KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS

Semester-II

18CHU 202 INORGANIC CHEMISTRY II: Metallurgy and S-Block and P- block elements 4H 4C

Instruction Hours/week:L: 4 T:0 P:0 Marks: Internal: 40 External: 60 Total:100

Scope

The course deals with the general principles involved in metallurgy. Further it deals with the S-block and P-block elements.

Programme objectives

To provide a knowledge on

1. The general principles of metallurgy
2. s-block elements
3. Complexes of s-block elements
4. Chemistry of p-block elements
5. Preparation, properties, structure and uses of some types of inorganic compounds.

Programme Outcome

It enables the students to

1. To understand the basic principles and methods involved in the metallurgy.
2. To understand the basic properties of s-block elements and their compounds.
3. To understand the Complex formation tendency of s-block elements and their structure.
4. To understand the basic properties of p-block elements and their compounds.
5. To understand the Preparation, properties, structure and uses of borazine, silicates, silicones, interhalogen compounds, Phosphonitrilic and clathrates.

Methodology

Blackboard teaching, Power point presentation and group discussion.

UNIT I

General Principles of Metallurgy

Chief modes of occurrence of metals based on standard electrode potentials. Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent. Electrolytic Reduction, Hydrometallurgy with reference to cyanide process for silver and gold. Methods of purification of metals: Electrolytic process, Van Arkel-de Boer process and Mond’s process, Zone refining.

UNIT II

Chemistry of *s* Block Elements:

(i) General characteristics: melting point, flame colour, reducing nature, diagonal relationships and anomalous behavior of first member of each group.
(ii) Reactions of alkali and alkaline earth metals with oxygen, hydrogen, nitrogen and water.

(iii) Common features such as ease of formation, thermal stability and solubility of the following alkali and alkaline earth metal compounds: hydrides, oxides, peroxides, superoxides, carbonates, nitrates, sulphates.

UNIT III

Complexes of s-block elements:

(i) Complex formation tendency of s-block elements; structure of the following complexes: crown ethers and cryptates of Group I; basic beryllium acetate, beryllium nitrate, EDTA complexes of calcium and magnesium.

(ii) Solutions of alkali metals in liquid ammonia and their properties.

UNIT IV

Chemistry of *p* Block Elements:

Electronic configuration, atomic and ionic size, metallic/non-metallic character, melting point, ionization enthalpy, electron gain enthalpy, electronegativity, Allotropy of C, P, S; inert pair effect, diagonal relationship between B and Si and anomalous behaviour of first member of each group.

Structure, bonding and properties: acidic/basic nature, stability, ionic/covalent nature, oxidation/reduction, hydrolysis, action of heat of the following:

Hydrides : hydrides of Group 13 (only diborane), Group 14, Group 15 (EH_3 where E = N, P, As, Sb, Bi), Group 16 and Group 17.
Oxides : oxides of phosphorus, sulphur and chlorine
Oxoacids : oxoacids of phosphorus and chlorine; peroxy acids of sulphur Halides: halides of silicon and phosphorus

UNIT V

Preparation, properties, structure and uses of the following compounds:

- ✓ Borazine
- ✓ Silicates, silicones,
- ✓ Phosphonitrilic halides {$(PNCl_2)_n$ where n = 3 and 4}
- ✓ Interhalogen and pseudohalogen compounds
- ✓ Clathrate compounds of noble gases, xenon fluorides (MO treatment of XeF_2).

Suggested Readings:

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.

2. Douglas .B.E, Mc Daniel, D.H. & Alexander J.J. (1994). *Concepts & Models of Inorganic Chemistry*. 3rdEd. N.Y. : John Wiley Sons.

Reference Books:

1. Greenwood, N.N. & Earnshaw. (2005). *Chemistry of the Elements*, Butterworth-Heinemann.
2. Cotton, F.A. & Wilkinson, G. (1999). *Advanced Inorganic Chemistry*. Wiley, VCH.
3. Miessler, G. L. & Donald, A. Tarr. (2011). *Inorganic Chemistry*. 5th Ed.(adapted). Pearson,
4. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry*. *5th* Ed. Oxford University Press.
5. Puri, B.R., Sharma, L.R & Kalia, K.C (2002). Principles of Inorganic Chemistry. Vallabh Publications.

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COIMBATORE-21

DEPARTMENT OF CHEMISTRY

LECTURE PLAN

STAFF NAME: B.Prabha **SUB.CODE**:18CHU202

SUBJECT NAME: METALLURGY AND S BLOCK & P BLOCK ELEMENTS

SEMESTER: II **CLASS**: I B.Sc., CHEMISTRY

S.No	Lecture hour	Topics	Support material
		Unit - I	
1	1	**General Principles of Metallurgy** Chief modes of occurrence of metals based on standard electrode potentials	T1-P-165-168
2	1	Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent	T1-P-184-186
3	1	Electrolytic Reduction	T1-P-182, R4-P-139-153,391-394.
4	1	Hydrometallurgy with reference to cyanide process for gold and silver.	R4-P-185
5	1	Methods of purification of metals: Electrolytic process	T1-P-317-318,R4-P-404
6	1	Van Arkel-De Boer process	T1-P-686-687,R4-P-399
7	1	Mond’s process, Zone refining	T1-P-180, R4-P-405, R4-P-413
8	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 1= 8		
	Unit – II		
1.	1	**Chemistry of *s* Block Elements:** General characteristics: melting point, flame colour, reducing nature.	T1-P-285-288, R5-P-419-422

2.	1	Diagonal relationships and anomalous behaviour of first member of each group.	T1-P-309-311,455, R5-P-431-432
3.	1	Reactions of alkali and alkaline earth metals with oxygen, hydrogen, nitrogen and water.	T1-P-309-311,455, R5-P-431-432
4.		Common features such as ease of formation, thermal stability	
5.	1	solubility of the hydrides, oxides of alkali and alkaline earth metal compounds:	T1-P-298-302, R5-P-462-463
6.	1	solubility of the Peroxides, superoxides, carbonates of alkali and alkaline earth metal compounds	T1-P-290-293, R4-P-440-442, R5-P-438-440
7.	1	Solubility of nitrates, sulphates of alkaline and alkaline earth metals	T1-P-295-296, R4-P-442-447
8.	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 2 = 8		
		Unit - III	
1.	1	Complex formation tendency of s-block elements.	T1-P-305-306, R5-P-427
2.	1	structure of the following complexes: crown ethers, cryptates of Group I	T1-P-306-308, R5-P-428-429
3.	1	basic beryllium acetate, beryllium nitrate,	T1-P-350-351, R5-P-467-468
4.	1	EDTA complexes of calcium and magnesium	T1-P-351, R5-P-470-471
5.	1	Solutions of alkali metals in liquid ammonia	T1-P-302-303, R5-P-425,
6.	1	Solutions of alkali metals in liquid ammonia and their properties.	T1-P-335, R5-P-425
7.	1	Recapitulation and discussion of important questions	
	Total No of Hours Planned For Unit 3 = 7		
		Unit - IV	
1.	1	**Chemistry of *p* Block Elements:** Electronic configuration, atomic and ionic size, metallic/non-metallic character	T1-P-366-368, R5-P-688-691, 673-680
2.	1	melting point, ionization enthalpy, electron gain enthalpy, electronegativity	T1-P-368-370, R5-P-479-480
3.	1	Allotropy of C, P, S and inert pair effect	T1-P-365,407,R5-P-526,529-531,588,651

4.	1	Diagonal relationship between B and Si and anomalous behaviour of first member of each group.	T1-P- 389, R5-P-526,481,647
5.	1	**Structure, bonding and properties: acidic/basic nature, stability, ionic/covalent nature, oxidation/reduction, hydrolysis, action of heat of the following:** Hydrides: hydrides of Group 13 (only diborane),	T1-P-395, R5-P-502-507
6.	1	Group 14, Group 15 (EH_3 where E = N, P, As, Sb, Bi),	T1-P-478,551, R5-P-536,598
7.	1	Group 16, Group 17	T1-P-565, R4-P-897-900, R5-P-657,693,902-908
8.	1	Oxides: oxides of phosphorus, sulphur and chlorine	T1-P-508,518, R5-P-604,662,701-702
9.	1	Oxoacids: oxoacids of phosphorus and chlorine, peroxoacids of sulphur, Halides: halides of silicon and phosphorus	T1-P-457,461,495-498, 511,563 R5-P-616,671,710,601
	Total No of Hours Planned For Unit 4 = 9		
		Unit - V	
1.	1	Preparation, properties, structure and uses of Borazine	T1-P-394-395 R5-P-514-515
2.	1	Preparation, properties, structure and uses of silicates, silicones	T1-P-445,R5-P-566-574
3.	1	Preparation, properties, structure and uses of Phosphonitrilic halides $\{(PNCl_2)_n$ where n = 3 and 4$\}$	T1-P-524-525
4.	1	Preparation, properties, structure and uses of Interhalogen and pseudohalogen compounds	T1-P-621-627,631 R5-P-711-722,722-724
5.	1	Preparation, properties, structure and uses of Clathrate compounds of noble gases and xenon fluorides (MO treatment of XeF_2).	R5-P-711-712, R4-P-712-714, R4-P-706-711
6.		Recapitulation and discussion of important questions	
7.	1	ESE Question paper discussion	
8.	1	ESE Question paper discussion	
	Total No of Hours Planned For Unit 5 = 8		

Total Hours Planned	**40**	

Text Books:

1. T_1: Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.

Reference Book:

1. R_2: Cotton, F.A & Wilkinson, G. (1999). Advanced Inorganic Chemistry. Wiley, VCH.
2. R_4: Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry*. 5th Ed. Oxford University Press.
3. R_5: Puri, B.R., Sharma, L.R & Kalia, K.C (2002). Principles of Inorganic Chemistry. Vallabh Publications.

UNIT-I

SYLLABUS

Chief modes of occurrence of metals based on standard electrode potentials. Ellingham diagrams for reduction of metal oxides using carbon and carbon monoxide as reducing agent. Electrolytic Reduction, Hydrometallurgy with reference to cyanide process for silver and gold. Methods of purification of metals: Electrolytic process, Van Arkel-de Boer process and Mond's process, Zone refining.

What are Minerals and Ores?

Metals occur in nature sometimes free (i.e., in uncombined state) but mostly in the combined state (i.e., as compounds with other elements). When a metal is found free or in uncombined state it is said to occur as **native.** Metals found in the native state are copper, silver, gold, mercury and platinum. Others are found in the combined state.

The natural materials found in the earth in which the metals occur in the combined state are called **Minerals.** Those minerals from which the metals may be extracted conveniently and economically are called **Ores.** Thus, all ores are minerals but all minerals are not ores. For example, all clays contain aluminium but these are not ores of aluminium, since the extraction of aluminium metal from these clays is too much coumbersome and not economically worthwhile.

Aluminium, for example, is the most common metal in the Earth's crust, occurring in all sorts of minerals. However, it isn't economically worthwhile to extract it from most of these minerals. Instead, the usual ore of aluminium is bauxite – which contains from 50 - 70% of aluminium oxide.

Copper is much rarer, but fortunately can be found in high-grade ores (ones containing a high percentage of copper) in particular places. Because copper is a valuable metal, it is also worth extracting it from low-grade ores as well.

Ores are commonly oxides - for example:

Bauxite	
haematite	
Rutile	TiO_2

or sulphides - for example:

Pyrite	FeS

chalcopyrite $CuFeS_2$

and a whole lot of other things as well which we won't actually come across as a part of this topic for UK A level purposes.

What is mining process?

The process of taking out the ores from mines is called **mining.**

What is Metallurgy?

The process of extracting the metals from their ores and refining them is called **metallurgy.**

The process used for the metallurgy (i.e., extraction) of metals depends on the nature of the ore from which the metal is being extracted and also on the properties of the metal. Thus it is not possible to provide a universal method for the extraction of all the metals.

ELLINGHAM DIAGRAMS

A particular case of the free energy change accompanying a chemical reaction is the standard free energy of formation, which is the free energy change accompanying the formation of one mole of a compound from the constituent elements, all being in their standard states. The free energies of formation of the elements in their standard states are, by convention, taken to be zero. As discussed in the previous section, the free energies of formation change with temperature and, without any serious loss of accuracy, this temperature dependence can be taken to be linear.

An Ellingham diagram is a plot of ΔG versus temperature. Since ΔH and ΔS are essentially constant with temperature unless a phase change occurs, the free energy versus temperature plot can be drawn as a series of straight lines, where ΔS is the slope and ΔH is the y-intercept. The slope of the line changes when any of the materials involved melt or vaporize.

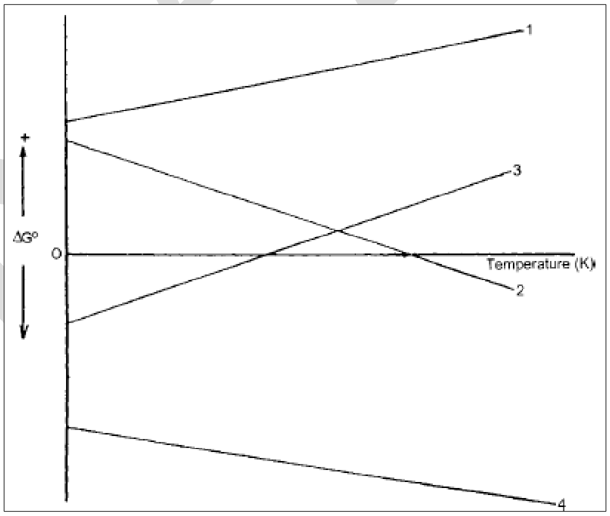
In 1944 Ellingham compiled, for the first time, diagrams depicting the temperature dependence of the standard free energies of formation of numerous oxides and sulphides. In the discussion presented here, attention will be confined to the oxide reaction and the essential features will be brought out in terms of a few illustrative free energy versus temperature lines (Ellingham lines) drawn for this reaction. Figure 3.4 shows one such plot. The plot is a straight line graph because is of the form $y = m x + c$ (with $m = -\Delta S0 = -(S - S)$ where S is the total entropy of the products and S is the total entropy of the reactants, and $c = \Delta H0$).

$M (s) + O_2 (g) \rightarrow MO_2 (s)$

$\Delta G_0 = \Delta H_0 - T \Delta S_0$

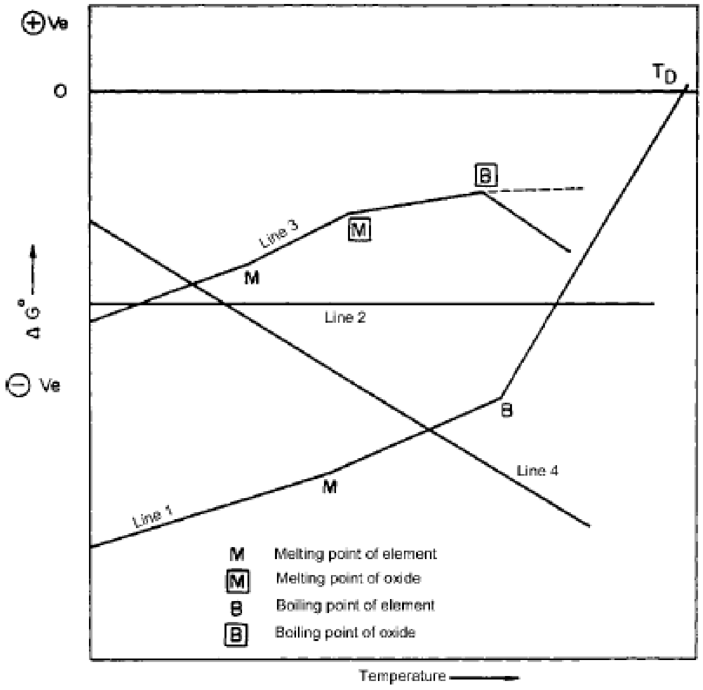
The intercept of the graph on the y axis is ΔH where ΔH is the standard enthalpy at 0 K. At 0 K, ΔG = ΔH. The slope of the graph is −ΔS0. Thus when the entropy is increasing (DS is positive), the slope of the graph is negative (m = −(+D S) = −D S). This situation is illustrated by lines 2 and 4 in Figure 3.4. Line 2 corresponds to an endothermic reaction with the entropy increasing. Line 4 corresponds to an exothermic reaction with entropy increasing. When the entropy is decreasing (ΔS is negative) the slope will be positive (m = − (−ΔS) = +ΔS). This situation is illustrated by lines 1 and 3 in Figure 3.4 Line 1 corresponds to an endothermic reaction with entropy decreasing (ΔG is always positive), and line 3 shows an exothermic reaction with entropy decreasing. The quantity plotted is free energy per mole of oxygen rather than per mole of the oxide. This facilitates a simple comparison, when data for more than one element are plotted, of the oxygen affinity of the different elements and enables one to obtain the free energy change corresponding to a reaction of the type by simple subtraction of the standard free energy values for the two compounds. Such a diagram allows one to read directly the value of ΔG0 at any temperature T1, and thus has the advantage of combining a great deal of information in a very simple presentation.

$M + NO \rightarrow MO + N$

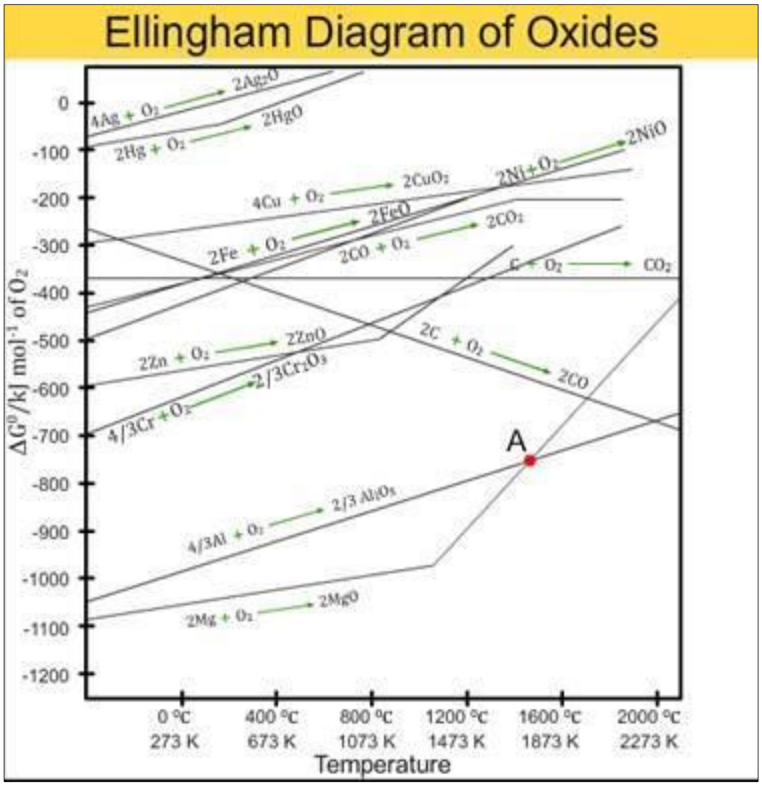


Effect of the sign of ΔH° and ΔS° on Ellingham lines

In an Ellingham diagram covering a wide temperature range, sharp changes in the slope of the line (ΔG0 versus T plot) occur at certain temperatures. At these temperatures phase transformations take place in the reactants or in the products. As the slope of the line corresponds to $-\Delta S0$, where $\Delta S0$ is the entropy change associated with oxide formation, the magnitude of the change in slope is determined by the value of the entropy change for the transformation. Since the entropy changes markedly at the melting and the boiling points of a metal as well as of its oxides, a change in the slope of the line in the Ellingham diagram may be anticipated at these temperatures. The various possibilities are shown in Figure 3.5 and Table 3.2. When the metal undergoes a phase change with rising temperature, its entropy increases by an amount equal to the enthalpy of the phase change divided by the absolute temperature at which the change occurs. When the phase change occurs in the reactants,augmentation of the entropy of the reactants results in the slope 0 0($m = -\Delta S = S - Sp$) becoming a larger positive value. Line 1 represents a typical case of phase transformation in reactant. If, on the other hand, there is a phase transformation in the product the slope becomes a smaller positive value because here the entropy of the product is augmented (S becomes more and m becomes a smaller positive value or even a negative value). In Figure 3.5, line 3 represents a typical case of phase transformation in the product. As regards the phase change, boiling results in a far greater augmentation of entropy than melting. Thus in the figure, sharper changes in slope occur at points marked B and B than at points marked M and M. Line 2 illustrates the special case where there is almost no entropy change associated with the oxidation reaction and where no phase transformation of the metal or its oxide occurs in the range of temperatures considered. Line 4 in the diagram pertains to another special situation which arises when oxidation causes an increase in entropy. For such reactions, $\Delta S0$ is positive and the slope of the Ellingham line is negative. The oxide becomes stabler as the temperature is increased. Typical examples of “line 1” behaviour are provided by magnesium, calcium, and zinc. The classic example of “line 2” behaviour is exhibited by carbon dioxide. However, this type of behaviour is not exhibited by any metal. The oxides of metals like lead and cadmium are examples of “line 3” behaviour. “Line 4” behaviour is exhibited by carbon monoxide, and volatile suboxides of several refractory metals.



Slopes of Ellingham lines



Hydrometallurgy

Hydrometallurgy is a method for obtaining metals from their ores. It is a technique within the field of extractive metallurgy involving the use of aqueous chemistry for the recovery of metals from ores, concentrates, and recycled or residual materials. Metal chemical processing techniques that complement hydrometallurgy are pyrometallurgy, vapour metallurgy and molten salt electrometallurgy. Hydrometallurgy is typically divided into three general areas:

- Leaching
- Solution concentration and purification
- Metal or metal compound recovery

Leaching gold with a cyanide solution remains the most widely used hydrometallurgical process for the extraction of gold from ores and concentrates. Despite the difficulties and hazards of working with cyanide, no other process has yet been proven to be an economic viable alternative.

A paper published by L. Elsner in 1846 first correctly identified the chemical reaction that forms the basis of all gold cyanide leaching processes:

$$4\ Au + 8\ NaCN + O_2 + 2\ H_2O \rightarrow 4\ Na[Au(CN)_2] + 4\ NaOH$$

The equation is well known, but the successful application of this reaction in a gold mining operation is rarely straightforward.

In a typical application, a slury of the ground ore is mixed with cyanide in the presence of activated carbon. The carbon has a very high affinity for the aurocyanide complex and adsorbs the gold out of solution resulting in very high loadings on the carbon (typically 1000-4000 g/t). At the end of the leach the loaded carbon is removed from the slurry and the adsorbed gold is stripped out at high temperature and pressure with sodium hydroxide and cyanide solutions to form a high value electrolyte solution. Gold bullion is then recovered from the electrolyte by electrowinning.

Extraction of Silver

Extraction of Silver by cyanide process and its uses

Silver also occurs both in combined state as well as in free state. The important ores of silver are: Argentite (Ag_2S), Copper silver glance, Horn silver, Ruby silver. The silver ores are found along with gold ores in some parts of India.

Extraction

Silver is extracted from the ore-argentite (Ag2SAg2S). The process of extraction of silver is called as cyanide process as sodium cyanide solution is used. The ore is crushed, concentrated and then treated with sodium cyanide solution. This reaction forms sodium argento cyanide Na[Ag(CN)2]Na[Ag(CN)2].

AgS+4NaCN⇌2Na[Ag(CN)2]+Na2S(1)(1)AgS+4NaCN⇌2Na[Ag(CN)2]+Na2S

The solution of sodium argento cyanide combines with zinc dust and forms sodium tetra cyanozicate and precipitated silver. This precipitated silver is called spongy silver.

