitate of barium phosphate (BaHPO <sub>4</sub> ) is produced, soluble in dilute acids e.g. HNO <sub>3</sub> or HCl and insoluble in excess of barium chloride.  Na <sub>2</sub> HPO <sub>4</sub> + BaCl <sub>2</sub> → BaHPO <sub>4</sub> ↓ + 2NaCl	A white ppt. of barium borate from concentrated solutions Ba(BO <sub>2</sub> ) <sub>2</sub> is produced, soluble in dilute acids and in excess of barium chloride.  Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> + 3H <sub>2</sub> O + BaCl <sub>2</sub> → Ba(BO <sub>2</sub> ) <sub>2</sub> + 2H <sub>3</sub> BO <sub>3</sub> + 2NaCl	A white precipitate of barium sulphate (BaSO <sub>4</sub> ) is formed which is insoluble in dilute acids and in excess of barium chloride.  Na <sub>2</sub> SO <sub>4</sub> + BaCl <sub>2</sub> → BaSO <sub>4</sub> ↓ + 2NaCl
Confirmatory tests: 1) Salt solution + silver nitrate (AgNO <sub>3</sub> )	A yellow precipitate of silver phosphate (Ag <sub>3</sub> PO <sub>4</sub> ) is formed, which is readly soluble in dil. HNO <sub>3</sub> and ammonia.	A white ppt. of silver borate (AgBO <sub>2</sub> ) is formed, from concentrated solution, which give brown ppt. after boiling. (also a brown ppt. is formed with diluted solution)  Na <sub>2</sub> B <sub>4</sub> O <sub>1</sub> + 3H <sub>2</sub> O + 2AgNO <sub>3</sub> → 2AgBO <sub>2</sub> + 2H <sub>3</sub> BO <sub>3</sub> + 2NaNO <sub>3</sub> 2AgBO <sub>2</sub> + 3H <sub>2</sub> O → Ag <sub>2</sub> O + 2H <sub>3</sub> BO <sub>3</sub>	A white ppt. of silver sulphate (Ag <sub>2</sub> SO <sub>4</sub> ) is formed with concentrated solution. Na <sub>2</sub> SO <sub>4</sub> + 2AgNO <sub>3</sub> → Ag <sub>2</sub> SO <sub>4</sub> ↓+ 2NaNO <sub>3</sub>





BaSO4 is white





## For phosphates:

0.5 ml of salt solution + 4 ml of ammonium molybdate solution + 0.5 ml of conc. HNO<sub>3</sub>:

Form a canary yellow precipitate of ammonium phosphomolybdate (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>.H<sub>2</sub>O in the cold or by gentle warming. (notes the volume needed in this test).

## For sulphates:

## Salt solution + lead acetate:

A white precipitate of lead sulphate is formed, which is redadly soluble in hot concentrated ammonium acetate or conc. H<sub>2</sub>SO<sub>4</sub>

 $K_2SO_4+Pb(CH_3COO)_2 \rightarrow PbSO_4\downarrow +2CH_3COOK$ 

 $PbSO_4 + H_2SO_4 \rightarrow Pb(HSO_4)_2$ 



#### Scheme for the identification of acid radicals

#### 1) Solid salt + dil. HCl:

Observation	Effervescence and a colourless odouless gas is evolved.	Pungent brown fumes are evolved.	Colourless gas with Pungent odour, which turns an acidified dichromate paper green, is evolved.	Colourless gas with pungent odour, which turns an acidified potassium dichreomate paper green, is evolved, and a yellow precipitate of sulphur appears.	Colourless gas is evolved which is characterized by its bad odour and turning a lead acetate paper black	The salt does not react with dil.HCl.
Results	The gas is CO: The anion is carbonate or bicarbonate.	The gas is NO <sub>2</sub> . The anion is Nitrite	The gas is SO <sub>2</sub> and the green colour is. Ct <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> . The anion is sulphite	The gas is SO <sub>2</sub> , the ppt is S and the green colour is C <sub>12</sub> (SO <sub>4</sub> ) <sub>3</sub> . The anion is thiosulphate.	The gas is H <sub>2</sub> S, and the black colour is PbS. The anion is sulphide	The anion is no from group 1.  (Go to step 2).

To differentiate between carbonate and bicarbonate

Salt solution + magnesium sulphate solution;
 For salbonate. White precipitate of magnesium carbonate (MgCO<sub>2</sub>).

For bicarbonate: No ppt in the cold, as magnesium bicarbonate is soluble, but on heating, a white ppt of magnesium carbonate is obtained Salt solution + mercuric chloride solution:
 For carbonate: Reddish brown precipitate of mercuric carbonate (HgCO<sub>2</sub>).

carbonate (HgCO<sub>3</sub>).

For bicarbonate: No ppt. in the cold, but on heating a reddish-brown ppt. of mercuric carbonate is obtained.

#### 2) Solid salt + conc. H2SO4:

Observation	Effervescence with the evolution of a colourless gas which forms white fumes with NH <sub>4</sub> OH.	Raddish 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. If no results, heat carefully.	-V.S. The salt does not react with conc. H <sub>2</sub> SO <sub>4</sub>
Results	The gas is HCl and the white fumes are NH4Cl. The anion is chloride.	The gas is Br <sub>2</sub> . The anion is Bromide.	The gas is I <sub>2</sub> . The anion is iodide.	The gas is NO <sub>2</sub> . Tha anion is Nitrate.	The anion is not from group 2. (Go to step 3).

#### 3) Salt solution + BaCl2:

Observation	A white precipitate is produced, soluble in dilute acids e.g. HNO <sub>3</sub> or HCl and insoluble in excess of barium chloride.	A white ppt. from concentrated solutions is produced, soluble in dilute acids and in excess of barium chloride	A white precipitate is formed which is insoluble in dilute acids and in excess of barium chloride.
Results	The white precipitate is barium phosphate (BaHPO <sub>4</sub> ). The anion is phosphate.	The white ppt. is barjum borate Ba(BO <sub>2</sub> ). The anion is Borate.	A white precipitate is barium sulphate (BaSO <sub>4</sub> ) The anion is sulphate

	phosphate	borate	Sulphate
Observation	A yellow precipitate is formed, which is readly soluble in dil. HNO <sub>3</sub> and ammonia.	A white ppt. is formed from concentrated solution, which give brown ppt. after boiling. (also, a brown ppt. is formed with diluted solution.)	A white ppt. is formed, with concentrated solution
Results	The yellow ppt. is silver phosphate (Ag <sub>3</sub> PO <sub>4</sub> ). The anion is phosphate.	The white ppt. is silver borate (AgBO <sub>2</sub> ). The anion is borate.	The white ppt. is silver sulphate (Ag <sub>2</sub> SO <sub>4</sub> ) The anion is sulphate.

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## Oxidation States and Colors

Metal	+1	+2	+3	+4	+5	+6	+7
Sc			Colorless				
Ti			Violet	Colorless			
V		Violet	Green	blue	Yellow		
Cr		Blue	Green			Yellow (CrO <sub>4</sub> <sup>2-</sup> ) orange (Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	
Mn		Pale pink		Brown		Dark green (MnO <sub>4</sub> <sup>2-</sup> )	Intense purple (MnO <sub>4</sub> -)
Fe		Pale green	Yellow or brown				
Со		Pink	Orange/y ellow				
Ni		Green					
Cu		Blue					
Zn		colorless					

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