Zn+2Na[Ag(CN)2]→Na2[Zn(CN)4]+2Ag(2)(2)Zn+2Na[Ag(CN)2]→Na2[Zn(CN)4]+2Ag

The spongy silver is fused with potassium nitrate to obtain pure silver. Then the silver obtained is purified by electrolytic process.

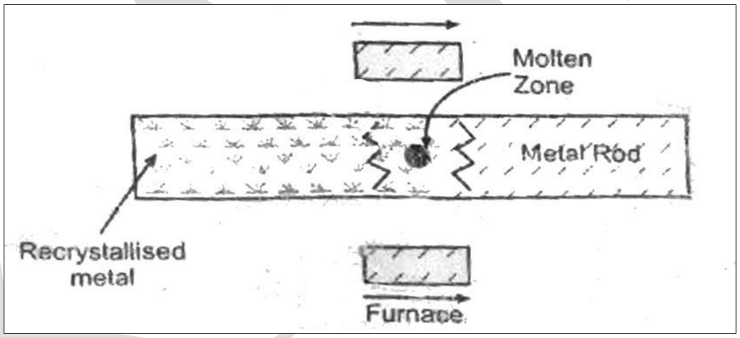
__ELECTROLYTIC REDUCTION:__

Very active metals like Na, K, Ca, Al etc. are produced by the electrolysis of their fused anhydrous salt. For example, sodium is produced by the electrolysis of fused sodium chloride:

$$\begin{aligned} &\mathrm{NaCl} \longrightarrow \mathrm{Na^+ + Cl^-} \\ &\mathrm{Na^+ + e} \longrightarrow \mathrm{Na} \quad \text{(at the cathode)} \\ &\left.\begin{aligned} &\mathrm{Cl^-} \longrightarrow \mathrm{Cl + e} \\ &\mathrm{2\,Cl} \longrightarrow \mathrm{Cl_2} \end{aligned}\right\} \text{(at the anode)} \end{aligned}$$

On electrolysis

__ZONE REFINING OR FRACTIONAL CRYSTALLIZATION:__ Metals like silicon, germanium and gallium are used as semi-conductors. These metals may be of very high purity and such purity is achieved by zone refining.



A circular heating coil passes slowly along a tube containing impure metals. At the heated zone the rod melts. As the heat passes on, the pure metal crystallizes while impurities pass into adjacent molten part. The impurities are in this way swept into the end of the rod and removed.

MOND’S PROCESS

The Mond process, sometimes known as the carbonyl process, is a technique created by Ludwig Mond in 1890, to extract and purify nickel. The process was used commercially before the end of the 19th century. This process converts nickel oxides into pure nickel.

This process involves the fact that carbon monoxide combines with nickel readily and reversibly to give nickel carbonyl. No other element forms a carbonyl compound under the mild conditions used in the process

This process has three steps:

1. Nickel oxide reacts with Syngas at 200 °C to give nickel, together with impurities including iron and cobalt.

$NiO(s) + H_2(g) \rightarrow Ni(s) + H_2O(g)$

2. The impure nickel reacts with carbon monoxide at 50–60 °C to form the gas nickel carbonyl, leaving the impurities as solids.

$Ni(s) + 4\ CO(g) \rightarrow Ni(CO)_4(g)$

3. The mixture of nickel carbonyl and Syngas is heated to 220–250 °C, resulting in decomposition back to nickel and carbon monoxide:

$Ni(CO)_4(g) \rightarrow Ni(s) + 4\ CO(g)$

Steps 2 and 3 illustrate a chemical transport reaction, exploiting the properties that (1) carbon monoxide and nickel readily combine to give a volatile complex and (2) this complex degrades back to nickel and carbon monoxide at higher temperatures. The decomposition may be engineered to produce powder, but more commonly an existing substrate is coated with nickel. For example, nickel pellets are made by dropping small, hot pellets through the carbonyl gas; this deposits a layer of nickel onto the pellets.

This process has also been used for plating nickel onto other metals, where a complex shape or sharp corners have made precise results difficult to achieve by electroplating. Although the results are good, the toxicity makes it impractical as an industrial process. Such parts are now plated by electroless nickel plating instead.

Van Arkel De Boer Process or Hot Wire Process:

Metals like Ti, Be, Th are refined by this process.

Impure titanium is heated with limited amount of iodine in evacuated glass apparatus at 470 K when solid TiI_4 is formed. The vapour of TiI_4 is then allowed to enter an evacuated quartz bulb a tungsten filament placed at its centre and electrically heated 1670 K. The vapour is decomposed to the metal in contact with filament and the metal is deposited on the filament which thicker. The metal is chipped off from the filament.

$$\underset{\textit{impure}}{Ti(s)} + 2\,I_2(g) \xrightarrow{470\text{ K}} TiI_4(g)$$

$$TiI_4(g) \xrightarrow{1670\text{ K}} Ti(s)\text{ pure} + 2\,I_2(g)$$

The vapours of regenerated iodine react with more titanium.

This method produces titanium of very high purity. This method is very expensive and is employed for the preparation of very pure metals for special uses.

Zone refining is used to get metal in the ultrapure state. This method is based on the principle that when impure molten metal is allowed to cool down the pure metal is crystalline out (solidify) first while the impurities present in the metal remains in the liquid phase.

In this method, the impure metal is placed in a pipe and the circular heater is fitted at one end of melt impure metal over that region.Then the heated is move to another portion to cool, the pure metal crystallises out but the impurities remains in a liquid phase and passed into the adjacent molten zone. In this way, the impurities are swept away to another end which is finally discarded. The process is repeated to get metal in the highly pure state.This method is used to purify Ga, Ge and Si.

Or in another language zone refining can be defined as the method of zone refining is used to obtain metals of very high purity. It is based on the principle that the impurity has the greatest solubility in a liquid than in the solid state of the metal.

A circular mobile heater around the rod of an impure metal at one end and is slowly moved along the rod. At the heated zone, the rod melts.As the heated moves forward the pure metal crystallises while the impurities pass into the adjacent molten zone. The process is repeated several times when the impurities are completely swept into the end of the rod which is finally discarded. Semi-conductors, silicon germanium, gallium and indium are purified by this method.

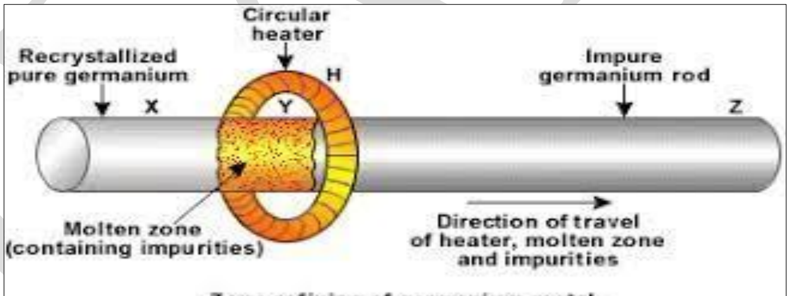
ZONE REFINING

Zone melting (or **zone refining** or **floating zone process** or **travelling melting zone**) is a group of similar methods of purifying crystals, in which a narrow region of a crystal is melted, and this molten zone is moved along the crystal. The molten region melts impure solid at its forward edge and leaves a wake of purer material solidified behind it as it moves through the ingot. The impurities concentrate in the melt, and are moved to one end of the ingot. Zone refining was invented by John Desmond Bernal[1] and further developed by William Gardner Pfann in Bell Labs as a method to prepare high purity materials, mainly semiconductors, for manufacturing transistors. Its early use was on germanium for this purpose, but it can be extended to virtually any solute-solvent system having an appreciable concentration difference between solid and liquid phases at equilibrium. This process is also known as the float zone process, particularly in semiconductor materials processing.

APPLICATIONS

Solar cells

In solar cells float zone processing is particularly useful because the single crystal silicon grown has desirable properties. The bulk charge carrier lifetime in float-zone silicon is the highest among various manufacturing processes. Float-zone carrier lifetimes are around 1000 microseconds compared to 20-200 microseconds with Czochralski process, and 1–30 microseconds with cast multi-crystalline silicon. A longer bulk lifetime increases the efficiency of solar cells significantly.



Zone refining of germanium metal.

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.
2. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry*. 5th Ed. Oxford University. Press.

POSSIBLE QUESTIONS:

Part-A (1 Mark)

Multiple Choice Questions (Each Question Carry One Mark)

1. Ellinghan diagrams can be used to predict the converion

(a) **Metals into their oxides** (b)Metal oxide into metal

(c) Impure metal into pure metal (d)Ore into metal

2. Which is the correct statement for the limitations of Ellighan diagram

(a)It didnot suggest the reduction of metal oxide by a given RA

(b)It tells the rate of the reduction reaction

(c) Do not tells anything about the rate at which the reduction reaction takes place

(d) It has no limitations

3. Which of the following is used in ointments for the treatment of ring worms

(a)Ti salts (b)**Tl salts** (c)Ga salts (d)Mo salts

4. The ore of Ti is….. (a)Tl_2O (b)**TiO_2** (c)$CaTiO_3$ (d)$TiCl_4$

5. Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?

(a)K2O < Na2O < Al2O3 < MgO (b)**Al2O3 < MgO < Na2O < K2O**

(c)MgO < K2O < Al2O3 < Na2O (d)MgO < K2O < Na2O < Al2O3

6. The correct order of stability for the following super oxides is:

(a)Na_2O (b)Na_2O_2 (c)**K_2O** (d)KO_2

7. The chemical formula of feldspar is:

(a) **$KAlSi_3O_8$** (b)Na_3AlF_6 (c)$NaAlO_2$ (d)$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

8. Among the alkali metals, the metal with the highest ionization potential is:

(a)Na (b)**Li** (c)Rb (d)Cs

9. Which of the following is used in ointments for the treatment of ring worms

(a)Ti salts (b)**Tl salts**

(c)Ga salts (d)Mo salts

10. Which one of the following is used for the manufacture of surgical instruments

(a)WO_3 (b) Cu (c)W (d)**W with Co and Cr**

11. Impure Ti metal can be purified by which of the following process

(a)Zone refining (b) **Van Arkel method**

(c)Electrolytic refinig (d)Kroll process

12. For the dyeing of wool and silk which of the following is used

(a)**Mo compounds** (b)W compounds

(c)V compounds (d)Ti compounds

13. Tl salts is used in ointments for the treatment of

(a) Ittching **(b) Ring worms** (c) Cracks (d) Burn wounds

14. Chemical formula for Ammonium Molybdate

(a)$(NH_4)_2MoO_4$ (b)NH_3 MoO_4

(c) NH_4 MoO_4 (d)$(NH_4)2MoO_4$. H_2O

15. What happen when the elmenite ore is heated with HCl in a current of chlorine

(a) **Converted into TiO_2** (b)Converted into Ti

(c)Converted into $TiCl_4$ (d)Converted into impure Ti metal

16. Find the ore of molydenum among the following

(a) Carnotite (b)Rutile (c)Eilmenite (d)**Wul-fenite**

17. Molybdenite ore is

(a) **MoS_2** (b)MoO_3

(c)$PbMoO_4$ (d)$MoS_2.7H_2O$

18. What happen when the elmenite ore is heated with HCl in a current of chlorine

(a)Converted into TiO_2 (b)Converted into Ti

(c)Converted into TiCl4 (d)Converted into impure Ti metal

19. Which of the followng Ti alloy can be used as filaments in vacuum tubes in place of Pt-Ir alloy

(a) Ti - Pt alloy (b)Ti - Cr alloy

(c)Ti - Co alloy **(d)Ti with Co and Ni alloy**

20. Rare earth element is……

(a) Ti (b)Mn (c)V **(d)TI**

PART- B (Each Carry 2 Marks)

1. What is standard electrode potential?
2. What is ore and minerals?
3. Define mining?
4. What are the difference between ore and minerals?
5. What is elligham diagram?
6. Write any two application of elligham diagram?
7. Define Fractional crystallization process?
8. What is metallurgy?
9. Write a note on electrolysis?
10. Write the applications of Monds process?
11. Define Hydrometallurgy?
12. Write the ores of gold and silver?

Part-C (Each Carry 6 Marks)

1. Explain Ellingham diagram for reduction of metal oxides using Carbon and carbon monoxide as reducing agent.
2. Write a note on van arkel-de boer process and Mond's process
3. Write a note on zone refining and electrolytic process.
4. What is Elligham diagram explain it brief.
5. Explain hydrometallurgy with reference to cyanide process for silver and gold.
6. Describe any two methods of purification of metals?
7. How to purify the Copper and Iron by electrolysis?
8. What are the characterization and application of elligham diagram?

18CHU202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2017 onwards)
Department of Chemistry
II- semester
Inorganic Chemistry- II (Metallurgy and S,P-Block Elements

UNIT I- Objective Questions for online examination (Each carry 1 Marks)

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
Ellinghan diagrams can be used to predict the converion	metals into their oxides	metal oxide into metal	impure metal into pure metal	ore into metal	metals into metal oxides
Which is the correct statement for the limitations of Ellighan diagram	It didnot suggest the reduction of metal oxide by a given RA	It tells the rate of the reduction reaction	Do not tells anything about the rate at which the reduction reaction takes place	it has no limitations	Do not tells anything about the rate at which the reduction reaction takes place
Which of the following is used in ointments for the treatment of ring worms	Ti salts	Tl salts	Ga salts	Mo salts	Tl salts
The ore of Ti is	Tl_2O	TiO_2	$CaTiO_3$	TiCl4	TiO_2
titanox is a mixture of	$TiO_2 + BaSO_4$	$TiO_2 + MgSO_4$	TiO_2 + Ag	$TiO_2 + CaSO_4$	$TiO_2 + BaSO_4$
Which one of the following is used for the manufacture of surgical instruments	WO_3	WO_2	W	W with Co and Cr	W with Co and Cr
Chemical formula for tungsten ore is	(Fe, Mn) WO_4	(Fe, Mn)WO_3	2(Fe, Mn)WO_5	Na_2WO_4	(Fe, Mn) WO_4
Molybdenite ore is	MoS_2	MoO3	PbMoO4	MoS2.7H2O	MoS_2
Name the catalyst used in the Contact process	V_2O_5	V_2O_3	VCl_5	V_2O_4	V_2O_5
Chemical formula for Ammonium Molybdate	$(NH_4)_2MoO_4$	NH_3 MoO_4	NH_4 MoO_4	$(NH_4)_2MoO_4$. H_2O	$(NH_4)_2MoO_4$
The standard free energy change of the formation of metal oxides is	positive	negative	one	zero	negative
Name of the ore which has the chemical formula of FeTiO3	Rutile	Titanate	Elmenite	Titanium	Elmenite

What happen when the elmenite ore is heated with HCl in a current of chlorine	Converted into TiO2	Converted into Ti	Converted into TiCl4	Converted into impure Ti metal	Converted into TiO2
Impure Ti metal can be purified by which of the following process	Zone refining	Van Arkel method	Electrolytic refinig	Kroll process	Van Arkel method
In alumino thermic proces, TiO2 is reduced with Ti which is the reducing agent	NaS	Na	Al	Mg	Al
Ferro titanium alloy is which of the following mixture	Ti + Cr	Ti + Ni	Fe + Ti	Fe + TiO2	Fe + Ti
Which of the followng Ti alloy can be used as filaments in vacuum tubes in place of Pt-Ir alloy	Ti - Pt alloy	Ti - Cr alloy	Ti - Co alloy	Ti with Co and Ni alloy	Ti with Co and Ni alloy
Vanadium can be extracted from which of the following ore	Ammonium Metavanadate	Sodium Vanadate	Vanodinite	Potassium Vanadate	Vanodinite
Carnotite is the ore of	Ti	Tl	V	Mn	V
The name of NH4VO3 which is obtained from vanodinite ore	Ammonium orthovanadate	Ammonium vanadate	Ammonium meta vanadate	Vanadate	Amonium mata vanadate
Pure V metal is obtained by alumino thermic reduction of	VCl5	VCl3	V_2O_5	VI4	V_2O_5
Titanium metal combines with the non-metal like carbon form	TiC	CO	CO2	Ti + CO alloy	TiC
When vanadium is easily attacked by carbon , it forms	V(NO3)3	NH4VO3	V2O5	VNO3	V(NO3)3
Rare earth element is	Ti	Mn	V	TI	Tl
Thalliferrous is the ore of	Ti	Tl	Fe	Ga	Tl
Flue dust is ontained from the roasting of	carnotite	vanodinite	Thalliferrous pyrites	carnollite	Thalliferrous pyrites
On the electrolysis of TlI with hot con.H2SO4 to get	Tl2SO4	TlSO4	TlI4	TlO2	Tl2SO4
Tl is more reactive than In and Ga due to its tendency to form	Tl2CO3	to form nitrides	to form Tl- Ag alloy	to form unipositive ion	to form unipositive ion

Which of the following is used as fungicide, germicide and for killing rats and destroying vermin	Ti salts	Mo salts	Tl salts	V salts	Tl salts
Thallium compounds has been used for the preparation of crooks glasses due to their	stability	high boiling point	high melting point	high refractive index	high refractive index
The chief ore of molybdenum are	molybdenite	wulframite	molbdenum trioxide	molybdenum sulphide	molydenite ore
Find the ore of molydenum among the following	carnotite	rutile	eilmenite	wul-fenite	wul-fenite
Formula for the ore of molybdenite is	MoS2	MoO3	PbMoO4	MoCl5	MoS2
On heating the crystals of ammonium molybdate (NH4)2MoO4, give	Pure Mo metal	MoO3	Mo	MoCl5	MoO3
Which one of the following reducing agent is used for the reduction of MoO3 into Mo metal	magnesium	Sodium	carbon	chlorine	Carbon
pure Mo metal is obtained from Impure Mo by heated with	CO2	CO	C	Al	CO
Which of the folllowing is used to detect and estimate phosphate and arsenic in chemical analysis of	(NH4)2MoO4	MoS2	MoO3	MoCl5	(NH4)2MoO4
For the dyeing of wool and silk which of the following is used	Mo compounds	W compounds	V compounds	Ti compounds	Mo compounds
Molybdenum is used in thermo-couples for the measurement of	high pressure	High temperaturre	high voltage	heat	High temperature
The chief ore of tungsten is	wolframite	Magnesite	carnotite	tungsten tri oxide	wolframite
The alloy of W along with Co and Cr is known under the name of	Stellite	tungtic acid	carnotite	chromite	stellite
What is the other name of titanium dioxide	titanous oxide	titanium oxide	titanous	titanic compound	titanium dioxide
Among the following which one is the crystalline form of titanium dioxide	Brookite	titanous	titanic compound	titania	brookite

The naturally occurring source of the metal from which the metal can be economically extracted is called its	mineral	gangue	ore	native ore	mineral
Which of the following species has a square planar geometry?	[Zn(NH3)4]2+	[Fe(CN)6]4-	[Cr(C2O4)3]3-	[Ni(CN)4]2-	[Ni(CN)4]2-
The hexafluoroferrate(III) has a magnetic moment of 6.0 B.M; this implies that	It is unstable	it involves sp3d2 hybridization	it involves d2sp3 hybridization	it should be coloured	it involves d2sp3 hybridization
Froth floatation is suitable for concentration of	oxide ores	carbonate ores	halide ores	sulphide ores	oxide ores
The various compounds of metals which occur in nature and are obtained by mining are called	minerals	ores	gangue	matrix	minerals
The art of winning the a metal from its ore is known as	minerals	ores	metallurgy	matrix	metallurgy
The ore which is mined is usually associated with rocky impurities called	flux	salt	slag	gangue	gangue
The lime is generally used as	flux	matrix	slag	gangue	flux
The metal ion present in chlorophyll is	Mg(II)	Fe(II)	Ca(II)	Mn(II)	Mg(II)
Which one of the following is a double salt?	nickel tetracarbonyl	sodium chloride	barium sulphate	ferrous ammonium sulphate	ferrous ammonium sulphate
Cinnabar has the composition	CuFeS2	ZnS	HgS	PbS	HgS
The main constituent of zinc blende is	CuFeS2	CuS	PbS	ZnS	ZnS
Which of the following is not characteristic of the metallurgical process of smelting?	It involves reduction	high temperature is used	carbon is commonly used for reduction in smelting	excess of air is required for smelting	excess of air is required for smelting
Which of the following metals can be obtained by the electrolytic reduction of its fused halide	Fe	Hg	Na	W	Na
Germanium and gallium may be purified by	electrolysis	recrystallization	distillation	zone refining	zone refining
The heating of an ore in a furnace in the absence of air to expel moisture and air is called	roasting	dehydration	poling	calcination	calcination
A method of purifying copper ore involves	poling	smelting	magnetic separation	electrolysis	poling

UNIT-II
SYLLABUS

i) General characteristics: melting point, flame colour, reducing nature, diagonal anomalous behavior of first member of each group
ii) Reactions of alkali and alkaline earth metals with oxygen, hydrogen, nitrogen and water.

iii) Common features such as ease of formation, thermal stability and solubility of the following alkali and alkaline earth metal compounds: hydrides, oxides, peroxides, superoxides, carbonates, nitrates, sulphates.

METALLIC CHARACTER AND ELECTRONEGATIVITY

The members of Group I and II are all metals. They are silvery coloured and tarnish in air. They show relatively weak metallic bonding because they have only one or two valence electrons.

Group I Metal	Symbol	Atomic number	Electronic structure	Electronegativity	Crystal structure
Lithium	Li	3	$[He]2s^1$	1.0	BCC
Sodium	Na	11	$[Ne]3s^1$	0.9	BCC
Potassium	K	19	$[Ar]4s^1$	0.8	BCC
Rubidium	Rb	37	$[Kr]5s^1$	0.8	BCC
Caesium	Cs	55	$[Xe]6s^1$	0.7	BCC
Francium	Fr	87	$[Rn]7s^1$	/	BCC

Group II Metal	Symbol	Atomic number	Electronic structure	Electronegativity	Crystal structure
Beryllium	Be	4	$[He]2s^2$	1.5	HCP
Magnesium	Mg	12	$[Ne]3s^2$	1.2	HCP
Calcium	Ca	20	$[Ar]4s^2$	1.0	FCC
Strotium	Sr	38	$[Kr]5s^2$	1.0	FCC
Barium	Ba	56	$[Xe]6s^2$	0.9	BCC
Radium	Ra	88	$[Rn]7s^2$	/	BCC

Alkali metals are all soft, silvery metals, with its lower member (like Cs) softer than its upper member and tarnishing more rapidly in air (therefore they are often kept immersed in paraffin). They all crystallize with body-centred cubic lattice, so that all of them have low densities as there are more space in the metallic lattice. The low core charge(+1) of the atoms results in very poor control of the outer shell s electrons, which are easily delocalized or lost from the atoms. As a result, metallic bond among atoms is weak and the metals can be easily cut with a knife, besides having low melting and boiling points.

Alkaline earth metals are grey metals and are harder than alkali metals, although they can still be cut with a knife. The lower member barium is very soft, and it tarnishes rapidly. Metallic bond among atoms is stronger than their Group I counterparts; and the melting points and boiling points of the elements are all higher, as a result of the effect of increased core charge (+2) and decreased atomic radius. Beryllium and magnesium have hexagonal close packed structures, whilst calcium and strontium have face-centred cubic close packed structures -- the more efficient packing of the atoms accounts for the higher density of alkaline earth metals.

All s-block elements have **low electronegativity** values, i.e., they are **electropositive**, with a tendency to lose their outer electrons relatively easily. As each group is descended, the elements become more and more electropositive -- the elements tend to lose electrons more readily. This is because the outer shell is further from the nucleus as each group is descended. Group II elements are more electronegative (less electropositive) than Group I elements in the same period, as the nuclear charge has increased by one.

FORMATION OF BASIC OXIDES AND HYDROXIDES

Group I Metal	Oxides formed	Hydroxides formed
Li	Li_2O	LiOH
Na	Na_2O ,Na_2O_2	NaOH
K	K_2O_2, KO_2	KOH
Rb	Rb_2O_2, RbO_2	RbOH
Cs	Cs_2O_2, CsO_2	CsOH

Group II Metals	Oxides formed	Hydroxides formed
Be	BeO	$Be(OH)_2$
Mg	MgO	$Mg(OH)_2$
Ca	CaO	$Ca(OH)_2$
Sr	SrO	$Sr(OH)_2$
Ba	BaO	$Ba(OH)_2$

Group I and II metal oxides have ionic lattices and are highly basic. Some oxides react exothermically with water to give the hydroxides. For example :

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)}$$

Magnesium oxide is slightly soluble in water and dissolves in acids to give salts :

$$MgO_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_2O_{(l)}$$

All Group I metal hydroxides are soluble in water. They are among the strongest bases known.

The properties of Group II metal hydroxides are summarized as in table :

Hydroxide	$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
Solubility	Insoluble		Solubility increasing	---------------------	→
Basic strength	Amphoteric		Base strength increasing	-------------------	→

PREDOMINANTLY IONIC BONDING WITH FIXED OXIDATION STATE IN THEIR COMPOUNDS

The s-block elements form compounds that are predominantly ionic in nature, showing fixed oxidation states of +1 in Group I and +2 in Group II.

Alkali metals have one electron in their outermost s -orbital, with completely filled inner orbitals. Hence they show only +1 oxidation state because their first ionization enthalpies are low.

Consider the enthalpy change for the formation of $NaCl_{2(s)}$ from Na metal and chlorine gas in the standard state. Since the second electron of sodium must be removed from a noble gas electronic structure [Ne], its second ionization enthalpy is very high, about 8000 kJ mol^{-1}. This amount of energy can not be repaid by the exothermic processes, and therefore sodium is restricted to the chemistry of a monovalent ion with a fixed oxidation state of +1.

Alkali earth metals have two electrons in their outermost s-orbital, with completely filled inner orbitals. Hence they show +2 oxidation state only as the sum of first and second ionization enthalpies is also relatively low.

In all their compounds the elements of Group II have the oxidation state of +2. The considerable endothermic contribution from the double ionization of a Group II metal M to M^{2+} is compensated by the very large lattice enthalpy. However, the third ionization of M, corresponding to the removal of an electron from an inner shell, is so large that the energy required cannot be recovered. Hence these elements do not occur with oxidation state +3.

Characteristic flame colour of salts

S-block elements give characteristic colours in the flame test (except Be and Mg). In the flame test, their electrons are excited to a higher energy level. When the electron drops back to the original lower level, the extra energy is given out. In the case of s-block elements, the amount of energy given out is small, hence it lies in the visible light region. These elements, therefore, have coloured flames:

Group I Metal salt	Flame colour
Li	red
Na	golden yellow
K	lilac
Rb	red
Cs	blue

Group II Metals salt	Flame colour
Be	None
Mg	None
Ca	brick red
Sr	crimson
Ba	apple green

The procedure to carry out flame test on alkali and alkaline earth metal compounds in the laboratory is shown below :

1. A platinum or nichrome wire is first cleaned by dipping it into a little concentrated hydrochloric acid, and then heating it in a non-luminous Bunsen flame till no special colour is imparted to the flame. The concentrated hydrochloric acid converts any contaminated salts to their corresponding chlorides, which are usually more volatile to be vaporized off.
2. The clean wire is then dipped into a fresh portion of concentrated hydrochloric acid, and then into a small sample of powdered compound whose flame colour is to be determined.
3. The wire is moved, first through the cooler part of a non-luminous Bunsen flame by approaching from underneath, so that even very volatile substances could colour the flame long enough to be observable.
4. The wire must be cleaned before testing for a new compound and a fresh portion of acid used.

WEAK TENDENCY TO FORM COMPLEXES

A **complex** is a polyatomic ion or molecule formed when molecular or ionic groups (called **ligands**) form dative covalent bonds with a **central metal atom or cation**. Complex formation is a common feature with d-block metal ions.

The formation of such complexes is due to the presence of low energy empty d-orbitals in the d-block metal ions that can accept the lone pairs from the surrounding ligands.

S-block metal ions rarely form complexes because they do not have low energy vacant orbitals available for the bonding with the lone pairs of surrounding ligands.

The alkali metal ions have least tendency towards complex formation. The relatively large size of their ions, completely filled inner orbitals, and low charge (+1) are responsible for such behaviour.

The alkaline earth metal ions have a relatively greater tendency to form complexes than alkali metal ions. It can be explained in terms of the higher charge (+2) and smaller size of the Group II cations. Beryllium forms a particular wide range of complexes for this reason.

Variation in properties of the s-block elements and their compounds

Variations in atomic radii, hydration enthalpies, ionization enthalpies and melting points

Atomic and ionic radii

Group I Element	Atomic radius (nm)	Ionic(M^+) radius (nm)
Li	0.123	0.060
Na	0.157	0.095
K	0.203	0.133
Rb	0.216	0.148
Cs	0.235	0.169

Group II Element	Atomic radius (nm)	Ionic(M^{2+}) radius (nm)
Be	0.089	0.031
Mg	0.136	0.065
Ca	0.174	0.099
Sr	0.191	0.113
Ba	0.198	0.135

a. Explain why atomic and ionic size increase down each group.
As each group is descended, the next atom in each group has another shell of electrons around the nucleus.

b. Explain why Group I atoms and ions are larger than their Group II neighbours in the same period.
Each Group II atom has one more electron in the outer shell and one more proton in the nucleus than has the Group I atom in the same period. Since the screening of the outer s-electrons from the nucleus is the same for both atoms, the nucleus of the Group II atoms exerts a stronger attraction on the outer electrons because it has one more proton. This greater 'effective nuclear charge' of Group II atoms reduces their atomic radii.

The similarity in size of the lithium and magnesium ions leads to a number of chemical similarities in the compounds of the two elements.

Hydration enthalpies

Group I Ions	charge/radius	hydration enthalpy $kJmol^{-1}$
Li^+	16.7	-500
Na^+	10.5	-390
K^+	7.5	-305
Rb^+	6.8	-281
Cs^+	5.9	-248

Group II Ions	charge/radius	hydration enthalpy $kJmol^{-1}$
Be^{2+}	66.6	-2385
Mg^{2+}	30.8	-1891
Ca^{2+}	20.2	-1561
Sr^{2+}	18.2	-1414
Ba^{2+}	15.5	-1273

The hydration enthalpy is the enthalpy change when polar water molecules cluster around a metal ion :

$$M^{+}_{(g)} + aq. \rightarrow M^{+}_{(aq)}$$

or

$$M^{2+}_{(g)} + aq. \rightarrow M^{2+}_{(aq)}$$

As each group is descended, the enthalpy of hydration of an ion become less negative. The larger the ion, the weaker the electric field around it and water molecules are attracted less strongly. This means that fewer water molecules are attracted to the ion and the enthalpy of hydration, resulting from this electrostatic attraction is smaller.

Group II ions have hydration enthalpies higher than their Group I counterparts, as they are doubly charged positive ions of smaller ionic radius. This higher charge density results in a greater electrostatic attraction between water molecules and Group II ions and more negative enthalpy of hydration.

Ionization enthalpies

Group I Element	First I.E. $kJ\ mol^{-1}$	Second I.E. $kJ\ mol^{-1}$	Third I.E. $kJ\ mol^{-1}$
Li	520	7300	11800
Na	500	4600	6900
K	420	3100	4400
Rb	400	2700	3800
Cs	380	2400	3300

Group II Element	First I.E. $kJ\ mol^{-1}$	Second I.E. $kJ\ mol^{-1}$	Third I.E. $kJ\ mol^{-1}$
Be	900	1800	14800
Mg	740	1500	7700
Ca	590	1100	4900
Sr	550	1100	4200
Ba	500	1000	3390

a. For each element in Group I, explain why the first ionization enthalpy is so much smaller than the other two.
The outer s-electron is relatively easy to remove because it is well shielded from the nucleus by the inner electrons. Removal of a second electron involves the removal of an electron with stable noble gas electronic configuration from an inner shell, which is closer and not so well shielded from the nucleus; it is therefore more strongly held by the nucleus.

b. Explain the relatively large difference between the second and the third ionization enthalpies for all Group II elements.
The two outer s-electrons are relatively easy to remove because they are **well shielded** from the nucleus by the inner electrons. Removal of a third electron is relatively difficult because the inner electrons, which have stable noble gas electronic configuration, are closer and not so well shielded from the nucleus.

c. Describe and explain the trend in ionization enthalpies as each group is descended.
Ionization enthalpy decreases as each group is descended. This is because the outer electrons are further out and progressively better shielded from the nucleus as each group is descended.

d. How do you expect the reactivity of the elements to change on going down each group ?
Reactivity increases down each group because the outer electrons are less strongly held.

e. How would you expect the reactivity of the elements to change going across from Group I to Group II in the same period ?

Reactivity decreases because one electron is more easily lost than two.

Melting points

Group I Element	Crystal structure	Melting point ℃
Li	BCC	181
Na	BCC	98
K	BCC	63
Rb	BCC	39
Cs	BCC	29

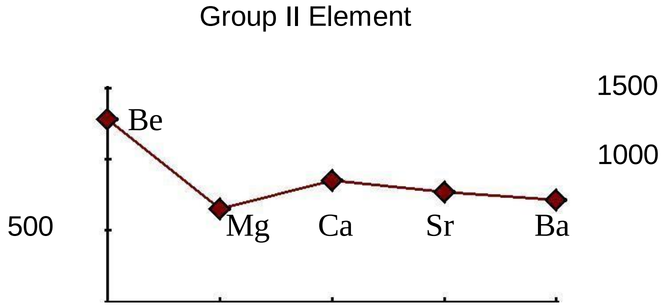
Group II Element	Crystal structure	Melting point ℃
Be	HCP	1283
Mg	HCP	650
Ca	FCC	850
Sr	FCC	770
Ba	BCC	714

Most of the differences in melting points can be interpreted in terms of the strength of metallic bonds. The strength of these bonds are dependent on the following factors :

1. atomic size,
2. number of electrons in the outer shell of each atom,
3. metallic crystal structure.

Melting points generally decrease down each group. A metal is regarded as a fairly closely-packed assembly of positive ions held together by a mobile electron 'cloud'. As each group is descended, the number of electrons in the cloud remains the same but the ionic size increases. Therefore, the electron cloud becomes more diffuse resulting in weaker attractive forces between the cloud and the ions.

The melting points in Group II are higher than for the corresponding Group I elements because the ions of Group II are doubly charged and smaller than their Group I neighbours. Thus, the alkaline -earth elements contribute two electrons per atom to the mobile electron 'cloud' whereas the alkali metals only contribute one electron per atom. The greater number of electrons and the smaller ionic size of the Group II elements help to increase the density of the electron cloud and thus increase the attractive forces between the mobile electrons and the cationic lattice.



In Group I all the metals have the same crystal structure whereas those of Group II are of more than one type. Since crystal structure affects physical properties, the irregularity in melting points can be explained in terms of **change of crystal structures**. Liquid sodium has been used as a coolant in some nuclear reactors. Give reasons why you think it is preferable to water.

Sodium has a fairly low melting point for a metal and is a liquid over a range of about 800℃. Water is usually a liquid between 0 and 100℃. In comparison to sodium, this is a much narrower range so that the boiling point is too low to be useful for nuclear reactors. Furthermore, sodium is a far better conductor of heat than water, and despite its lower heat capacity, a flow of sodium can remove heat from a reactor more efficiently. (Liquid sodium also presents fewer corrosion problems than water)

Reactions of the elements with oxygen and water

Alkali metals

The elements of Group I are called alkali metals because they react with water to form alkaline solutions. They are very reactive and have to be stored under paraffin oil to protect them from air and moisture. The alkali metals have low first ionization enthalpies and form ions easily by losing one electron thereby forming a univalent ion with a noble gas like structure. They react readily with water, dilute acids and most non-metals. The order of the reactivity of the elements is :

Cs > Rb > K > Na > Li

Alkaline earth metals

The Group II elements are called alkaline earth metals because many of their compounds are found as minerals in rocks. This is possible because the compounds are insoluble in water, so they are not washed away by rain. The alkaline earth metals are less reactive than alkali metals due to greater ionization enthalpies. The order of the reactivity of the elements is :

Ba > Sr > Ca > Mg > Be

Reaction with oxygen

With the exception of lithium and beryllium, all s-block elements produce more than one oxide. The three types of oxides are all ionic, and the ions are related as follows :

$$O^{2-} \longrightarrow O_2^{2-} \longrightarrow O_2^{-}$$

Lithium will melt when heated and eventually burns to form the monoxide and some lithium nitride :

$2\,Li_{(s)} + 1\,O_{2(g)} \rightarrow Li_2O_{(s)}$

$3\,Li_{(s)} + 1\,N_{2(g)} \rightarrow Li_3N_{(s)}$

Sodium burns in air with a yellow flame. The white product remaining is not pure sodium oxide. In fact, it is mainly sodium peroxide :

Potassium, rubidium and caesium ignite spontaneously to form peroxides and superoxides :

All alkali earth metals burn brilliantly when heated in air to form a mixture of oxide and nitride. The rate of reaction and the proportion of nitride formed increases down the group :s)

$$2Mg + 1\,O_{2(g)} \rightarrow MgO_{(s)}$$

$$3\,Mg_{(s)} + 1\,N_{2(g)} \rightarrow Mg_3N_{2(s)}$$

There are no Group II superoxides as the cations have too great polarising power.

When barium peroxide is heated, it decomposes to produce a colourless gas. Write an equation for this decomposition.

Reaction with water

The reactivity of alkali metals increases markedly down the group. Lithium reacts quietly or very slowly with water. Sodium reacts vigorously with water. Potassium reacts so vigorously with water that the hydrogen formed catches fire because sufficient heat is generated in the reaction between potassium and water to ignite the hydrogen. Both rubidium and caesium react explosively.

Beryllium does not react with water even when hot.

Magnesium reacts very slowly with cold water but reacts vigorously with steam at red heat.

Calcium reacts vigorously with cold water, producing hydrogen and whitish suspension of calcium hydroxide, some of which dissolves.

Barium react very vigorously to produce hydrogen and barium hydroxide.

Reaction of the oxides with water, acids and alkalis

Types of oxides	Elements which form oxides directly in adequate supply of air
monoxide, O^{2-}	Li Be Mg Ca Sr Ba
peroxide, O_2^{2-}	Na
superoxide, O_2^{-}	K Rb Cs

All alkali metal oxides are basic oxides and thus react with water to form hydroxides, and with acids to form salts and water.

$$\mathbf{O^{2-}_{(s)} + H_2O_{(l)} \rightarrow 2OH^{-}_{(aq)}}$$

$$O^{2-}_{(s)} + 2H^{+}_{(aq)} \rightarrow H_2O_{(l)}$$

Alkali metal oxides are decomposed by cold water. They react with acid readily and have no reaction with alkalis.

$$Na_2O_{(s)} + H_2O_{(l)} \rightarrow 2\,Na^{+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

Group II metal oxides are much less soluble than those of Group I due to their higher lattice enthalpies. Except **beryllium oxide**, which **is amphoteric**, the other alkaline earth metal oxides are basic. The basic strength increases from magnesium oxide to barium oxide. This is because the ionic size increases from Mg^{2+} to Ba^{2+}. Solubility of the oxides increases from magnesium to barium due to the decreasing magnitude of lattice enthalpies.

Magnesium oxide is slightly soluble in water producing an insoluble hydroxide :

$$MgO_{(s)} + H_2O_{(l)} \rightarrow Mg^{2+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

All the other oxides slake rapidly in water to give alkaline solutions of their hydroxides with considerable evolution of heat :

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

$$BaO_{(s)} + H_2O_{(l)} \rightarrow Ba^{2+}_{(aq)} + 2\,OH^{-}_{(aq)}$$

All Group II oxides react with acids to form salts and water:

$$MgO_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_2O_{(l)}$$

Beryllium oxide is virtually insoluble. It is amphoteric and reacts with both acids and alkalis:

$$BeO_{(s)} + 2HNO_{3(aq)} \rightarrow$$

$$BeO_{(s)} + 2NaOH_{(aq)} + H_2O_{(l)} \rightarrow$$

All **peroxides** and **superoxides** of s-block elements are decomposed by cold water :

$$O_2^{2-}{}_{(s)} + 2\,H_2O_{(l)} \rightarrow 2\,OH^-{}_{(aq)} + H_2O_{2(aq)}$$

$$2\,O_2^-{}_{(s)} + 2\,H_2O_{(l)} \rightarrow 2\,OH^-{}_{(aq)} + H_2O_{2(aq)} + O_{2(g)}$$

a. At 0℃, sodium peroxide reacts with water without the evolution of oxygen. Hydrogen peroxide is detected at this temperature. Write an equation for this reaction.

b. At 25℃, sodium peroxide reacts with water with the evolution of oxygen. The evolution of oxygen at higher temperature is believed to be due to a secondary reaction. Write an equation for this reaction.

c. Predict the reaction between barium peroxide and ice-cold water.

d. Hydrogen peroxide can be prepared in the laboratory by adding barium peroxide to ice-cold dilute sulphuric acid. Write an equation for this reaction.

Relative thermal stabilities of the carbonates and hydroxides

The thermal stability of an ionic compound depends on the charge and the size of the ions. If the cation has a greater polarizing power (smaller size and higher charge), it will distort the electron cloud of the neighbouring large anion to a greater extent, and hence the compound becomes less stable. Most carbonates and hydroxides readily undergo decomposition on heating to give oxides.

Down each group, as the size of the cation increases, the polarizing power of the cation decreases. The compound with large cation become more stable. Hence, the thermal stability of carbonates and hydroxides of both group I and Group II metals increases down the group.

Group II metals are much smaller than Group I metal ions and have a higher charge. Consequently, their polarizing power is greater. Carbonates and hydroxides of Group II metals are less stable to thermal decomposition than those of Group I metals.

Carbonates

Except for lithium carbonate, the alkali metal carbonates are stable to heat.

The relative instability of lithium carbonate can be explained in terms of the gain in lattice enthalpy when the very small cation, Li^+ is combined with the smaller oxide ion instead of the much larger carbonate ion.

All Group II carbonates are decomposed on heating.

$$MCO_{3(S)} \rightarrow MO_{(s)} + CO_{2(g)}$$

The decomposition temperatures of the Group II carbonates are shown below :

$BeCO_3$	$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$
100℃	540℃	900℃	1290℃	1360℃

The thermal stability of the carbonates increases down the group because as the group is descended, the polarizing power of the cation decreases. Thus, cations of the upper elements distort the anion electron clouds far more than those of the lower elements do.

Hydroxides

Lithium hydroxide is the only Group I metal hydroxides which decomposes at Bunsen burner temperatures because the small Li^+ ion has considerable polarizing power which polarizes the electron cloud of hydroxide ion to such extent that decomposition occurs on heating.

The thermal stability of Group II hydroxides increases down the group because polarizing power decreases with increasing size of the cation.

$$\mathbf{M(OH)_{2(s)} \xrightarrow{\Delta} MO_{(s)} + H_2O_{(g)} \qquad \Delta H}$$

The data given below does back up the trend in the thermal stability of the Group II hydroxides because more and more endothermic as the group is descended. This suggests that the thermal decomposition process become less energetically favorable as the group is descended.

Hydroxides	**$Be(OH)_2$**	**$Mg(OH)_2$**	**$Ca(OH)_2$**	**$Sr(OH)_2$**	**$Ba(OH)_2$**
ΔH / kJ mol^{-1}	+54	+81	+109	+127	+146

Relative solubilities of the sulphates(VI) and hydroxides

Enthalpy change of solution can be used for comparing the relative solubility of ionic compounds. For the dissolution of a salt **MX** , the enthalpy change of solution can be related to hydration and lattice enthalpy by the following enthalpy diagram :

$$\mathbf{\Delta H_{solution} = - \Delta H_{lattice} + \Delta H_{hydration}}$$

If the magnitude of $\Delta H_{hydration}$ is greater than that of $\Delta H_{lattice}$, then $\Delta H_{solution}$ is negative (exothermic) and the compound will be soluble.

Compound	**Solubility mol per 100g 0f water**
LiOH	0.516
NaOH	1.05
KOH	1.71
RbOH	1.69
$MgCrO_4$	8500×10^{-4}
$CaCrO_4$	870×10^{-4}
$SrCrO_4$	5.9×10^{-4}
$BaCrO_4$	0.011×10^{-4}

Compound	**Solubility mol per 100g 0f water**
$Mg(OH)_2$	0.02×10^{-3}
$Ca(OH)_2$	1.5×10^{-3}
$Sr(OH)_2$	3.4×10^{-3}
$Ba(OH)_2$	15×10^{-3}
$MgSO_4$	3600×10^{-4}
$CaSO_4$	11×10^{-4}
$SrSO_4$	0.62×10^{-4}
$BaSO_4$	0.009×10^{-4}

Sulphates(VI) and hydroxides of Group I metals are more soluble than those of Group II metals.

This is because Group I metal ions have smaller charges and larger sizes, and $\Delta H_{lattice}$ of their compounds are smaller in magnitude than those of Group II compounds. Consequently, $\Delta H_{solution}$ is more negative.

For the hydroxides of Group II metals, the size of the anions and cations are of the same order of magnitude. Down the group, less energy is required to break the lattice as the size of cations increases,

but the change in $\Delta H_{hydration}$ is comparatively small. As a result, the $\Delta H_{solution}$ becomes more negative and the solubility of Group II hydroxides increases down the group.

For the sulphates(VI) of Group II metals, the cations are much smaller than the anions. Down the

group, the change in size of the cations does not cause a significant change in $\Delta H_{lattice}$, but $\Delta H_{hydration}$ becomes less negative. As a result, $\Delta H_{solution}$ becomes less negative and the solubility of Group II sulphates(VI) decreases down the group.

What are the trends in solubility of the Group II chromates(VI) ? Explain why the trend occur.

The solubility of the Group II chromates(VI) generally decreases down the group. As CrO_4^{2-} ion is much larger than the cations, the change in size of the cations does not cause a significant change in

$\Delta H_{lattice}$. The solubility of the Group II chromates(VI) decreases down the group because $\Delta H_{hydration}$ becomes less negative as cations becomes larger in size.

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.
2. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry*. 5th Ed. Oxford University Press.

POSSIBLE QUESTIONS:

Part-A (1 Mark)

Multiple Choice Questions (Each Question Carry One Mark)

1. Titanox is a mixture of……… (a)**TiO_2 + $BaSO_4$** (b)TiO_2 + $MgSO_4$

(c)TiO_2 + Ag (c)TiO_2 + $CaSO_4$

2. For the dyeing of wool and silk which of the following is used

(a) **Mo compounds** (b)W compounds (c)V compounds (d)Ti compounds

3. Molybdenum is used in thermo-couples for the measurement of

(a) High pressure (b)**High temperature** (c)High voltage (d)Heat

4. The chief ore of tungsten is

(a) **Wolframite** (b)Magnesite (c)Carnotite (d)Tungsten tri oxide

5. Alkali metals are:

(a) Oxidising agents (b)Dehydrating agents

(c)**Reducing agents** (d)hydrating agents

6. A elements are named as alkali metals because

(a) Their oxides are basic (b) **Their oxide and hydroxides are watersoluble**

(c) Hydroxides are water soluble (d) They are found in earth

7. Which element is produced at the cathode during the electrolysis of brine in Nelsons cell?

(a)**H_2** (b)Na (c)CO_2 (d)O_2

8. Ammonia may be prepared by heating ammonium chloride with

(a) Water (b)NaCl (c)**Aqueous sodium hydroxide** (d)H_2SO4

9. DMG is used for the detection of

(a) Zn^{2+} (b) Ca^{2+}

(c)Fe^{2+} (d) **Ni^{2+}**

10. The metal ion present in haemoglobin is

(a) Mg(II) (b) **Fe(II)**

(c) Mn(II) (d) Ca(II)

11. Which of the following is not an ore

(a) Bauxite (b)Malachite

(c)Zinc blende (d)**Pig iron**

12. Removal of rocky impurities from the ore is known as

(a)**Concentration** (b)Froath floatation

(c)Magnetic seperation (d)Ore dressing

13. The indicator used in EDTA titration is

(a) Phenolphthalein (b)Methyl orange (c) Starch (d) **Eriochrome Black-T**

14. Metallurgy is defined as the process of

(a) **Extracting metal in pure form** (b**)**creating alloys of metals

(c)making metals live long (d)Extracting ore from its mineral

15. The process of heating the ore strongly in excess of air so that the volatile impurities are removed and the ore is changed to oxide is known as

(a) Calcination (b)Froth floatation(c)**Roasting** (d)Leaching

16. Argentite is the ore of

(a) Gold (b)Zinc (c)**Silver** (d)Mercury

17. The type of indicator used in EDTA titration is,

(a)neutralization indicator (b) **metal ion indicator**

(c)redox indicator (d) precipitation indicator

18. From the following which metal occur in their native state

(a) Tungsten (b)Vanadium (c)Gallium **(d)Silver**

19. The process of making small pieces of ores is known as

(a)Crushing **(b)**Pulverising

(c)concentration (d)ore dressing

20. The rocky materials such as sand, lime stone and clay are called under the name

(a)Flux **(b)Gangue** (c)sludge (d)mud

PART- B (Each Carry 2 Marks)

1. What are the alkali metals?
2. List out the alkaline earth metals?
3. Write down the flame colours of 1s and 2s elements?

4. What is oxidation?
5. Define reduction process?
6. What happens to melting point of S block elements descending down the group?
7. Write a note on reducing nature of S-block elements?
8. Write a note on reaction of alkali metals with oxygen?
9. Write a note on reaction of 1s and 2s metals with Hydrogen?
10. What are the differences between alkali and alkaline earth metals?
11. Define diagonal relationship?
12. What is Oxosalts? Give some examples?

Part-C (Each Carry 6 Marks)

1. Analyse the anomalous behaviour of Lithium.
2. Compare solubilities of alkali and alkaline earth metal compounds
3. Compare chemical reactions of alkali and alkaline earth metals with oxygen and water.
4. Discuss the solubility and thermal stability of alkaline earth metals.
5. Discuss the diagonal relationship between Li and Mg.
6. Explain all possible chemical reactions for alkaline earth metals.
7. Describe the anomalous behaviour of Be.
8. Give a brief account on ease of formation, thermal stability, solubility of alkaline earth metal compounds.
9. Discuss the diagonal relationship between Be and Al.
10. Describe the reaction of alkali metals with nitrogen, hydrogen, oxygen and water?
11. Write a note on carbonates, sulphates and nitrates of alkali metals?
12. Explain the chemical reaction of alikaline earth metal with nitrogen, hydrogen, oxygen and water?
13. Discuss about the oxides, peroxides and super oxides of alkali metals
14. Briefly explain about the oxosalts of alkaline earth metals?
15. Explain brief i) hydrides ii) oxides of alkaline earth metals?

18CHU202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2017 onwards)
Department of Chemistry
II- semester
Inorganic Chemistry- II (Metallurgy and S,P-Block Elements)

UNIT II- Objective Questions for online examination (Each carry 1 Marks)

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
Which of the following ligands is not capable of forming a chelate with metals?	EDTA	ethylene diamine	ONO-	oxalate	ONO-
DMG is used for the detection of	Zn2+	Ca2+	Fe2+	Ni2+	Ni2+
Pick out the neutral ligand?	chloride	cyanide	hydroxide	carbon monoxide	carbon monoxide
Which one of the following is a bidentate ligand?	chloride	water	oxalate	ammonia	oxalate
The type of indicator used in EDTA titration is,	neutralization indicator	metal ion indicator	redox indicator	precipitation indicator	metal ion indicator
Which is not true with EDTA?	relatively low price	high water solubility	good chelating agent	denticity is four	denticity is four
The indicator used in EDTA titration is	phenolphthalein	methyl orange	starch	Eriochrome Block-T	Eriochrome Block-T
The metal ion largely responsible for hardness of water are	Ca(II) and Mg(II)	Ca(II) and Zn(II)	Ca(II) and Cu(II)	Mg(II) and Al(III)	Ca(II) and Zn(II)
The metal ion present in haemoglobin is	Mg(II)	Fe(II)	Mn(II)	Ca(II)	Fe(II)
The metal ion in haemoglobin assumes	square planar structure	tetrahedron structure	octahedron structure	linear structure	octahedron structure
The percentage of iron in haemoglobin is	0.347	1.23	3.47	2.31	0.347
The molecular mass of haemoglobin in around	6450	64500	645000	6450000	64500
What type of protein is haemoglobin?	simple protein	fibrous protein	conjugated protein	globular protein	conjugated protein

Metallurgy is defined as the process of	Extracting metal in pure form from its ore	creating alloys of metals	making metals live long	Extracting ore from its mineral	Extracting metal in pure form from its ore
Which of the following is not an ore	Bauxite	Malachite	Zinc blende	Pig iron	Pig iron
Minerals from which the metals can be extracted are called	Metals	minerals	Mining	ores	Ores
The process of taking out the ores from mines is known as	Mining	Metallurgy	Extraction	Purification	Mining
Chemical formula for Haematite ore is	Fe2O3	Fe2O4	FeO	FeO.Cr2O3	Fe2O3
Name of the ore which has the formula of Cu(OH)2.CuCO3	Malachite	Dolamite	Monosite	Magnesite	Malachite
Name any one noble metal among the following	Zinc	Iron	Gold	Titanium	Gold
From the following which metal occur in their native state	Tungsten	Vanadium	Gallium	Silver	Silver
Choose the occur in the form of their compounds	Silver	Cinnabar	Gold	Platinum	Cinnabar
alkali metals are strong reducing agents due to	Low ionisation energy	large ionic radii	high enthalpy of hydration	potential value	low ionisation energy
Among the alkali metals, caesium should be	Least ionisable	Lightest of all	more electropositive than fransium	having low b.p and m.p	having low b.p and m.p
Alkali metal chloride soluble in pyridine is	LiCl	CsCl	NaCl	KCl	LiCl
The process of heating the ore strongly in excess of air so that the volatile impurities are removed and the ore is changed to oxide is known as	Calcination	Froth floatoion	Roasting	Leaching	Roasting
The process of making small pieces of ores is known as	Crushing	Pulverising	concentration	ore dressing	Crushing
Finely powdered ore can be obtained by which of the following process	Crushing	Grinding	Pulverisation	ore dressing	Pulverisation
Wilfley table and Hydraulic classifier methods are collectively called as	Froth floatation	Gravity seperation	Leaching	Electromagnetic seperation	Gravity seperation

Which of the following metal is used in aliminothermic process	Fe	Zn	Al	Ni	Al
Removal of rocky impurities from the ore is known as	Concentration	Froath floatation	Magnetic seperation	Ore dressing	Concentration
The rocky materials such as sand, lime stone and clay are called under the name	Flux	Gangue	sludge	mud	Gangue
Identify the process when an ore is heated in the absence of O2	Smelting	calcination	Roasting	Carbonisation	Calcination
The reagent used to facillitate the froth floation process is called	Activator	Flux	Sludge	slurry	Activator
Argentite is the ore of	Gold	Zinc	Silver	Mercury	Silver
In the extraction of copper from its sulphide ore, the metal is formed by the reduction of Cu2O with	FeS	Co	Cu2S	SO2	Cu2S
Which metal is obtained from haematite ore	Copper	Silver	Iron	Gold	Iron
In alumino thermic process which is used a s reducing agent	Ca powder	Mg powder	Al powder	Fe powder	Al powder
Which of the following metal cannot be reduced with carbon, because it forms	W, their metal carbide	Al, their metal carbide	Mn, their metal carbide	Ti, their metal carbide	Al, their metal carbide
The metallurgical process in which a metal is obtained in a fused state is called	Roasting	Calcination	Smelting	froath floatation	Smelting
In the metallurgical process, the flux used for removing acidic impurities are	Sodium carbonate	lime stone	Sodium chloride	Silica	Silica
From the following which one is known as basic flux	CaO	SiO2	CaSiO3	CaCO3	CaCO3
Function of flux is to remove	the acidic impurities	the basic impurities	non-fusible impurities as fusible slag	rocky impurities	non-fusible impurities as fusible slag
Which of the following is known as acidic flux	CaCO3	MgCO3	SiO2	Fe2O3	SiO2
Whai tpye of product can be obtained by calcination of Bauxite is	Al2O3	Al2(OH)3	Al2O3 + 2H2O	AlO	Al2O3 + 2H2O

Smelting of CuO with carbon gives	Cu	CuO	Cu + CO	CO2	Cu + CO
Slurry is known as the mixture of	Finely powdered ore and water	metal + Amalgam	Finely powdered ore	Finely powdered ore and Hg	Finely powdered ore and water
In aluminothermic process, Aluminium acting as	Oxidising agent	a flux	a reducing agent	a gangue	a reducing agent
Identify the process when an ore is heated in the presence of excess of air	Smelting	calcination	Roasting	Carbonisation	Roasting
Zone refinfing is based on the principle that	Impurities of low boiling metals can be separated by distillation	Impurities are more soluble in molten metal than in solid metal	Different compounds of a mixture are differently adsorbed on an adsorbent	Vapours of volatile compound can be decomposed in pure metal	Impurities are more soluble in molten metal than in solid metal
Which metal ore is obtained in the name of argentite or horn silver	Hg	Ag	Au	Pt	Ag
In electrolytic refining method, the impurities are collected below the	cathode	anode	electrode	vessel	anode
In electrolytic refining method, pure metal cane be deposited on	anode	electrolyte	cathode	electrode	cathode
Anode mud (or) anode sludge is also known as	pure metal	electrolyte	metal solution	impurities	Impurities
Zone refining method is also known as	Electrolytic refining	Vapour phase method	fractional crystalisation	chromatography method	fractional crystallisation
In which method high purity metals can be obtained	Vapour phase method	Electrolytic refining	Zone refining	Solvent extraction	Zone refining
Molecular formula of Glauber's salt is:	MgSO4.7H2O	FeSO4.7H2O	CuSO4.5H2O	Na2SO4.10H2O	Na2SO4.10H2O
Which one of the following orders presents the correct sequence of the increasing basic nature of the given oxides?	K2O < Na2O < Al2O3 < MgO	Al2O3 < MgO < Na2O < K2O	MgO < K2O < Al2O3 < Na2O	MgO < K2O < Na2O < Al2O3	Al2O3 < MgO < Na2O < K2O

UNIT III

SYLLABUS

(i) Complex formation tendency of s-block elements; structure of the following complexes: crown ethers and cryptates of Group I; basic beryllium acetate, beryllium nitrate, EDTA complexes of calcium and magnesium.
(ii) Solutions of alkali metals in liquid ammonia and their properties.

COMPLEX FORMATION TENDENCY OF S-BLOCK ELEMENTS

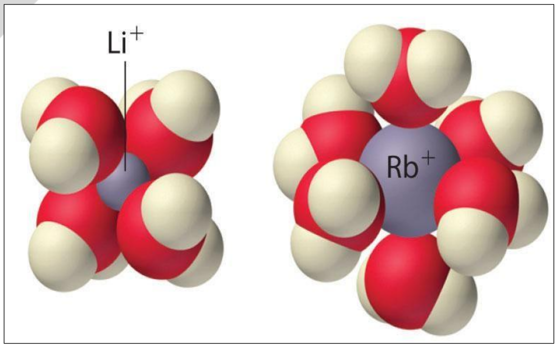
Group I metals stand out from the other groups in their weak tendency to form complexes. This is predictable because the factors favouring complex formation are small size, high charge, and empty orbitals of low energy for forming the bonds, and Group I metal ions are very large and have a low charge (+1).

A number of aqua complexes are known such as $[Li(H_20)_4\}^+$ and a primary hydration shell of four H_20 molecules arranged tetrahedrally is found in various crystalline salts. Na^+ and K^+ also have the same primary hydration shell. But Rb^+ and Cs^+ coordinate six H20 molecules. Stable complexes are formed with phosphine oxides; for example, complexes of formula $(LiX \cdot 4Ph_3PO)$, $[LiX \cdot 5Ph_3PO]$ and $[NaX \cdot 5Ph_3PO]$ are known where X is a large anion such as $Cl0_4^-$, I^-, NO_3^- or SbF_6^- (There is a slight tendency to form ammine complexes such as $[Li(NH_3)_4]L$. Weak complexes of sulphates, peroxosulphates and thiosulphates, and also hexacyanoferrates, are known in solution.

However, some organic chelating agents (particularly salicaldehyde and β-diketones) are extremely strong complexing agents, and Group I ions form complexes with these. These ligands are very strong complexing agents because they are multidentate, that is they have more than one donor group so they form more than one bond to the metal, and also because they form a ring or chelate compound by bonding to the metal.

Examples include salicaldehyde, acetylacetone, benzoylacetone, methyl salicylate, o-nitrophenol, and o-nitrocresol. The metal usually attains a coordination number of 4 or 6 (see Figure1).

An important development in the chemistry of the alkali metals is the discovery of complexes with polyethers. and 'cryptate complexes' with macrocyclic molecules with nitrogen and oxygen.



The tetrahedral $[Li(H_2O)_4]^+$and octahedral $[Rb(H_2O)_6]^+$complexes. The Li^+ ion is so small that it can accommodate only four water molecules around it, but the larger alkali metal cations tend to bind six water molecules.

Because of their higher positive charge (+2) and smaller ionic radii, the alkaline earth metals have a much greater tendency to form complexes with Lewis bases than do the alkali metals. This tendency is most important for the lightest cation (Be^{2+}) and decreases rapidly with the increasing radius of the metal ion.

The chemistry of Be^{2+} is dominated by its behavior as a Lewis acid, forming complexes with Lewis bases that produce an octet of electrons around beryllium. For example, Be^{2+} salts dissolve in water to form acidic solutions that contain the tetrahedral $[Be(H_2O)_4]^{2+}$ ion. Because of its high charge-to-radius ratio, the Be^{2+} ion polarizes coordinated water molecules, thereby increasing their acidity:

$[Be(H_2O)_4]^{2+}(aq) \rightarrow [Be(H_2O)_3(OH)]^+(aq) + H^+(aq)$

Similarly, in the presence of a strong base, beryllium and its salts form the tetrahedral hydroxo complex: $[Be(OH)_4]^{2-}$. Hence beryllium oxide is amphoteric. Beryllium also forms a very stable tetrahedral fluoride complex: $[BeF_4]^{2-}$. Recall that beryllium halides behave like Lewis acids by forming adducts with Lewis bases.

The heavier alkaline earth metals also form complexes, but usually with a coordination number of 6 or higher. Complex formation is most important for the smaller cations (Mg^{2+} and Ca^{2+}). Thus aqueous solutions of Mg^{2+} contain the octahedral $[Mg(H_2O)_6]^{2+}$ ion. Like the alkali metals, the alkaline earth metals form complexes with neutral cyclic ligands like the crown ethers.

STRUCTURE OF CROWN ETHERS

Crown ethers are cyclic chemical compounds that consist of a ring containing several ether groups. The most common crown ethers are oligomers of ethylene oxide, the repeating unit being ethyleneoxy, i.e., $–CH_2CH_2O–$. Important members of this series are the tetramer (*n* = 4), the pentamer (*n* = 5), and the hexamer (*n* = 6). The term "crown" refers to the resemblance between the structure of a crown ether bound to a cation, and a crown sitting on a person's head. The first number in a crown ether's name refers to the number of atoms in the cycle, and the second number refers to the number of those atoms that are oxygen. Crown ethers are much broader than the oligomers of ethylene oxide; an important group are derived from catechol.

The crown ethers are an interesting class of complexing agents first synthesized by Pedersen in 1967. An example is dibenzo-18-crown-6, and the name indicates that there are two benzene rings in the compound, 18 atoms make up a crown-shaped ring, and six of the ring atoms are oxygen.

These six oxygen atoms may complex with a metal ion, even with large ions like Group I ions that are not very good at forming complexes. The organic part of the molecule is puckered to give the crown arrangement, and the oxygen atoms with their lone pairs are nearly planar about the metal ion at the centre of the ring. The bonding of the metal ion to the polyether is largely electrostatic, and a close fit between the size of the metal ion and the size of the hole in the centre of the polyether is essential.

Cyclic polyethers can have varying sizes of ring; for example. benzo-12- crown-4 has a ring of 12 atoms. four of which are oxygen. The polyethers form complexes selectively with the alkali metal ions. The size of the ring opening in the crown determines the size of the metal ion which may be accommodated. Thus a Crown-4 (a cyclic polyether with four oxygens) is selective for Li+. Na+ prefers crown-5. and K + prefers crown-6. II is possible to get complexes with the unusual coordination number of 10, for example K^+ (dibeozo-30-crown-JO).

Crown ethers form a number of crystalline complexes, b4t more importantly they are sometimes added to organic solvents to make them dissolve inorganic salts which. being ionic. would not normally dissolve .. Polyethers of this type act as ion carriers.

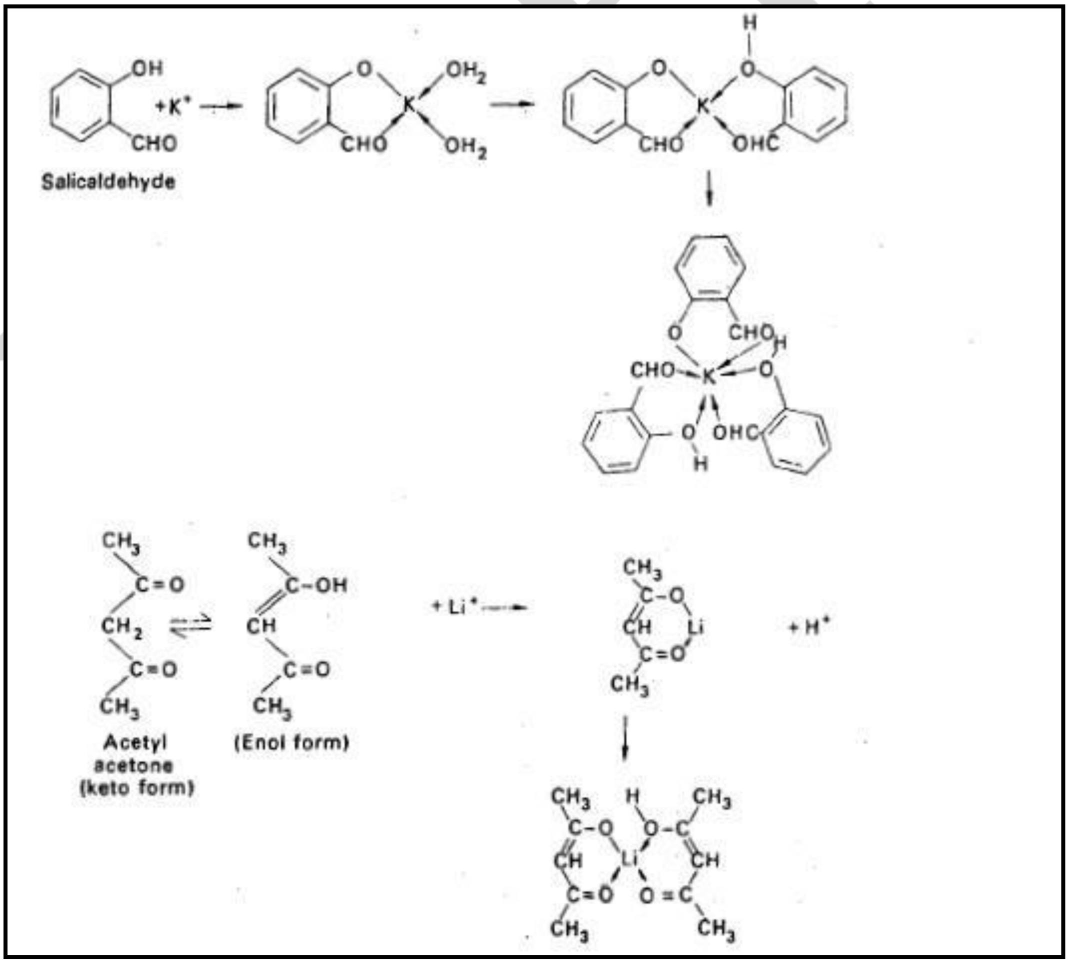


Figure 1. Salicaldehyde and acetylacetone complexes.

inside living cells to transport ions across cell membranes, and thus maintain the balance between Na+ and K+ inside and outside cells.

- The crown ethers also form some unusual complexes called electrides.
- These are black and paramagnetic, and have fortfiulae such as Cs+[(crownether)e^{-}.
- The structure consists of a Cs+ ion, and the crown ether with an electron in the ceilttal hole instead of a metal ion.
- The cryptates are even more selective and evenstronger complexing agents than are the crown ethers.
- They differ from the crown ethers by using nitrogen atoms as well as oxygen atoms to bond to the metal ion, and as they are polycyclic they cafl surround the metal ion completely.

A typical crypt is the molecule $N[CH_2CH_20CH_2CH_20CH_2CH_2]_3N$. This is called (2. 2, 2-crypt) and forms a complex [Rb(crypt)]CNS · H_20 in which six oxygen atoms and two nitrogen atoms in the crypt molecule bond to the metal ion, giving the metal ion a coordination number of 8.

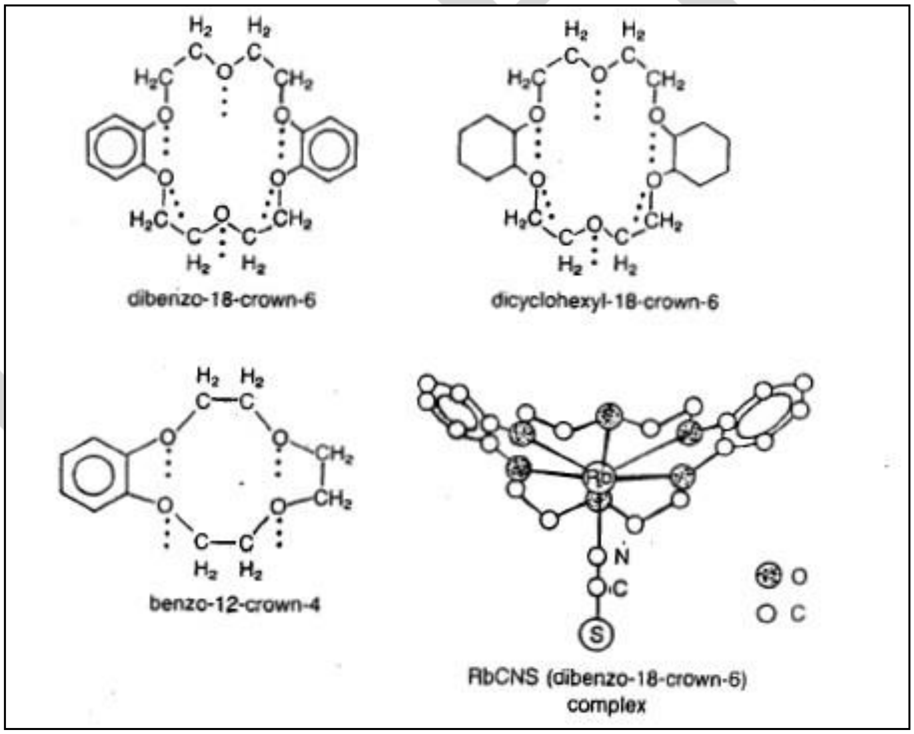


Figure 2 Structures .of some crown ethers.

The ligand completely wraps round the metal ion, hiding it: hence the name crypt. The complex presents a hydrocarbon exterior, and so is soluble in organic solvents. Such complexes are used for solvent extraction, stabilizing uncommon oxidation states, and promoting otherwise improbable reactions.

An unusual compound [Na(2; 2, 2-crypt)] $^{+}Na^{-}$ can be formed by cooling a solution of Na in ethylamine with 2, 2, 2-crypt. The compound is crystalline and is endothermic. Presumably it is only formed because of the complexing power of the crypt, and the lattice energy of the crystal. It is stable below -10 °C. The interesting feature is the formation of the Na^{-} sodide ion. The K^{-} potasside ion has been made in a similar way, but is less stable. These alkalide compounds are yellow brown in colour, and are diamagnetic.

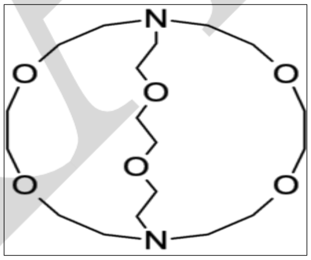
CRYPTATES OF GROUP I

Cryptands are a family of synthetic bi- and polycyclic multidentate ligands for a variety of cations. The Nobel Prize for Chemistry in 1987 was given to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen for their efforts in discovering and determining uses of cryptands and crown ethers, thus launching the now flourishing field of supramolecular chemistry.The term cryptand implies that this ligand binds substrates in a crypt, interring the guest as in a burial. These molecules are three-dimensional analogues of crown ethers but are more selective and strong as complexes for the guest ions. The resulting complexes are lipophilic.

Structure

The most common and most important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; the formal IUPAC name for this compound is 1,10-diaza-4,7,13,16,21,24 hexaoxabicyclo[8.8.8]hexacosane.

This compound is termed [2.2.2]cryptand where the numbers indicate the number of ether oxygen atoms (and hence binding sites) in each of the three bridges between the amine nitrogen "caps". Many cryptands are commercially available under the tradename "Kryptofix". All-amine cryptands exhibit particularly high affinity for alkali metal cations, which has allowed the isolation of salts of K^{-}.



Properties

The 3-dimensional interior cavity of a cryptand provides a binding site – or host – for "guest" ions.

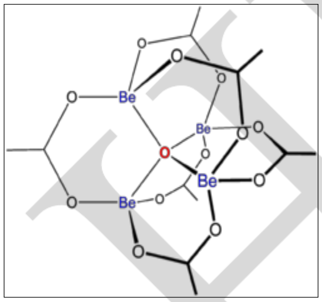
The complex between the cationic guest and the cryptand is called a cryptate. Cryptands form complexes with many "hard cations" including NH^{+}_{4}, lanthanoids, alkali metals, and alkaline earth metals. In contrast to crown ethers, cryptands bind the guest ions using both nitrogen and oxygen donors. This three-dimensional encapsulation mode confers some size-selectivity, enabling discrimination among alkali metal cations (e.g. Na^{+} vs. K^{+}).

Uses

Cryptands are more expensive and difficult to prepare, but offer much better selectivity and strength of binding than other complexants for alkali metals, such as crown ethers. They are able to bind otherwise insoluble salts into organic solvents. They can also be used as phase transfer catalysts by transferring ions from one phase to another. Cryptands enabled the synthesis of the alkalides and electrides. They have also been used in the crystallization of Zintl ions such as Sn.

BASIC BERYLLIUM ACETATE

Basic beryllium acetate is the chemical compound with the formula $Be_4O(O_2CCH_3)_6$. Although this compound has no applications and has been only lightly studied, it adopts a distinctive structure. The compound is a colourless solid that is soluble in organic solvents.



Preparation

It can be prepared by treating basic beryllium carbonate with hot acetic acid.

Basic beryllium acetate is insoluble in water but soluble in chloroform, consistent with it being nonpolar.

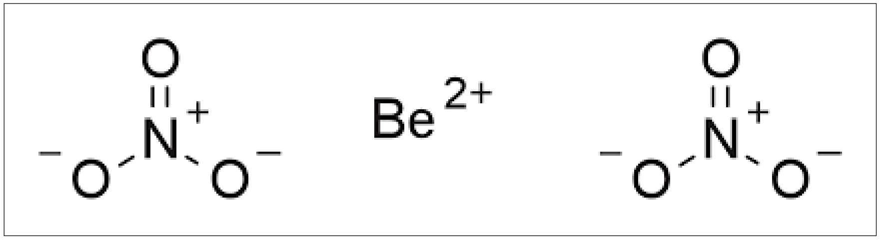
It melts and sublimes in a vacuum without decomposition.

Structure

"Basic acetates" consist of an ensemble of metal centres bound to a central oxide ion, and a collection of acetate ligands. Basic beryllium acetate has a tetrahedral Be_4O^{6+} core with acetates ($CH_3CO_2^-$) spanning each of the pairs of Be^{2+} centres.It is diamondoid, consisting of interlocking six-membered Be_2O_3C rings. The structure is relevant to its considerable stability (the compound is distillable at 330 °C).

BERYLLIUM NITRATE

Beryllium nitrate, also known as **beryllium dinitrate**, is an ionic beryllium salt of nitric acid with the chemical formula $Be(NO_3)_2$.Each formula unit is composed of one Be^{2+} cation and two NO_3^- anions.



Hazards

Beryllium nitrate is a toxic chemical, like all other beryllium compounds. It is also an irritant in small doses. When burned, it gives off irritating or toxic fumes. However, when massive short-term exposure occurs, acute pneumonitis can set in, but symptoms do not manifest themselves for 3 days.

Preparation

Beryllium nitrate can be prepared by reacting beryllium hydroxide in nitric acid.

$$Be(OH)_2 + 2\ HNO_3 \rightarrow Be(NO_3)_2 + 2\ H_2O$$

EDTA COMPLEXES OF CALCIUM AND MAGNESIUM

Many metal ions form slightly dissociated complex ions. The formation of these can serve as the basis of accurate and convenient titrations for such metal ions. Such determinations are referred to as complexometric titrations. The accuracy of these titrations is high and they offer the possibility of determinations of metal ions at concentrations at the millimole level. Many cations will form complexes in solution with a variety of substances that have a pair of unshared electrons (e.g. on N, O, S atoms in the molecule) capable of satisfying the coordination number of the metal. The metal ion acts as a Lewis acid (electron pair acceptor) and the complexing agent is a Lewis base (electron pair donor). The number of molecules of the complexing agent, called the ligand, will depend on the coordination number of the metal and on the number of complexing groups on the ligand molecule. Simple complexing agents such as ammonia are rarely used as titrating agents because a sharp end point corresponding to a stoichiometric complex is generally difficult to achieve. This is true since the stepwise formation constants are frequently close together and not very large, and a single stoichiometric complex cannot be observed. Certain ligands that have two or more complexing groups on the molecule, however, do form well-defined complexes and can be used as titrating agents. One such reagent that is widely used is ethylenediaminetetraacetic acid (EDTA).

An organic agent which has two or more groups capable of complexing with a metal ion is called a chelating agent. The complex which is formed in this manner is called a chelate. Titration with such a chelating agent is called a chelometric titration which is a particular type of complexometric titration. A pair of unshared electrons capable of complexing with a metal ion is located on each of the two nitrogen atoms and each of the four carboxyl groups. Thus there are six complexing groups in EDTA. We represent EDTA by the symbol H_4Y, which recognizes the fact that it is a tetraprotic acid. The four hydrogens in the formula refer to the four acidic hydrogens on the four carboxyl groups. It is the unprotonated ligand Y^{4-} that is responsible for the formation of complexes with metal ions.

The present analysis is concerned with the determination of Ca by the use of a complexometric titration of the type that is described above. The titration is performed by adding a standard solution of EDTA to the sample containing the Ca. The reaction that takes place is the following:

$$Ca^{2+} + Y^{4-} <===> CaY^{2-}$$

Before the equivalence point, the Ca^{2+} concentration is nearly equal to the amount of unchelated (unreacted) calcium since the dissociation of the chelate is slight. At the equivalence point and beyond, pCa is determined from the dissociation of the chelate at the given pH. The equivalence point is detected through the use of an indicator which is itself a chelating agent. The specific indicator used is Eriochrome Black T. It contains three ionizable protons and we will represent it by the formula H_3In. In neutral or somewhat basic solutions, it is a doubly dissociated ion, HIn^{2-}, which is blue in color. Eriochrome Black T cannot be used as an indicator for the titration of calcium with EDTA, since it forms too weak a complex with calcium to give a sharp end point. Therefore, a solution containing the magnesium complex of EDTA, MgY^{2-}, is introduced into the titration mixture. Since Ca^{2+} forms a more stable complex with EDTA than magnesium, the following reaction occurs:

$$MgY^{2-} + Ca^{2+} <===> CaY^{2-} + Mg^{2+}$$

The magnesium that is released in this manner then reacts with the doubly ionized ion of the Eriochrome Black T. The complex that is formed between magnesium and that ion is red, hence at the start of the Ca titration the solution is red. This reaction can be written as follows:

$$Mg^{2+} + HIn^{2-} <===> MgIn^{-} + H^{+}$$

(blue) <===> (red)

The solution is then titrated with a standard solution of EDTA. At the beginning of the titration, the EDTA reacts with the remaining calcium ion that has not been complexed. After all the calcium has reacted the next portion of EDTA reacts with the magnesium complex which was formed earlier. The added EDTA competes favorably with the red magnesium-indicator complex ($MgIn^-$), to give MgY^{2-} and HIn^{2-} and thereby giving a blue color at the end point.

$$MgIn^- + H^+ + Y^{4-} <===> MgY^{2-} + HIn^{2-}$$

(red) <===> (blue)

EXPERIMENTAL

Preparation of a 0.0100 M EDTA Solution

Dry about 2 g of EDTA dihydrate, $Na_2H_2Y_2$ $2H_2O$, in a drying oven at 80C for one hour. Then accurately weigh out about .95 g ± 0.lmg. Quantitatively transfer the EDTA into a 250 mL **volumetric flask,** add distilled water with mixing then dilute to the mark with distilled water. Mix well by inverting and shaking the tightly stoppered flask. Label this solution "Standard EDTA".

Preparation of the Mg-EDTA Complex Indicator.

Mix 0.744 g of dried EDTA with 0.492 g of $MgSO_4$ in 100 mL of distilled water. Divide the solution into two 50 mL portions. To one portion add a few drops of phenolphthalein. Dropwise, counting the drops, add sufficient 0.1 M NaOH solution to turn the solution faintly pink. ONCE THE NUMBER OF DROPS OF NaOH HAS BEEN DETERMINED, DISCARD THIS SOLUTION. To the second 50mL portion add the same number of drops of 0.1 M NaOH solution as were added to the first portion, then dilute to about 95 mL with distilled water. Add 2 mL of pH 10 buffer solution and add a few drops of Eriochrome Black T indicator solution. At this stage there are two possibilities, the solution is either red or blue. If the solution is red, Mg^{2+} is in excess. In that case add 0.0100 M EDTA solution dropwise until the solution just turns blue. If the solution is originally blue then EDTA is in excess and in that case add

0.01 M $MgSO_4$ solution dropwise until the solution just turns red, then add 0.100 M EDTA dropwise to just turn the solution blue again.

Preparation of the Powdered Milk Solution

Dry approximately 5 g of powdered milk at 80C for one hour in a drying-oven. Accurately weigh about 3 g of dry milk into a 250 mL beaker and add approximately 100 mL of distilled water. Stir to dissolve. Transfer quantitatively with repeated washings with distilled water into a 250 mL volumetric flask. Let stand for a sufficient length of time, so that all bubbles disperse. If foaming occurs it can be suppressed by the addition of 1 or 2 drops of n-octanol. Then dilute to the calibration mark with distilled water. Then mix well by stoppering the flask and then inverting and shaking it repeatedly.

Titration of Milk Solution

Pipet an exact 50 mL aliquot of the milk solution into a 250 mL Erlenmeyer flask. Add about 2 mL of pH 10 buffer, 10 mL of Mg-EDTA Indicator solution and 3 drops of Eriochrome Black T indicator. Titrate with the standard 0.0100 M EDTA solution to a color change from red to blue. Titrate at least two more milk samples using the same procedure as before.

Treatment of Data and Report

From your experimental data calculate the percentage of Ca in the powdered milk for each aliquot that you titrated. Then calculate an average percentage.

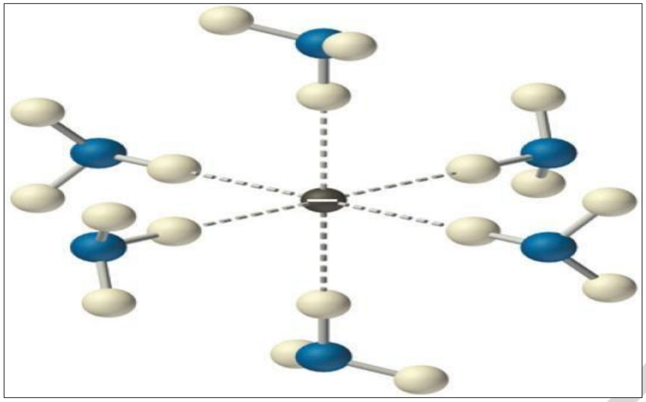
On the report sheet provided report the following data:

1. Milk unknown number
2. Weight of milk sample used.
3. Volume of EDTA solution used for each samples.
4. Percentage of Ca for each sample.
5. The average percentage of Ca.
6. The average deviation from the mean for the percent Ca in the samples
7. Pages in your lab notebook containing the pertinent data.

SOLUTION OF ALKALI METALS IN LIQUID AMMONIA AND THEIR PROPERTIES

A remarkable feature of the alkali metals is their ability to dissolve reversibly in liquid ammonia. Just as in their reactions with water, reacting alkali metals with liquid ammonia eventually produces hydrogen gas and the metal salt of the conjugate base of the solvent—in this case, the *amide* ion (NH_2^-) rather than hydroxide:

$$M(s) + NH_3(l) \rightarrow 12H_2(g) + M^+(am) + NH_2^-(am)$$



Solvated electrons. *The presence of solvated electrons (e^-, NH_3) in solutions of alkali metals in liquid ammonia is indicated by the intense color of the solution and its electrical conductivity.*

Where the (am) designation refers to an ammonia solution, analogous to (aq) used to indicate aqueous solutions. Without a catalyst, the reaction in tends to be rather slow. In many cases, the alkali metal amide salt (MNH_2) is not very soluble in liquid ammonia and precipitates, but when dissolved, very concentrated solutions of the alkali metal are produced. One mole of Cs metal, for example, will dissolve in as little as 53 mL (40 g) of liquid ammonia. The pure metal is easily recovered when the ammonia evaporates.

Solutions of alkali metals in liquid ammonia are intensely colored and good conductors of electricity due to the presence of *solvated electrons*(e^-, NH_3), which are not attached to single atoms. A solvated electron is loosely associated with a cavity in the ammonia solvent that is stabilized by hydrogen bonds. Alkali metal–liquid ammonia solutions of about 3 M or less are deep blue and conduct electricity about 10 times better than an aqueous NaCl solution because of the high mobility of the solvated electrons. As the concentration of the metal increases above 3 M, the color changes to metallic bronze or gold, and the conductivity increases to a value comparable with that of the pure liquid metals.

In addition to solvated electrons, solutions of alkali metals in liquid ammonia contain the metal cation (M^+), the neutral metal atom (M), metal dimers (M_2), and the metal anion (M^-). The anion is formed by adding an electron to the singly occupied *ns* valence orbital of the metal atom. Even in the absence of a catalyst, these solutions are not very stable and eventually decompose to the thermodynamically favored products: $M^+NH_2^-$ and hydrogen gas. Nonetheless, the solvated electron is a potent reductant that is often used in synthetic chemistry.

Focusing on ammonia solutions, all of the alkali metals, as well as Ca, Sr, Ba, Eu, and Yb (also Mg using an electrolytic process dissolve to give the characteristic blue solutions. Other amines, such as methylamine and ethylamine, are also suitable solvents.

A lithium ammonia solution at −60 °C is saturated at about 16 mol% metal (MPM). When the concentration is increased in this range electrical conductivity increases from 10^{-2} to 10^{4} $ohm^{-1}cm^{-1}$ (larger than liquid mercury). At around 8 MPM, a "transition to the metallic state" (TMS) takes place (also called a "metal to nonmetal transition" (MNMT)). At 4 MPM a liquid-liquid phase separation takes place: the less dense gold-color phase becomes immiscible from a more dense blue phase. Above 8 MPM the solution is bronze/gold-colored. In the same concentration range the overall density decreases by 30%.

Dilute solutions are paramagnetic and at around 0.5 MPM all electrons are paired up and the solution becomes diamagnetic. Several models exist to describe the spin-paired species: as an ion trimer; as an ion-triple—a cluster of two single-electron solvated-electron species in association with a cation; or as a cluster of two solvated electrons and two solvated cations.

Solvated electrons produced by dissolution of reducing metals in ammonia and amines are the anions of salts called electrides. Such salts can be isolated by the addition of macrocyclic ligands such as crown ether and cryptands. These ligands bind strongly the cations and prevent their re-reduction by the electron.

Its standard electrode potential value is -2.77 V. Equivalent conductivity 177 Mho cm^{2} is similar to that of hydroxide ion.

Reactivity and applications

The solvated electron reacts with oxygen to form a superoxide radical ($O_2^{\cdot-}$), which is a potent oxidant. With nitrous oxide, solvated electrons react to form hydroxyl radicals ($HO^{\cdot}$). The solvated electrons can be scavenged from both aqueous and organic systems with nitrobenzene or sulfur hexafluoride.

A common use of sodium dissolved in liquid ammonia is the Birch reduction. Other reactions where sodium is used as a reducing agent also are assumed to involve solvated electrons, e.g. the use of sodium in ethanol as in the Bouveault–Blanc reduction.

Diffusion

The diffusivity of the solvated electron in liquid ammonia can be determined using potential-step chronoamperometry.

History

The first recorded observation of the color of metal-electride solutions is generally attributed to Sir Humphry Davy. In 1807–1809, he examined the addition of grains of potassium to gaseous ammonia (liquefaction of ammonia was invented in 1823). James Ballantyne Hannay and J. Hogarth repeated the experiments with sodium in 1879–1880. W. Weyl in 1844 and C.A. Seely in 1871 were the first to use liquid ammonia. Hamilton Cady in 1897 was the first to relate the ionizing properties of ammonia to that of water. Charles A. Kraus measured the electrical conductance of metal ammonia solutions and in 1907 was the first to attribute it the electrons liberated from the metal.In 1918, G. E. Gibson and W. L. Argo introduced the solvated electron concept.They noted based on absorption spectra that different metals and different solvents (methylamine, ethylamine) produce the same blue color, attributed to a common species, the solvated electron. In the 1970s, solid salts containing electrons as the anion were characterized.

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.
2. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry.* 5th Ed. Oxford University Press.

POSSIBLE QUESTIONS:

Part-A (1 Mark)

Multiple Choice Questions (Each Question Carry One Mark)

1. The oxides of beryllium BeO is

(a) Acidic (b) Basic (c) **Amphoteric** (d) Neutral

2. Downs cell is used to prepare…..

(a) Sodium carbonate (b) Sodium bicarbonate
(c) **Sodium metal** (d) Sodium hydroxide

3. Al and Ga form

(a) acidic oxides (b) **amphoteric oxides** (c) basic oxides (d) carbonates

4. Bi has an exceptionally low melting point due to the Bi has an exceptionally low melting point due to

(a) **the non availability of 's' electrons**. (b) the non availability of 'f' electrons.
(c) the non availability of 'd' electrons. (d) the non availability of 'p' electrons.

5. Among the alkali metals, the metal with the highest ionization potential is:

(a) Na (b) **Li** (c) Rb (d) Cs

6. Nitrates of which pair of elements give different products on thermal decomposition?

(a) Na K (b) Mg Ca (c) **Li Na** (d) Li Ca

7. The ore CaSO4.H2O has the general name

(a) **Gypsum** (b) Dolomite (c) Calcite (d) Plaster of Paris

8. In diaphragm cell level of brine in anode compartment is kept slightly higher which prevents

(a) **Hydroxide ions to reach anode** (b) Chlorine gas to mix
(c) Cathode to decay (d) NaCl

9. The chemical formula of feldspar is:

(a) **$KAlSi_3O_8$** (b) Na_3AlF_6
(c) $NaAlO_2$ (d) $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

10. Carbonates of lithium are not stable like that of sodium due to

(a) Low electronegativity (b) **Low electropositivity**
(c) Low charge density (d) High charge density

11. The ore $CaSO_4.H_2O$ has the general name

(a) **Gypsum** (b) Dolomite (c) Calcite (d) Plaster of Paris

12. In diaphragm cell level of brine in anode compartment is kept slightly higher which prevents

(a) **Hydroxide ions to reach anode** (b) Chlorine gas to mix

(c) Cathode to decay (d) NaCl

13. Calcium carbide is prepared by heating lime with coke at

(a) 2500ºC (b) 2600ºC (c) 2700ºC (d) **2800ºC**

14. Valence shell configuration of indium

(a) **$3s^2 p^1$** (b) $3s^2 p^2$ (c) $3s^2 p^3$ (d) $2s^2 p^1$

15. Boron is a…….

(a) **Non metal**, (b) Metal (c) Metalloid (d) Semiconductor

16. Boron forms ……….

(a) **Acidic oxides** (b) Basic oxides (c) Acidic and basic oxides (d) carbonates

17. The alloy of W along with Co and Cr is known under the name of

(a) **Stellite** (b) Tungtic acid (c) Carnotite (d) Chromite

18. What is the other name of titanium dioxide

(a) Titanous oxide (b) **Titanium oxide** (c) Titanous (d) Titanic compound

19. Among the following which one is the crystalline form of titanium dioxide

(a) **Brookite** (b) Titanous (c) Titanic compound (d) Titania

20. Which of the following ligands is not capable of forming a chelate with metals?

(a) **EDTA** (b) Ethylene diamine (c) ONO- (d) Oxalate

PART- B (Each Carry 2 Marks)

1. What are crown ethers?
2. Write a note on EDTA complexes of calcium.
3. Explain the structure of beryllium acetate.
4. Write a note on structure of beryllium nitrate.
5. Write any two property of 1s element present in the solution of ammonia?
6. Give any two example of Mg-EDTA complex?
7. What is the biological importance of EDTA complexes?
8. List out any four crown ethers structures?
9. Give any two uses of beryllium acetate and beryllium nitrate
10. What is cryptates?

Part-C (Each Carry 6 Marks)

1. Explain the structure of crown ethers of group I.
2. Describe the solutions of alkali metals in liquid ammonia and their properties.
3. Explain the structure of cryptates of group I.
4. Write a note on EDTA complexes of calcium and magnesium.
5. Explain the structure of crown ether and basic beryllium acetate.
6. Explain the structure of crown ethers and beryllium nitrate.

18CHU202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2017 onwards)
Department of Chemistry
II- semester
Inorganic Chemistry- II (Metallurgy and S,P-Block Elements

UNIT III- Objective Questions for online examination (Each carry 1 Marks)

Question	Option 1	Option 2	Option 3	Option 4	Answer
The correct order of stability for the following super oxides is:	$KO_2 > RbO_2 > CsO_2$	$RbO_2 > CsO_2 > KO_2$	$CsO_2 > RbO_2 > KO_2$	$KO_2 > CsO_2 > RbO_2$	$CsO_2 > RbO_2 > KO_2$
The correct order of stability for the following super oxides is:	Na_2O	Na_2O_2	K_2O	KO_2	KO_2
The chemical formula of feldspar is:	$KAlSi_3O_8$	Na_3AlF_6	$NaAlO_2$	$K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$	$KAlSi_3O_8$
What are the products formed when Li_2CO_3 undergoes decomposition?	Li_2O_2, CO	Li_2O, CO	Li_2O,CO_2	LiO_2, CO	Li_2O,CO_2
Among the alkali metals, the metal with the highest ionization potential is:	Na	Li	Rb	Cs	Li
Alkali metals are:	Oxidising agents	dehydrating agents	reducing agents	hydrating agents	reducing agents
A elements are named as alkali metals because	Their oxides are basic	Their oxide and hydroxides are water soluble	hydroxides are water soluble	They are found in earth	Their oxide and hydroxides are water soluble
The word Alkali means	Base	Basic salt	Ashes	Spirit	Ashes
Formula of Chile saltpetre is	$NaNO_3$	$CaCO_3$	Ba $(NO_3)_2$	NH_4Cl	$NaNO_3$
The elements which are very abundant in earth crust are	Si & Al	Ca & Mg	B & Al	si	Si & Al
The oxides of beryllium BeO is	Acidic	Basic	Amphoteric	Neutral	Amphoteric
Which element is necessary for normal leaf development?	Si	Ba	Mg	Ca	Ca

Li is different from its family members due to	small size	high charge density	less electropositivity	high electropositivity	high electropositivity
Carbonates of lithium are not stable like that of sodium due to	Low electronegativity	Low electropositivity	Low charge density	High charge density	Low electropositivity
Nitrates of which pair of elements give different products on thermal decomposition?	Na K	Mg Ca	Li Na	Li Ca	Li Na
Which one of the following is not an alkali metal?	Francium	Caesium	Rubidium	Radium	Radium
Which of the following sulphates is not soluble in water?	Sodium sulphate	Potassium sulphate	Zinc sulphate	Barium sulphate	Barium sulphate
The element cesium bears resemblance with	Ca	Co	Mn	Fe	Ca
The ore $CaSO_4.H_2O$ has the general name	Gypsum	Dolomite	Calcite	Plaster of Paris	Gypsum
Downs cell is used to prepare	Sodium carbonate	Sodium bicarbonate	Sodium metal	Sodium hydroxide	Sodium metal
Which element is produced at the cathode during the electrolysis of brine in Nelsons cell?	H_2	Na	CO_2	O_2	H_2
Ammonia may be prepared by heating ammonium chloride with	Water	NaCl	Aqueous sodium hydroxide	H2SO4	Aqueous sodium hydroxide
Calcium carbide is prepared by heating lime with coke at	2500C	2600C	2700C	2800C	2800C
Crystals of $Na_2CO3. 10H_2O$ when exposed to air	Lose water and remain solid	Gain water and remain solid	Gain water and become liquid	Remains unchanged	Lose water and remain solid
Which one of the following substances conducts electricity by the movement of ions?	Graphite	Copper	Molten sodium chloride	Mercury	Molten sodium chloride
Which one of the following gives white precipitate with aqueous solution of BaC?2?	$NaHCO_3$	$NaNO_3$	Na_2CO_3	Na_2CrO_4	Na_2CO_3
Which one of the following carbonate is water insoluble?	Na_2CO_3	K_2CO_3	$(NH_4)_2CO_3$	$CaCO_3$	$CaCO_3$
The deliquescence is a property in which a solid	Absorbs moisture and remains solid	Absorbs moisture and turns to liquid form	Loses water of crystallization	Increases the number of water of crystallization	Absorbs moisture and turns to liquid form

In diaphragm cell hydrogen is discharged by the reduction of	Water	HCI	Na+	NaCl	Water
In diaphragm cell level of brine in anode compartment is kept slightly higher which prevents	Hydroxide ions to reach anode	Chlorine gas to mix	Cathode to decay	NaCl	Hydroxide ions to reach anode
Gypsum is applied to the soil as a source of	Ca and P	S and P	Ca and S	P and O	Ca and S
Alkali and alkaline earth metals impart colours when heated over burner. It is due to	Smaller electronegativity of alkali metals	Smaller ionic radius of these metals	De-excitation of electrons from higher energy levels to low energy level	Excitation of electrons from low energy levels to higher energy levels	De-excitation of electrons from higher energy levels to low energy level
Which one of the following alkali metals forms only normal oxide when it reacts with O_2?	Lithium	Sodium	Potassium	Rubidium	Lithium
First ionization potential of alkaline earth metal is greater than alkali metals because	They are more reactive	They have greater atomic radii	They have smaller atomic sizes	They are less reactive	They have smaller atomic sizes
Which one of the following pairs shown diagonal relationship in the periodic table?	Sodium and Lithium		Lithium and magnesium	Lithium and beryllium	Lithium and magnesium
NaOH is named as caustic soda because	It corrodes the organic tissues	It is used in soda water	It reacts with chlorine gas	It reacts with fats to form soap	It corrodes the organic tissues
Sodium is not observed in +2 oxidation state because of its	high first ionization potential	high second ioniation potential	high ionic radius	high electronegativity	high second ioniation potential
Carnalite has chemical formula	KCI	$KCI.MgCl_2.6H_2O$	$Na_2B_4O_7.10H_2O$	$CaCO_3.MgCO_3$	$KCI.MgCl_2.6H_2O$
Magnesium metal does not burn in the vessel containing	N2	O2	N2 and O2	Ne	Ne
Electrolysis of dilute solution of NaCl results at the anode	sodium	hydrogen	chlorine	oxygen	oxygen
Second ionization potential of alkali metals are very high due to	being s-block elements	inert gas configurations	ns1 electronic configuration	being metals	inert gas configurations
Which ion will have maximum value of heat of hydration?	$A1^{+3}$	Cs^+	Ba^+	Mg^{+2}	$A1^{+3}$
Which one can form complex?	Na	Cr	Li	K	Li
Which one is natron?	Na_2CO_3	$Na_2CO_3.10H_2O$	$Na_2CO_3.H_2O$	$NaHCO_3$	$Na_2CO_3.H_2O$

Addition of 2% gypsum in cement	Triggers hydration	Triggers hydrolysis	Prevents rapid hardening	hydrolysis	Prevents rapid hardening
Which one is least ionic in nature and decompose on heating.	LiOH	NaOH	KOH	CsOH	LiOH
The temporary hardness of water is due to calcium bicarbonate can be removed by adding	$CaCO_3$	Ca(OH)	CaCl	HCl	Ca(OH)
Calcium is obtained by	Electrolysis of molten $CaCl_2$	Electrolysis of solution of $CaCl_2$ in water	Reduction of $CaCl_2$ with carbon	Roasting of limestone	Electrolysis of molten $CaCl_2$
A solution of sodium metal in liquid ammonia is strongly reducing due to the presence of	Sodium atoms	Sodium hydride	Sodium aminde	Solvated electrons	Solvated electrons
Heavy water is	H_2O	Water obtained by repeated distillation	D_2O	Water at 4°C	D_2O
Molecular formula of Glauber's salt is	$MgSO_4. 7H_2O$	$CuSO_4.5H_2O$	$FeSO_4.7H_2O$	$NaSO_4.10H_2O$	$NaSO_4.10H_2O$
The oxide that gives H_2O on treatment with a dilute acid is	PbO_2	Na_2O_2	MnO_2	TiO_2	Na2O2
Nitrogen dioxide cannot be obtained by heating	KNO_3	$Pb(NO_3)$	$Cu(NO_3)$	$AgNO_3$	$Pb(NO_3)$
A solution of sodium sulphate in water is electrolysided using inert electrodes. The products at cathode and anode are respectively	H_2, O_2	O_2, H_2	O_2, Na	O_2, SO_2	O_2, H_2
The metallic luster exhibited by sodium metal is explained by	Diffusion of sodium ions	Oscillation of loose electron	Excitation of free protons	Existence of body centred cubit lattice	Excitation of free protons
The oxidation state of the most electronegative element is the products of the reaction, $BaO_2$with dil. H_2SO_4 are	0 and –1	–1 and –2	–2 and 0	–2 and –1	–1 and –2
Hydrolysis of one mole of peroxodisulphuric acid produces	Two moles of sulphuric acid	Two moles of peroxomono sulpuric acid	One mole of sulphuric acid and one mole of peroxomono sulphuric acid	One mole of sulphuric acid, one mole of peroxomono sulphuric acid and one mole of hydrogen peroxide	One mole of sulphuric acid and one mole of peroxomono sulphuric acid

A dilute aqueous solution of Na2SO4 is electrolysed using platinum electrodes. The products at the anode and cathode are respectively	O_2, H_2	SO_3, Na	O_2, Na	S_2O_8, H_2	O_2, H_2
A sodium salt of an unknown anion when treated with $MgCl_2$ gives white precipitate only on boiling. The anion is	SO_4	HCO_3	CO_3	NO_3	HCO_3
Atomic size of all elements in the 'P' block	increases as we move from IIIA to VIIA.	decreases as we move from IIIA to VIIA.	no change as we move from IIIA to VIIA.	increases and then decreases as we move from IIIA to VIIA.	decreases as we move from IIIA to VIIA.

UNIT IV

SYLLABUS

Chemistry of *p* Block Elements:
Electronic configuration, atomic and ionic size, metallic/non-metallic character, melting point, ionization enthalpy, electron gain enthalpy, electronegativity, Allotropy of C, P, S; inert pair effect, diagonal relationship between B and Si and anomalous behaviour of first member of each group.
Structure, bonding and properties: acidic/basic nature, stability, ionic/covalent nature, oxidation/reduction, hydrolysis, action of heat of the following:

Hydrides : hydrides of Group 13 (only diborane), Group 14, Group 15 (EH_3 where E = N, P, As, Sb, Bi), Group 16 and Group 17.
Oxides : oxides of phosphorus, sulphur and chlorine
Oxoacids : oxoacids of phosphorus and chlorine; peroxy acids of sulphur Halides: halides of silicon and phosphorus

CHEMISTRY OF P BLOCK ELEMENTS

What Are P-Block Elements?

The **p-block** is on the right side of the periodic table and includes elements from the six columns beginning with column 3A and ending with column 8A (or columns 13-18 on some versions of the periodic table). Helium, which is in the top of column 8A, is not included in the p-block. In the periodic table shown here, the p-block is colored orange.

P-block elements are unified by the fact that their valence electrons (outermost electrons) are in the p orbital. The p orbital consists of six lobed shapes coming off a central point at evenly spaced angles. The p orbital can hold a maximum of six electrons, hence why there are six columns in the p-block. Elements in column 3A, the first column of the p-block, have one valence electron. Elements in column 4A, the second column of the p-block, have two valence electrons. The trend continues this way until we reach column 8A, which has six valence electrons.

There are 35 elements that live in the p-block, which can be seen here.

The p-block is home to the biggest variety of elements and is the only block that contains all three types of elements: metals, nonmetals, and metalloids. Generally, the p-block elements are best described in terms of element type or column number.

Properties of P-Block Metals

P-block metals have classic metal characteristics: they are shiny, they are good conductors of heat and electricity, and they lose electrons easily. Generally, these metals have high melting points and readily react with nonmetals to form ionic compounds. **Ionic compounds** form when a positive metal ion bonds with a negative nonmetal ion.

Of the p-block metals, several have fascinating properties. Gallium, in the 3rd row of column 3A, is a metal that can melt in the palm of your hand. Tin, in the fourth row of column 4A, is an abundant, flexible, and extremely useful metal. It is an important component of many metal alloys like bronze, solder, and pewter.

Sitting right beneath tin is lead, a toxic metal with an intriguing history. Ancient peoples used lead for a variety of things, from food sweeteners to pottery glazes to eating utensils. Unbeknownst to these ancient civilizations, lead is quite toxic. Many historians suspect that lead poisoning is related to the fall of Roman civilization. For a long time, lead was used in the manufacturing of paints. It was only within the last century that lead paint use has been restricted due to its toxic nature.

PROPERTIES OF P-BLOCK METALLOIDS

Metalloids have properties of both metals and nonmetals, but the term 'metalloid' lacks a strict definition. All of the elements that are commonly recognized as metalloids are in the p-block: boron, silicon, germanium, arsenic, antinomy, and tellurium.

Silicon is perhaps the most famous metalloid. It is the second most abundant element in Earth's crust and one of the main ingredients in glass. It is used to make microchips for computers and other electronic devices. So valuable is silicon to the technology industry that Silicon Valley in California is named after it.

Germanium has properties very similar to silicon, yet this element is much more rare. Arsenic is a toxic metalloid that has been used throughout history as an additive to metal alloys, paints, and even makeup.

Properties of P-Block Nonmetals

Most of the p-block elements are nonmetals. These elements generally have low boiling points, are poor conductors, and do not lose electrons easily. Some nonmetals are solids at room temperature, while others are gases. One nonmetal in the p-block, bromine, is a liquid at room temperature.

Carbon, phosphorus, sulfur, selenium, and iodine regularly occur as solids. Pure carbon commonly occurs as graphite or diamond, but it can bond with other elements to form a variety of compounds. Carbon is considered to be the most important element to life because most compounds essential to living things contain carbon. Phosphorus, sulfur, selenium, and iodine make brittle solids of various colors.

Nitrogen and oxygen often occur as gases, and both elements are important to living organisms. Nitrogen is the most abundant element in our atmosphere; approximately 78% of it is made of nitrogen. In its gaseous form, oxygen makes up 20% of our atmosphere.

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 VA 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 p-block 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 :- O_2 , which makes up 21 percent of the earth's atmosphere, or O_3 (ozone), which slowly decomposes to O_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.
b) 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.

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.

DIAGONAL RELATIONSHIP BETWEEN BORON AND SILICON

Due to its small size and similar charge/mass ratio, boron differs from other group 13 members, but it resembles closely with silicon, the second element of group 14 to exhibit diagonal relationship. Some important similarities between boron and silicon are given below,

(1) Both boron and silicon are typical non-metals, having high m.pt. b.pt nearly same densities (B=2.35gml^{-1} S=2.34 g//ml). low atomic volumes and bad conductor of current. However both are used as semiconductors.

(2) Both of them do not form cation and form only covalent compounds.

(3) Both exists in amorphous and crystalline state and exhibit allotropy.

(4) Both possess closer electronegativity values (B=2.0; Si=1.8).

(5) Both form numerous volatile hydrides which spontaneously catch fire on exposure to air and are easily hydrolysed.

(6) The chlorides of both are liquid, fume in most air and readily hydrolysed by water.

$BCl_3 + 3H_2O \rightarrow B(OH)_3 + 3HCl$
$SiCl_4 + H_2O \rightarrow Si(OH)_4 + 4HCl$

(7) Both form weak acids like H_3BO_3 and H_2SiO_3.

(8) Both form binary compounds with several metals to give borides and silicide. These borides and silicide react with H_3PO_4 to give mixture of boranes and silanes.

$3Mg+2B \rightarrow Mg_3B_2$; $Mg_3B_2 + H_3PO_4 \rightarrow$ Mixture of boranes

(Magnesium boride)

$2Mg + Si \rightarrow Mg_2Si$; $Mg_2Si + H_3PO_4 \rightarrow$ Mixture of silanes

(magnesium silicide)

(9) The carbides of both Boron and silicon (B_4C and SiC) are very hard and used as abrasive.

(10) Oxides of both are acidic and can be reduced by limited amount of Mg In excess of Mg boride and silicide are formed.

$B_2O_3 + 3Mg \rightarrow 3MgO + 2B$; $SiO_2 + 2Mg \rightarrow 2MgO + Si$

(11) Both the metals and their oxides are readily soluble in alkalies.

$2B + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2$

(borate)

$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2$

(silicate)

$B_2O_3 + 6NaOH \rightarrow 2Na_3BO_3 + 3H_2O$

$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$

Both borates and silicates have tetrahedral structural units and respectively. Boro silicates are known in which boron replaces silicon in the three dimensional lattice. Boron can however form planar BO_3 units.

(12) Acids of both these elements form volatile esters on heating with alcohol in presence of conc. H_2SO_4.

$B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O$

$Si(OH)_4 + 4ROH \rightarrow Si(OR)_4 + 4H_2O$

HYDRIDES OF GROUP 13

Group 13 hydride

Group 13 hydrides are chemical compounds containing both hydrogen atoms and boron family atoms (elements of group 13: boron, aluminium, gallium, indium, thallium).

Trihydrides

The simplest series has the chemical formula XH_3, with X representing any of the boron family.

Compound	Chemical formula	
boron trihydride (borane)	BH_3	
aluminium trihydride (alane)	AlH_3	
gallium trihydride (gallane)	GaH_3	
indium trihydride (indigane)	InH_3	
thallium trihydride (thallane)	TlH_3	

The great variety of boranes show a huge covalent cluster chemistry, but the heavier group 13 hydrides do not. Despite their formulae, however, they tend to form polymers. Alane is a strong reducing agent with octahedrally coordinated aluminium atoms. Gallane is even harder to synthesise and decomposes to gallium and hydrogen at room temperature. Indigane and thallane are too unstable to exist for any significant time when not coordinated.

They have a trigonal planar molecular geometry, contrasting with the trigonal pyramidal geometry of the pnictogen hydrides.

Tetrahydrides

The tetrahydride series has the chemical formula XH_4, with X representing any of the carbon family. Methane is commonly the result of the decomposition of organic matter, and is a greenhouse gas. The other hydrides are generally unstable, poisonous metal hydrides.

They take on a pyramidal structure, and as such are not polar molecules like the other p-block hydrides.

Unlike other light hydrides such as ammonia, water and hydrogen fluoride, methane does not exhibit any anomalous effects attributed to hydrogen bonding and so its properties conform well to the prevailing trend of heavier group 14 hydrides.

Compound	Chemical formula
carbon tetrahydride hydrogen carbide methane (carbane)	CH_4
silicon tetrahydride hydrogen silicide (silane)	SiH_4
germanium tetrahydride hydrogen germanide (germane)	GeH_4
tin tetrahydride hydrogen stannide (stannane)	SnH_4
lead tetrahydride hydrogen plumbide (plumbane)	PbH_4

Hexahydrides

This series has the chemical formula X_2H_6. Ethane is commonly found alongside methane in natural gas. The other hydrides are even less stable than the tetrahydrides.

Compound	**Chemical formula**
dicarbon hexahydride ethane (dicarbane)	C_2H_6
disilicon hexahydride (disilane)	Si_2H_6
digermanium hexahydride (digermane)	Ge_2H_6
ditin hexahydride (distannane)	Sn_2H_6

Higher group 14 hydrides

All straight-chain saturated group 14 hydrides follow the formula X_nH_{2n+2}, the same formula for the alkanes.

Cubane, a Platonic hydrocarbon and prismane

Many other group 14 hydrides are known. Carbon forms a huge variety of hydrocarbons (with propane and butane following methane and ethane among the alkanes, but also including alkenes, alkynes, cyclic and branched compounds, as well as aromatic hydrocarbons such as benzene, toluene and limonene), whose study forms the core of organic chemistry.

Alongside hydrogen, carbon can form compounds with the chemically similar halogens, forming haloalkanes. The simplest of this series, the halomethanes, contain compounds such as dichloromethane and iodoform. Other such important chemicals include vinyl chloride, which is used in the production of PVC.

The other group 14 elements have a lower tendency to catenate. Silanes Si_nH_{2n+2} are known for n = 1–8 (thermal stability decreasing as n increases), as are cyclosilanes Si_5H_{10} and Si_6H_{12}. They are very reactive, pyrophoric colourless gases or volatile liquids that spontaneously catch fire or explode in air. Their volatility is intermediate between the alkanes and the germanes.Unsaturated silanes, the silenes and silynes, have been characterized spectroscopically. The first members of each respectively are disilene and disilyne, the silicon analogues of ethylene and acetylene). The first five germanes Ge_nH_{2n+2} are known, and they are fairly similar to the silanes.Stannane, a strong reducing agent slowly decomposes at room temperature to tin and hydrogen gas, and is decomposed by concentrated aqueous acids or alkalis; distannane, Sn_2H_6 is still more unstable and longer stannanes are unknown. Plumbane is very poorly characterised and is only known in trace amounts: even at low temperatures, synthesis methods that yield the other MH_4 compounds fail to give PbH_4. No other plumbanes are known.

Compounds containing hydrogen and multiple group 14 elements are known, one of the most famous of these being tetraethyllead.

Category:Group 16 hydrides

The Group 16 hydrides are:

- **O**: water, H_2O; hydrogen peroxide, H_2O_2; trioxidane H_2O_3
- **S**: hydrogen sulfide, H_2S; hydrogen disulfide, H_2S_2
- **Se**: hydrogen selenide, H_2Se
- **Te**: hydrogen telluride, H_2Te
- **Po**: hydrogen polonide, H_2Po

Subcategories

This category has the following 9 subcategories, out of 9 total.

H

- ► Hydrogen diselenide (2 F)
- ► Hydrogen disulfide (5 F)
- ► Hydrogen peroxide (3 C, 75 F)
- ► Hydrogen polonide (5 F)
- ► Hydrogen selenide (7 F)
- ► Hydrogen sulfide (21 F)
- ► Hydrogen telluride (7 F)

T

- ► Trioxidane (9 F)

W

- ► Water (54 C, 1 P, 966 F)

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OXIDES

Phosphorus pentoxide crystallizes in at least four forms or polymorphs. The most familiar one, a metastable form, shown in the figure, comprises molecules of P_4O_{10}. Weak van der Waals forces hold these molecules together in a hexagonal lattice (However, in spite of the high symmetry of the molecules, the crystal packing is not a close packing). The structure of the P_4O_{10} cage is reminiscent of adamantane with T_d symmetry point group.It is closely related to the corresponding anhydride of phosphorous acid, P_4O_6. The latter lacks terminal oxo groups. Its density is 2.30 g/cm^3. It boils at 423 °C under atmospheric pressure; if heated more rapidly it can sublimate. This form can be made by condensing the vapor of phosphorus pentoxide rapidly, the result is an extremely hygroscopic solid.

The other polymorphs are polymeric, but in each case the phosphorus atoms are bound by a tetrahedron of oxygen atoms, one of which forms a terminal P=O bond involving the donation of the terminal oxygen p-orbital electrons to the antibonding phosphorus-oxygen single bonds. The macromolecular form can be made by heating the compound in a sealed tube for several hours, and maintaining the melt at a high temperature before cooling the melt to the solid. The metastable orthorhombic, "O"-form (density 2.72 g/cm^3, melting point 562 °C), adopts a layered structure consisting of interconnected P_6O_6 rings, not unlike the structure adopted by certain polysilicates. The stable form is a higher density phase, also orthorhombic, the so-called O' form. It consists of a 3-dimensional framework, density 3.5 g/cm^3. The remaining polymorph is a glass or amorphous form; it can be made by fusing any of the other

Preparation

P_4O_{10} is prepared by burning elemental phosphorus with sufficient supply of air:

$$P_4 + 5\ O_2 \rightarrow P_4O_{10}$$

For most of the 20th century, phosphorus pentoxide was used to provide a supply of concentrated pure phosphoric acid. In the thermal process, the phosphorus pentoxide obtained by burning white phosphorus was dissolved in dilute phosphoric acid to produce concentrated acid. Improvements in filter technology is leading to the "wet phosphoric acid process" taking over from the thermal process, obviating the need to produce white phosphorus as a starting material. The dehydration of phosphoric acid to give phosphorus pentoxide is not possible as on heating metaphosphoric acid will boil without losing all its water.

Applications

Phosphorus pentoxide is a potent dehydrating agent as indicated by the exothermic nature of its hydrolysis:

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4\ (-177\ kJ)$$

However, its utility for drying is limited somewhat by its tendency to form a protective viscous coating that inhibits further dehydration by unspent material. A granular form of P_4O_{10} is used in desiccators. Consistent with its strong desiccating power, P_4O_{10} is used in organic synthesis for dehydration. The most important application is for the conversion of primary amides into nitriles:

$$P_4O_{10} + RC(O)NH_2 \rightarrow P_4O_9(OH)_2 + RCN$$

The indicated coproduct $P_4O_9(OH)_2$ is an idealized formula for undefined products resulting from the hydration of P_4O_{10}.

Alternatively, when combined with a carboxylic acid, the result is the corresponding anhydride[9]

$$P_4O_{10} + RCO_2H \rightarrow P_4O_9(OH)_2 + [RC(O)]_2O$$

The "Onodera reagent", a solution of P_4O_{10} in DMSO, is employed for the oxidation of alcohols.[10] This reaction is reminiscent of the Swern oxidation.

The desiccating power of P_4O_{10} is strong enough to convert many mineral acids to their anhydrides. Examples: HNO_3 is converted to N_2O_5; H_2SO_4 is converted to SO_3; $HClO_4$ is converted to Cl_2O_7; HCF_3SO_3 is converted to $(CF_3)_2S_2O_5$.

Related phosphorus oxides

Between the commercially important P_4O_6 and P_4O_{10}, phosphorus oxides are known with intermediate structures

Hazards

Phosphorus pentoxide is not flammable. It reacts vigorously with water and water-containing substances like wood or cotton, liberates much heat and may even cause fire. It is corrosive to metal and is very irritating – it may cause severe burns to the eye, skin, mucous membrane, and respiratory tract even at concentrations as low as 1 mg/m^3

oxides of sulphur

SO_2 is a bent molecule with C_{2v} symmetry point group. A valence bond theory approach considering just *s* and *p* orbitals would describe the bonding in terms of resonance between two resonance structures.

Two resonance structures of sulfur dioxide

The sulfur–oxygen bond has a bond order of 1.5. There is support for this simple approach that does not invoke *d* orbital participation. In terms of electron-counting formalism, the sulfur atom has an oxidation state of +4 and a formal charge of +1.

Occurrence

It is found on Earth and exists in very small concentrations and in the atmosphere at about 1 ppm

On other planets, it can be found in various concentrations, the most significant being the atmosphere of Venus, where it is the third-most significant atmospheric gas at 150 ppm. There, it condenses to form clouds, and is a key component of chemical reactions in the planet's atmosphere and contributes to global warmin It has been implicated as a key agent in the warming of early Mars, with estimates of concentrations in the lower atmosphere as high as 100 ppm, though it only exists in trace amounts. On both Venus and Mars, its primary source, like on Earth, is thought to be volcanic. The atmosphere of Io is 90% sulfur dioxide and trace amounts are thought to also exist in the atmosphere of Jupiter.

The blue auroral glows of Io's upper atmosphere are caused by volcanic sulfur dioxide.

As an ice, it is thought to exist in abundance on the Galilean moons—as sublimating ice or frost on the trailing hemisphere of Io, a natural satellite of Jupiter[12] and in the crust and mantle of Europa, Ganymede, and Callisto, possibly also in liquid form and readily reacting with water.

Production

Sulfur dioxide is primarily produced for sulfuric acid manufacture (see contact process). In the United States in 1979, 23.6 million tonnes of sulfur dioxide were used in this way, compared with 150 thousand tonnes used for other purposes. Most sulfur dioxide is produced by the combustion of elemental sulfur. Some sulfur dioxide is also produced by roasting pyrite and other sulfide ores in air.

Combustion routes

Sulfur dioxide is the product of the burning of sulfur or of burning materials that contain sulfur:

$$S + O_2 \rightarrow SO_2, \Delta H = -297 \text{ kJ/mol}$$

To aid combustion, liquefied sulfur (140–150 °C) is sprayed through an atomizing nozzle to generate fine drops of sulfur with a large surface area. The reaction is exothermic, and the combustion produces temperatures of 1000–1600 °C. The significant amount of heat produced is recovered by steam generation that can subsequently be converted to electricity.

The combustion of hydrogen sulfide and organosulfur compounds proceeds similarly. For example:

$$2\ H_2S + 3\ O_2 \rightarrow 2\ H_2O + 2\ SO_2$$

The roasting of sulfide ores such as pyrite, sphalerite, and cinnabar (mercury sulfide) also releases SO_2:

$$4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$$
$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$$
$$HgS + O_2 \rightarrow Hg + SO_2$$
$$4\ FeS + 7O_2 \rightarrow 2\ Fe_2O_3 + 4\ SO_2$$

A combination of these reactions is responsible for the largest source of sulfur dioxide, volcanic eruptions. These events can release millions of tonnes of SO_2.

Reduction of higher oxides

Sulfur dioxide can also be a byproduct in the manufacture of calcium silicate cement; $CaSO_4$ is heated with coke and sand in this process:

$$2\ CaSO_4 + 2\ SiO_2 + C \rightarrow 2\ CaSiO_3 + 2\ SO_2 + CO_2$$

Until the 1970s, commercial quantities of sulfuric acid and cement were produced by this process in Whitehaven, England. Upon being mixed with shale or marl, and roasted, the sulfate liberated sulfur dioxide gas, used in sulfuric acid production, the reaction also produced calcium silicate, a precursor in cement production.

On a laboratory scale, the action of hot concentrated sulfuric acid on copper turnings produces sulfur dioxide.

$Cu + 2 H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2 H_2O$

From sulfite

Sulfite results from the reaction of aqueous base and sulfur dioxide. The reverse reaction involves acidification of sodium metabisulfite:

$H_2SO_4 + Na_2S_2O_5 \rightarrow 2 SO_2 + Na_2SO_4 + H_2O$

Reactions

Industrial reactions

Treatment of basic solutions with sulfur dioxide affords sulfite salts:

$SO_2 + 2 NaOH \rightarrow Na_2SO_3 + H_2O$

Featuring sulfur in the +4 oxidation state, sulfur dioxide is a reducing agent. It is oxidized by halogens to give the sulfuryl halides, such as sulfuryl chloride:

$SO_2 + Cl_2 \rightarrow SO_2Cl_2$

Sulfur dioxide is the oxidising agent in the Claus process, which is conducted on a large scale in oil refineries. Here, sulfur dioxide is reduced by hydrogen sulfide to give elemental sulfur:

$SO_2 + 2 H_2S \rightarrow 3 S + 2 H_2O$

The sequential oxidation of sulfur dioxide followed by its hydration is used in the production of sulfuric acid.

$2 SO_2 + 2 H_2O + O_2 \rightarrow 2 H_2SO_4$

Laboratory reactions

Sulfur dioxide is one of the few common acidic yet reducing gases. It turns moist litmus pink (being acidic), then white (due to its bleaching effect). It may be identified by bubbling it through a dichromate solution, turning the solution from orange to green (Cr^{3+} (aq)). It can also reduce ferric ions to ferrous[*citation needed*]

Sulfur dioxide can react with certain 1,3-dienes in a cheletropic reaction to form cyclic sulfones. This reaction is exploited on an industrial scale for the synthesis of sulfolane, which is an important solvent in the petrochemical industry.

Sulfur dioxide can bind to metal ions as a ligand to form metal sulfur dioxide complexes, typically where the transition metal is in oxidation state 0 or +1. Many different bonding modes (geometries) are recognized, but in most cases, the ligand is monodentate, attached to the metal through sulfur, which can be either planar and pyramidal η^1.

Uses

Precursor to sulfuric acid

Sulfur dioxide is an intermediate in the production of sulfuric acid, being converted to sulfur trioxide, and then to oleum, which is made into sulfuric acid. Sulfur dioxide for this purpose is made when sulfur combines with oxygen. The method of converting sulfur dioxide to sulfuric acid is called the contact process. Several billion kilograms are produced annually for this purpose.

As a preservative

Sulfur dioxide is sometimes used as a preservative for dried apricots, dried figs, and other dried fruits, owing to its antimicrobial properties, and is called E220[18] when used in this way in Europe. As a preservative, it maintains the colorful appearance of the fruit and prevents rotting. It is also added to sulfured molasses.

In winemaking

Sulfur dioxide was used by the Romans in winemaking, when they discovered that burning sulfur candles inside empty wine vessels keeps them fresh and free from vinegar smell.

Sulfur dioxide is still an important compound in winemaking, and is measured in parts per million in wine. It is present even in so-called unsulfurated wine at concentrations of up to 10 mg/L. It serves as an antibiotic and antioxidant, protecting wine from spoilage by bacteria and oxidation. Its antimicrobial action also helps to minimize volatile acidity. Sulfur dioxide is responsible for the words "contains sulfites" found on wine labels.

Sulfur dioxide exists in wine in free and bound forms, and the combinations are referred to as total SO_2. Binding, for instance to the carbonyl group of acetaldehyde, varies with the wine in question. The free form exists in equilibrium between molecular SO_2 (as a dissolved gas) and bisulfite ion, which is in turn in equilibrium with sulfite ion. These equilibria depend on the pH of the wine. Lower pH shifts the equilibrium towards molecular (gaseous) SO_2, which is the active form, while at higher pH more SO_2 is found in the inactive sulfite and bisulfite forms. The molecular SO_2 is active as an antimicrobial and antioxidant, and this is also the form which may be perceived as a pungent odor at high levels. Wines with total SO_2 concentrations below 10 ppm do not require "contains sulfites" on the label by US and EU laws. The upper limit of total SO_2 allowed in wine in the US is 350 ppm; in the EU it is 160 ppm for red wines and 210 ppm for white and rosé wines. In low concentrations, SO_2 is mostly undetectable in wine, but at free SO_2 concentrations over 50 ppm, SO_2 becomes evident in the smell and taste of wine.

SO_2 is also a very important compound in winery sanitation. Wineries and equipment must be kept clean, and because bleach cannot be used in a winery due the risk of cork taint, a mixture of SO_2, water, and citric acid is commonly used to clean and sanitize equipment. Compounds of ozone (O_3) are now used extensively as cleaning products in wineries due to their efficiency, and because these compounds do not affect the wine or equipment.

As a reducing agent

Sulfur dioxide is also a good reductant. In the presence of water, sulfur dioxide is able to decolorize substances. Specifically, it is a useful reducing bleach for papers and delicate materials such as clothes. This bleaching effect normally does not last very long. Oxygen in the atmosphere reoxidizes the reduced dyes, restoring the color. In municipal wastewater treatment, sulfur dioxide is used to treat chlorinated wastewater prior to release. Sulfur dioxide reduces free and combined chlorine to chloride.

Sulfur dioxide is fairly soluble in water, and by both IR and Raman spectroscopy; the hypothetical sulfurous acid, H_2SO_3, is not present to any extent. However, such solutions do show spectra of the hydrogen sulfite ion, HSO_3^-, by reaction with water, and it is in fact the actual reducing agent present:

$$SO_2 + H_2O \rightarrow HSO_3^- + H^+$$

Biochemical and biomedical roles

Sulfur dioxide is toxic in large amounts. It or its conjugate base bisulfite is produced biologically as an intermediate in both sulfate-reducing organisms and in sulfur-oxidizing bacteria, as well. The role of sulfur dioxide in mammalian biology is not yet well understood. Sulfur dioxide blocks nerve signals from the pulmonary stretch receptors and abolishes the Hering–Breuer inflation reflex.

It was shown that endogenous sulfur dioxide plays a role in diminishing an experimental lung damage caused by oleic acid. Endogenous sulfur dioxide lowered lipid peroxidation, free radical formation, oxidative stress and inflammation during an experimental lung damage. Conversely, a successful lung damage caused a significant lowering of endogenous sulfur dioxide production, and an increase in lipid peroxidation, free radical formation, oxidative stress and inflammation. Moreover, blockade of an enzyme that produces endogenous SO_2 significantly increased the amount of lung tissue damage in the experiment. Conversely, adding acetylcysteine or glutathione to the rat diet increased the amount of endogenous SO_2 produced and decreased the lung damage, the free radical formation, oxidative stress, inflammation and apoptosis.

It is considered that endogenous sulfur dioxide plays a significant physiological role in regulating cardiac and blood vessel function, and aberrant or deficient sulfur dioxide metabolism can contribute to several different cardiovascular diseases, such as arterial hypertension, atherosclerosis, pulmonary arterial hypertension, stenocardia.

It was shown that in children with pulmonary arterial hypertension due to congenital heart diseases the level of homocysteine is higher and the level of endogenous sulfur dioxide is lower than in normal control

children. Moreover, these biochemical parameters strongly correlated to the severity of pulmonary arterial hypertension. Authors considered homocysteine to be one of useful biochemical markers of disease severity and sulfur dioxide metabolism to be one of potential therapeutic targets in those patients
Endogenous sulfur dioxide also has been shown to lower the proliferation rate of endothelial smooth muscle cells in blood vessels, via lowering the MAPK activity and activating adenylyl cyclase and protein kinase A. Smooth muscle cell proliferation is one of important mechanisms of hypertensive remodeling of blood vessels and their stenosis, so it is an important pathogenetic mechanism in arterial hypertension and atherosclerosis.

Endogenous sulfur dioxide in low concentrations causes endothelium-dependent vasodilation. In higher concentrations it causes endothelium-independent vasodilation and has a negative inotropic effect on cardiac output function, thus effectively lowering blood pressure and myocardial oxygen consumption.
The vasodilating and bronchodilating effects of sulfur dioxide are mediated via ATP-dependent calcium channels and L-type ("dihydropyridine") calcium channels. Endogenous sulfur dioxide is also a potent antiinflammatory, antioxidant and cytoprotective agent. It lowers blood pressure and slows hypertensive remodeling of blood vessels, especially thickening of their intima. It also regulates lipid metabolism
Endogenous sulfur dioxide also diminishes myocardial damage, caused by isoproterenol adrenergic hyperstimulation, and strengthens the myocardial antioxidant defense reserve.

As a refrigerant

Being easily condensed and possessing a high heat of evaporation, sulfur dioxide is a candidate material for refrigerants. Prior to the development of chlorofluorocarbons, sulfur dioxide was used as a refrigerant in home refrigerators.

As a reagent and solvent in the laboratory

Sulfur dioxide is a versatile inert solvent widely used for dissolving highly oxidizing salts. It is also used occasionally as a source of the sulfonyl group in organic synthesis. Treatment of aryl diazonium salts with sulfur dioxide and cuprous chloride yields the corresponding aryl sulfonyl chloride, for example:

Proposed use in climate engineering

Injections of sulfur dioxide in the stratosphere has been proposed in climate engineering. The cooling effect would be similar to what has been observed after the large explosive volcano eruption of Mount Pinatubo in 1991. However this form of geoengineering would have uncertain regional consequences on rainfall patterns, for example in monsoon regions.

As an air pollutant

A sulfur dioxide plume from the Halemaʻumaʻu vent, glows at night
Sulfur dioxide is a noticeable component in the atmosphere, especially following volcanic eruptions. According to the United States Environmental Protection Agency, the amount of sulfur dioxide released in the U.S. per year was:

A collection of estimates of past and future anthropogenic global sulphur dioxide emissions. The Cofala et al. estimates are for sensitivity studies on SO_2 emission policies, CLE: Current Legislation, MFR: Maximum Feasible Reductions. RCPs (Representative Concentration Pathways) are used in CMIP5 simulations for latest (2013–2014) IPCC 5th assessment report.

OXIDES OF CHLORINE

Chlorine dioxide is a neutral chlorine compound. It is very different from elementary chlorine, both in its chemical structure and in its behavior. One of the most important qualities of chlorine dioxide is its high water solubility, especially in cold water. Chlorine dioxide does not hydrolyze when it enters water; it remains a dissolved gas in solution. Chlorine dioxide is approximately 10 times more soluble in water than chlorine.

The molecule ClO_2 has an odd number of valence electrons, and therefore, it is a paramagnetic radical. Its electronic structure has long baffled chemists because none of the possible Lewis structures is very satisfactory. In 1933, L. O. Brockway proposed a structure that involved a three-electron bond. Chemist Linus Pauling further developed this idea and arrived at two resonance structures involving a double bond on one side and a single bond plus three-electron bond on the other.In Pauling's view the latter combination should represent a bond that is slightly *weaker* than the double bond. In molecular orbital theory this idea is commonplace if the third electron is placed in an anti-bonding orbital. Later work has confirmed that the HOMO is indeed an incompletely-filled orbital.

Preparation

Chlorine dioxide is a compound that can decompose extremely violently when separated from diluting substances. As a result, preparation methods that involve producing solutions of it without going through a gas-phase stage are often preferred. Arranging handling in a safe manner is essential.

In lab

In the laboratory, ClO_2 is prepared by oxidation of sodium chlorite:

$$NaClO_2 + ½ Cl_2 \rightarrow ClO_2 + NaCl$$

Chlorine dioxide can be prepared in laboratory by reaction of potassium chlorate with oxalic acid:

$$KClO_3 + H_2C_2O_4 \rightarrow ½ K_2C_2O_4 + ClO_2 + CO_2 + H_2O$$

$$KClO_3 + ½ H_2C_2O_4 + H_2SO_4 \rightarrow KHSO_4 + ClO_2 + CO_2 + H_2O$$

Pulp bleaching

Over 95% of the chlorine dioxide produced in the world today is made from sodium chlorate and is used for pulp bleaching. It is produced with high efficiency by reducing sodium chlorate in a strong acid solution with a suitable reducing agent such as methanol, hydrogen peroxide, hydrochloric acid or sulfur dioxide.[10] Modern technologies are based on methanol or hydrogen peroxide, as these chemistries allow the best economy and do not co-produce elemental chlorine. The overall reaction can be written as:

chlorate + acid + reducing agent → chlorine dioxide + by-products

As a typical example, the reaction of sodium chlorate with hydrochloric acid in a single reactor is believed to proceed through the following pathway:
The commercially more important production route uses methanol as the reducing agent and sulfuric acid for the acidity. Two advantages of not using the chloride-based processes are that there is no formation of elemental chlorine, and that sodium sulfate, a valuable chemical for the pulp mill, is a side-product. These methanol-based processes provide high efficiency and can be made very safe.

Disinfectant

A much smaller, but important, market for chlorine dioxide is for use as a disinfectant. Since 1999 a growing proportion of the chlorine dioxide made globally for water treatment and other small-scale applications has been made using the chlorate, hydrogen peroxide and sulfuric acid method, which can produce a chlorine-free product at high efficiency. Traditionally, chlorine dioxide for disinfection applications has been made by one of three methods using sodium chlorite or the sodium chlorite – hypochlorite method:

$$2 NaClO_2 + 2 HCl + NaOCl \rightarrow 2 ClO_2 + 3 NaCl + H_2O$$

or the sodium chlorite – hydrochloric acid method:

$$5 NaClO_2 + 4 HCl \rightarrow 5 NaCl + 4 ClO_2 + 2 H_2O$$

or the chlorite – sulfuric acid method:

$$8ClO_2^- + 4H_2SO_4 \rightarrow 4ClO_2 + 2HClO_3 + 4SO_4^{2-} + 2H_2O + 2HCl$$

All three sodium chlorite chemistries can produce chlorine dioxide with high chlorite conversion yield, but unlike the other processes the chlorite-sulfuric acid method produces completely chlorine-free chlorine dioxide, although it suffers from the requirement of 25% more chlorite to produce an equivalent amount of chlorine dioxide. Alternatively, hydrogen peroxide may be efficiently used in small-scale applications.

Other

Very pure chlorine dioxide can also be produced by electrolysis of a chlorite solution:

$$2\ NaClO_2 + 2\ H_2O \rightarrow 2\ ClO_2 + 2\ NaOH + H_2$$

High-purity chlorine dioxide gas (7.7% in air or nitrogen) can be produced by the gas–solid method, which reacts dilute chlorine gas with solid sodium chlorite:

$$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$$

These processes and several slight variations have been reviewed.

Handling properties

At gas-phase concentrations greater than 30% volume in air at STP (more correctly: at partial pressures above 10 kPa), ClO_2 may explosively decompose into chlorine and oxygen. The decomposition can be initiated by, for example, light, hot spots, chemical reaction, or pressure shock. Thus, chlorine dioxide gas is never handled in concentrated form, but is almost always handled as a dissolved gas in water in a concentration range of 0.5 to 10 grams per liter. Its solubility increases at lower temperatures, thus it is common to use chilled water (5 °C, or 41 °F) when storing at concentrations above 3 grams per liter. In many countries, such as the United States, chlorine dioxide gas may not be transported at any concentration and is almost always produced at the application site using a chlorine dioxide generator. In some countries,chlorine dioxide solutions below 3 grams per liter in concentration may be transported by land, however, they are relatively unstable and deteriorate quickly.

Uses

Chlorine dioxide is used for bleaching of wood pulp and for the disinfection (called chlorination) of municipal drinking water.As a disinfectant it is effective even at low concentrations because of its unique qualities.

Bleaching

Chlorine dioxide is sometimes used for bleaching of wood pulp in combination with chlorine, but it is used alone in ECF (elemental chlorine-free) bleaching sequences. It is used at moderately acidic pH (3.5 to 6). The use of chlorine dioxide minimizes the amount of organochlorine compounds produced.Chlorine dioxide (ECF technology) currently is the most important bleaching method worldwide. About 95% of all bleached Kraft pulp is made using chlorine dioxide in ECF bleaching sequences.

Chlorine dioxide is also used for the bleaching of flour.

Water chlorination

Further information: Water chlorination

Further information: Chlorine_Dioxide_Tablets § Chemical_disinfection

The Niagara Falls, New York, water treatment plant first used chlorine dioxide for drinking water treatment in 1944 for phenol destruction. Chlorine dioxide was introduced as a drinking water disinfectant on a large scale in 1956, when Brussels, Belgium, changed from chlorine to chlorine dioxide. Its most common use in water treatment is as a pre-oxidant prior to chlorination of drinking water to destroy natural water impurities that would otherwise produce trihalomethanes on exposure to free chlorine. Trihalomethanes are suspect carcinogenic disinfection by-products associated with chlorination of naturally occurring organics in the raw water. Chlorine dioxide is also superior to chlorine when operating above pH 7,4–33 in the presence of ammonia and amines and or for the control of biofilms in water distribution systems. Chlorine dioxide is used in many industrial water treatment applications as a biocide including cooling towers, process water, and food processing.

Chlorine dioxide is less corrosive than chlorine and superior for the control of legionella bacteria.

Chlorine dioxide is superior to some other secondary water disinfection methods in that chlorine dioxide: 1) is an EPA registered biocide, 2) is not negatively impacted by pH, 3) does not lose efficacy over time (the bacteria will not grow resistant to it) and 4) is not negatively impacted by silica and phosphate, which are commonly used potable water corrosion inhibitors.

It is more effective as a disinfectant than chlorine in most circumstances against waterborne pathogenic agents such as viruses, bacteria and protozoa – including the cysts of *Giardia* and the oocysts of *Cryptosporidium*.

The use of chlorine dioxide in water treatment leads to the formation of the by-product chlorite, which is currently limited to a maximum of 1 ppm in drinking water in the USA This EPA standard limits the use of chlorine dioxide in the USA to relatively high-quality wate, or water that is to be treated with iron-based coagulants (iron can reduce chlorite to chloride

Chlorine dioxide has many applications as an oxidizer or disinfectant. Chlorine dioxide can be used for air disinfection and was the principal agent used in the decontamination of buildings in the United States after the 2001 anthrax attacks. After the disaster of Hurricane Katrina in New Orleans, Louisiana, and the surrounding Gulf Coast, chlorine dioxide has been used to eradicate dangerous mold from houses inundated by the flood water.Because of its unique qualities, chlorine dioxide is an effective disinfectant even at low concentrations.

Other disinfection uses

Sometimes chlorine dioxide is used as a fumigant treatment to "sanitize" fruits such as blueberries, raspberries, and strawberries that develop molds and yeast.[*citation needed*]

Chlorine dioxide is used for the disinfection of endoscopes, such as under the trade name *Tristel*. It is also available in a "trio" consisting of a preceding "pre-clean" with surfactant and a succeeding "rinse" with deionised water and low-level antioxidant.

Chlorine dioxide also is used for control of zebra and quagga mussels in water intake

Chlorine dioxide also was shown to be effective in bedbug eradication.

Other uses

Chlorine dioxide is used as an oxidant for phenol destruction in waste water streams and for odor control in the air scrubbers of animal byproduct (rendering) plants. It is also available for use as a deodorant for cars and boats, in chlorine dioxide generating packages that are activated by water and left in the boat or car overnight.

Safety issues in water and supplements

Chlorine dioxide is toxic, hence limits on exposure to it are needed to ensure its safe use. The United States Environmental Protection Agency has set a maximum level of 0.8 mg/L for chlorine dioxide in drinking water.[31] The Occupational Safety and Health Administration (OSHA), an agency of the United States Department of Labor, has set an 8-hour permissible exposure limit of 0.1 ppm in air (0.3 mg/m^3) for people working with chlorine dioxide

On July 30, 2010 and again on October 1, 2010, the United States Food and Drug Administration (FDA) warned against the use of the product "Miracle Mineral Supplement", or "MMS", which when made up according to instructions produces chlorine dioxide. MMS has been marketed as a treatment for a variety of conditions, including HIV, cancer, autism, and acne. The FDA warnings informed consumers that MMS can cause serious harm to health and stated that it has received numerous reports of nausea, diarrhea, severe vomiting, and life-threatening low blood pressure caused by dehydration.

Oxo acids of phosphorus

Oxoacids are basically the acids that contain oxygen. Phosphorus forms a number of oxoacids, for example: H_3PO_4, H_3PO_3, etc. In oxoacids of phosphorus, phosphorus is tetrahedrally surrounded by other atoms. Generally, all these acids are known to form at least one P=O bond and one P–OH bond. P–P or P–H bonds are also found in addition to P=O bonds and P–OH bonds in oxoacids of phosphorus where the oxidation state of phosphorus is less than +5. These acids are generally seen to disproportionate to higher and lower oxidation states. For example, phosphorous acid on heating disproportionates to give phosphoric acid and phosphine.

Oxoacids of Phosphorus

$4H3PO3 \rightarrow 3H3PO4 + PH3$

The P-H bonds in oxoacids are not ionisable to give H^+ ions whereas the H atoms which are attached with oxygen in P-OH form are ionisable. Hence we can say that only the H atoms attached with oxygen cause basicity. As a result phosphorous acid, H_3PO_3 is dibasic due to the presence of two P-OH bonds whereas phosphoric acid, H_3PO_4 is tribasic due to the presence of three P-OH bonds. Oxoacids of phosphorus having P-H bonds have strong reducing properties. For example: hypophosphorous acid containing two P-H bonds acts as a good reducing agent.

$4\,AgNO3 + 2H2O + H3PO2 \rightarrow 4Ag + 4HNO3 + H3PO4$

Few popular oxoacids of phosphorus

Phosphorus acid, H_3PO_3: Phosphorous acid is a diprotic acid that is, it ionizes two protons. It is better described with the structural formula $HPO(OH)_2$. Phosphorous acid is prepared by hydrolysis of phosphorus trichloride with acid or steam.

$PCl3 + 3\,H2O \rightarrow HPO(OH)2 + 3\,HCl$

Phosphoric acid, H_3PO_4: Phosphoric acid is a triprotic acid that is, it ionizes three protons. It is a non-toxic acid, when pure and is a solid at room temperature and pressure. Phosphoric acid is prepared by adding sulfuric acid to tricalcium phosphate rock:

$Ca5(PO4)3X + 5\,H2SO4 + 10\,H2O \rightarrow 3H3PO4 + 5\,CaSO4.2H2O + HX$

X can be F, Cl, Br and OH

Oxo acids of chlorine

Halogens usually form four series of oxoacids, namely, hypohalous acids, halous acids, halic acids and perhalic acids. X represents the halogen, which may be fluorine, chlorine, bromine or iodine.

Oxidation states of the 4 series of oxoacids:

Halogen oxoacid series	General formulae	**Oxidation states**	**Halogen oxoacid**			
			F	Cl	Br	I
Hypohalous acids	HOX	+1	HOF	HOCl	HOBr	HOI
Halous acids	HOXO	+3	-	HOClO	-	-
Halic acids	$HOXO_2$	+5	-	$HOClO_2$	$HOBrO_2$	$HOIO_2$
Perhalic acids	$HOXO_3$	+7	-	$HOClO_3$	$HOBrO_3$	$HOIO_3$

STRUCTURES OF THE OXOACIDS OF HALOGENS:

In all of these oxoacids, the central halogen atom is sp3 hybridised.

One X-OH bond is essentially present in every oxoacid. In most of these oxoacids, "X=O" bonds are present. The double bond present in an oxoacid between the central halogen atom and oxygen is d pi - p pi in nature.

Hypohalous acids include hypofluorous acid, hypochlorous acid, hypobromous acid and hypoiodous acid.

The halogen has the oxidation state of +1 in hypohalous acids.

The respective hypohalite ions have a linear shape owing to the presence of three lone pairs of electrons on the central halogen atom.

Hypohalous acids, being less stable, tend to form halic acids.

$3HOX \rightarrow HOXO_2 + 3HX$

Hypohalous acid Halic acid Hydrogen halide

Only oxoacid of fluorine is hypofluorous acid. No higher oxoacid of fluorine is known due to the absence of d orbitals in the fluorine atom.

Halous acids, includes only chlorous acid. The chlorine in chlorous acid has the oxidation state of+3. The chlorite ion has a V - shape owing to the presence of two lone pairs on the central chlorine atom.

Halic acids, includes chloric acid, bromic acid and iodic acid. The halogen has the oxidation state of +5 in these oxoacids. The respective halate ions are pyramidal in shape owing to the presence of a lone pair of electrons on the central halogen atom.

Perhalic acids, includes perchloric acid, perbromic acid and periodic acid. The oxidation state of the halogen in these oxoacids is+7. The shape of the perhalate ion is tetrahedral.

In any series of oxoacids of halogens, the first member possesses high acidic strength. This is due to the high electro-negativity and small size of the respective halogens.
Ex: Among perhalic acids, perchloric acid has high acidic strength. As chlorine is more electro-negative than bromine or iodine, the shared electron pair lies relatively nearer to chlorine in a Cl-O bond than bromine in a Br-O bond or iodine in an I-O bond. As a consequence, the O-H bond becomes much weaker in case of perchloric acid, thereby facilitating the release of a proton readily.

$HOClO_3$ > $HOBrO_3$ > $HOIO_3$
Perchloric acid perbromic acid Periodic acid

The acidic strength of an oxoacid increases with an increase in the oxidation number of the halogen.
EX: Among the four oxoacids of chlorine, the acidic strength increases markedly from hypochlorous acid to perchloric acid.
Perchloric acid is the strongest acid among all the oxoacids of halogens.

PEROXY ACIDS OF SULPHUR

The **sulfur oxoacids** are chemical compounds that contain sulfur, oxygen and hydrogen. The best known and most important industrially is sulfuric acid. Sulfur has a number of oxoacids; however, some of these are known only from their salts (these are shown in italics in the table below). The acids that have been characterised contain a variety of structural features, for example:

- tetrahedral sulfur when coordinated to oxygen
- terminal and bridging oxygen atoms
- terminal peroxo groups
- terminal S=S
- chains of $(-S-)_n$

Halides of silicon

Comparison of SiX_4

The properties of the tetrahalosilanes, all of which are tetrahedral, are significantly affected by nature of the halide. These trends apply also to the mixed halides. Melting points, boiling points, and bond lengths increase with the atomic mass of the halide. The opposite trend is observed for the Si-X bond energies.

	SiF_4	**$SiCl_4$**	**$SiBr_4$**	**SiI_4**
b.p. (˚C)[2]	-90.3	56.8	155.0	290.0
m.p. (˚C)[2]	-95.0	-68.8	5.0	155.0
Si-X bond length (Å)	1.55	2.02	2.20	2.43
Si-X bond energy (kJ/mol)[3]	582	391	310	234

Lewis acidity

Covalently saturated silicon complexes like $SiBr_4$, along with tetrahalides of germanium (Ge) and tin (Sn), are Lewis acids.[4] Although silicon tetrahalides obey the octet rule, they add Lewis basic ligands to give adducts with the formula $SiBr_4L$ and $SiBr_4L_2$ (where L is a Lewis base).[5][6][7] The Lewis acidic properties of the tetrahalides tend to increase as follows: $SiI_4 < SiBr_4 < SiCl_4 < SiF_4$. This trend is attributed to the relative electronegativities of the halogens.[6][3]

The strength of the Si-X bonds decrease in the order: Si-F > Si-Cl > Si-Br > Si-I.[3][2]

Synthesis

Silicon tetrabromide is synthesized by the reaction of silicon with hydrogen bromide at 600 °C.[8]

$$Si + 4\ HBr \rightarrow SiBr_4 + 2\ H_2$$

Side products include dibromosilane (SiH_2Br_2) and tribromosilane ($SiHBr_3$).[8]

$$Si + 2\ HBr \rightarrow SiH_2Br_2$$

$$Si + 3\ HBr \rightarrow SiHBr_3 + H_2$$

Reactivity

Like other halosilanes, $SiBr_4$ can be converted to hydrides, alkoxides, amides, and alkyls, i.e., products with the following functional groups: Si-H, Si-OR, Si-NR_2, Si-R, and Si-X bonds respectively.

Silicon tetrabromide can be readily reduced by hydrides or complex hydrides.

$$4\ R_2AlH + SiBr_4 \rightarrow SiH_4 + 4\ R_2AlBr$$

Reactions with alcohols and amines proceeed as follows:

$$SiBr_4 + 4\ ROH \rightarrow Si(OR)_4 + 4\ HBr$$

$$SiBr_4 + 8\ HNR_2 \rightarrow Si(NR_2)_4 + 4\ HNR_2HBr$$

Grignard reactions with metal alkyl halides are particularly important reactions due to their production of organosilicon compounds which can be converted to silicones.

$$SiBr_4 + n\ RMgX \rightarrow R_nSiBr_{4-n} + n\ MgXBr$$

Redistribution reactions occur between two different silicon tetrahalides (as well as halogenated polysilanes) when heated to 100 ˚C, resulting in various mixed halosilanes. The melting points and boiling points of these mixed halosilanes generally increase as their molecular weights increase. (Can occur with X= H, F, Cl, Br, and I)

$$2\ SiBr_4 + 2\ SiCl_4 \rightarrow SiBr_3Cl + 2\ SiBr_2Cl_2 + SiBrCl_3$$

$$Si_2Cl_6 + Si_2Br_6 \rightarrow Si_2Cl_nBr_{6-n}$$

Silicon tetrabromide hydrolyzes readily when exposed to air causing it to fume:

$$SiBr_4 + 2\ H_2O \rightarrow SiO_2 + 4\ HBr$$

Silicon tetrabromide is stable in the presence of oxygen at room temperature, but bromosiloxanes form at 670-695 ˚C .

$$2\ SiBr_4 + 1/2\ O_2 \rightarrow Br_3SiOSiBr_3 + Br_2$$

Phosphorus halides

In the gas phase the phosphorus pentahalides have trigonal bipyramidal molecular geometry as explained by VSEPR theory.

Phosphorus pentafluoride is a relatively inert gas, notable as a mild Lewis acid and a fluoride ion acceptor. It is a fluxional molecule in which the axial (ax) and equatorial (eq) fluorine atoms interchange positions by the Berry pseudorotation mechanism.

Phosphorus pentachloride, phosphorus pentabromide, and phosphorus heptabromide are ionic in the solid and liquid states; PCl_5 is formulated as $PCl_4^+PCl_6^-$, but in contrast, PBr_5 is formulated as $PBr_4^+\ Br^-$, and PBr_7 is formulated as $PBr_4^+\ Br_3^-$. They are widely used as chlorinating and brominating agents in organic chemistry.

Oxidation state +3 (PX_3)

Chemical formula	CAS number	Melting point	Boiling point	P–X bond length	X–P–X bond angle	Dipole moment
PF_3	[7783-55-3]	-151.5°C	-101.8°C	156 pm	96.3°	1.03 D
PCl_3	[7719-12-2]	-93.6°C	76.1°C	204 pm	100°	0.56 D
PBr_3	[7789-60-8]	-41.5°C	173.2°C	222 pm	101°	
PI_3	[13455-01-1]	61.2°C	227°C	243 pm	102°	

The phosphorus(III) halides are the best known of the three series. They are usually prepared by direct reaction of the elements, or by transhalogenation.

Phosphorus trifluoride is used as a ligand in coordination chemistry, where it resembles carbon monoxide. Phosphorus trichloride is a major industrial chemical and widely used starting material for phosphorus chemistry. Phosphorus tribromide is used in organic chemistry to convert alcohols to alkyl bromides and carboxylic acids to acyl bromides (*e.g.* in the Hell-Volhard-Zelinsky reaction). Phosphorus triiodide also finds use in organic chemistry, as a mild oxygen acceptor.

The trihalides are fairly readily oxidized by chalcogens to give the corresponding oxyhalides or equivalents.

The **oxyhalides** may be prepared from the corresponding trihalides by reaction with organic peroxides or ozone: they are sometimes referred to as **phosphoryl halides**.

The **thiohalides**, also known as **thiophosphoryl halides** may be prepared from the trihalides by reaction with elemental sulfur in an inert solvent. The corresponding selenohalides are also known.

The oxyhalides and thiohalides are significantly more electrophilic than the corresponding phosphorus(III) species, and present a significant toxic hazard.

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.
2. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry*. 5th Ed. Oxford University Press.

POSSIBLE QUESTIONS:

Part-A (1 Mark)

Multiple Choice Questions (Each Question Carry One Mark)

1. DMG is used for the detection of

(a) Zn^{2+} (b) Ca^{2+} (c) Fe^{2+} (d) **Ni^{2+}**

2. Pick out the neutral ligand?

(a) Chloride (b) Cyanide (c) Hydroxide (d) **Carbon monoxide**

3. Catenation is not shown among

(a) Alkali and alkaline earth metals (b) **Halogens and noble gases**.

(c) Alkaline earth metals and noble gases. (d) Alkali metals and noble gases.

4. Carbon compounds are the best example of a group of

(a) **Covalently bonded compounds** (b) Ionic bonded compounds

(c) Metallic bonded compounds (d) Vanderwals bonded compounds

5. The general electronic configuration of nitrogen group is

(a) **$ns^2\ np^3$** (b) $ns^2\ np^4$ (c) $ns^1\ np^3$ (d) $ns^2\ np^4$

6. Bismuth has a……

(a) **+3 oxidation state** (b) +2 oxidation state

(c) +1 oxidation state (d) +4 oxidation state

7. Chalcogens have…..

(a) Two electrons in their outermost shell. (b) **Six electrons in their outermost shell**.

(c) Five electrons in their outermost shell. (d) Three electrons in their outermostshell.

8. The metallic character of chalcogens elements

(a) **Increases down the group** (b) No change down the group

(c) Decreases and then increases down the group(d) Decreases down the group

9. Elements of VII A have maximum electronegativity, with fluorine being the most electronegative atom present

(a) **Due to its smaller size.** (b) Due to its larger size.

(c) Due to first element in the periodic table. (d) Due to its least electropositivity

10. An example of catenation

(a) **S_8** (b) S_7 (c) S_6 (d) S_5

11. Valence shell configuration of Boron

(a) **$2s^2\ p^1$** (b) $2s^2\ p^3$ (c) $2s^2\ p^2$ (d) $2s^1\ p^1$

12. Carbon and silicon show

(a) **+4 oxidation states** (b) +1 oxidation state

(c) +3 oxidation state (d) +2 oxidation state

13. Catenation is the ability to form compounds in which the atoms are linked to each other in

(a) **Chains or rings**. (b) Vanderwals forces

(c) Covalent bond (d) Ionic bond

14. Boron is a…..

(a) Metal **(b) Nonmetal** (c) Metalloid (d) Semiconductor

15. The melting point and boiling point in carbon group

(a) **Decreases down the group** (b) No change down the group

(c) Decreases and then increases (d) Increases down the group

16. Halogens are…….

(a) **Highly electronegative** (b) Low electronegative

(c) Low electropositive (d) Highly electropositive

17. Halogens are

(a) C**oloured** (b) Non-coloured (c) Some are coloured (d) Some non coloured

18. PH3 produces smoky rings when it comes in content with air. This is because:

(a) It is inflammable (b) It combines with water vapour

(c) It combines with nitrogen (d) **It contains impurity of P_2H_4**

19. Xenon difluoride is a

(a) **linear molecule** (b) Square pyrimadal (c) See saw (d) Tetrahedral

20. Hexachlorophosphazene together with the related $(NPCl_2)_4$ are precursors to inorganic polymers called

(a) Hexachlorophosphazene (b) **Polyphosphazenes**.

(c) Hexaphosphazene (c) Chlorophosphazene

PART- B (Each Carry 2 Marks)

1. What happens to electronegativity of P block elements as we descending down the group.
2. Explain atomic and ionic size of P block elements.
3. Write down the electronic configuration of F.
4. Assess electronegativity of P block elements.
5. Write down the electronic configuration of silicon.
6. What is inert pair effect?

7. Give any two structures of hydrides of Group-15 elements?
8. Write any four applications of sulphur and phosphorous oxides?
9. Define peroxy sulphur halides?
10. Write any two properties of diborane?

Part-C (Each Carry 6 Marks)

1. Discuss the diagonal relationship between Boron and Silicon.
2. Discuss the structure and properties of oxides of phosphorus and sulphur.
3. Describe the structure, bonding and properties of hydrides of group 13.
4. Discuss the anomalous behaviour of Boron
5. Explain the anomalous behaviour of carbon in p block elements.
6. Draw the structure and bonding of halides of Si and P.
7. Analyse the structure, bonding and properties of peroxy acids of sulphur.

18CHU202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2017 onwards)
Department of Chemistry
II- semester
Inorganic Chemistry- II (Metallurgy and S,P-Block Elements

UNIT IV- Objective Questions for online examination (Each carry 1 Marks)

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
From carbon to lead in group IV A, the elements increase in size, due to the	additional shell added	high electronegativity	high electropositivity	high nuclear charge	additional shell added
Ionization energy, or the energy to remove an electron from the outermost shell of an element	decreases as we move along from IIIA to VIIA.	no change as we move along from IIIA to VIIA.	increases and then decreases as we move along from IIIA to VIIA.	increases as we move along from IIIA to VIIA.	increases as we move along from IIIA to VIIA.
Elements of VII A have maximum electronegativity, with fluorine being the most electronegative atom present	due to its smaller size.	due to its larger size.	due to first element in the periodic table.	due to its least electropositivity	due to its smaller size.
phosphorus exist in many forms like	red phosphorus, white phosphorus	yellow phosphorus, white phosphorus	blue phosphorus, white phosphorus	red phosphorus, violet phosphorus	red phosphorus, white phosphorus
Catenation is the ability to form compounds in which the atoms are linked to each other in	chains or rings.	vanderwals forces	covalent bond	ionic bond	chains or rings.
the element which has the greater tendency to combine with other carbon atoms to form quite large carbon structures.	carbon	sulphur	oxygen	nitrogen	carbon
an example of catenation	S8	S7	S6	S5	S8
Catenation is not shown among	alkali and alkaline earth metals	halogens and noble gases.	alkaline earth metals and noble gases.	alkali metals and noble gases.	halogens and noble gases.
Carbon compounds are the best example of a group of	covalently bonded compounds	ionic bonded compounds	metallic bonded compounds	vanderwals bonded compounds	covalently bonded compounds

Valence shell configuration of Boron	2s2 p1	2s2 p3	2s2 p2	2s1 p1	2s2 p1
Valence shell configuration of gallium	3s1 p1	3s2 p2	3s2 p3	2s2 p1	3s2 p1
Valence shell configuration of indium	$3s^2$ p^1	3s2 p2	3s2 p3	2s2 p1	$3s^2$ p^1
Boron is a	non metal,	metal	metalloid	semiconductor	non metal,
Boron forms	acidic oxides	basic oxides	acidic and basic oxides	carbonates	acidic oxides
Al and Ga form	acidic oxides	amphoteric oxides	basic oxides	carbonates	amphoteric oxides
In and Tl forms	basic oxides	acidic oxides	carbonates	acidic and basic oxides	basic oxides
Boron trihalides are covalent in character due to their	smaller size	larger size	high electropositivity	high nuclear charge	smaller size
Electronic configuration of tin	5s2p1s2p2	5s2p1s2p1	6s2p1s2p1	4s2p1s2p1	5s2p1s2p1
Electronic configuration of lead	6s2p1s2p1	6s2p1s2p2	5s2p1s2p1	4s2p1s2p1	6s2p1s2p1
The melting point and boiling point in carbon group	decreases down the group	no change down the group	decreases and then increases down the group	increases down the group	decreases down the group
Carbon and silicon show	+4 oxidation states	+1 oxidation state	+3 oxidation state	+2 oxidation state	+4 oxidation state
Ge, Sn and Pb show	+3 oxidation state.	+2 and +4 oxidation states.	+3 and +4 oxidation states.	+2 oxidation state	+2 and +4 oxidation states.
The general electronic configuration of nitrogen group is	ns^2 np^3	ns^2 np4	ns1 np^3	ns^2 np4	ns^2 np^3
nitrogen group elements have	5 electrons in their valence shell	3 electrons in their valence shell	4 electrons in their valence shell	6 electrons in their valence shell	5 electrons in their valence shell
Bi has an exceptionally low melting point due to the Bi has an exceptionally low melting point due to	the non availability of 's' electrons.	the non availability of 'f' electrons.	the non availability of 'd' electrons.	the non availability of 'p' electrons.	the non availability of 's' electrons.
Bismuth has a	+3 oxidation state	+2 oxidation state	+1 oxidation state	+4 oxidation state	+3 oxidation state
Chalcogens have	two electrons in their outermost shell.	six electrons in their outermost shell.	five electrons in their outermost shell.	three electrons in their outermost shell.	six electrons in their outermost shell.

The metallic character of chalcogens elements	increases down the group	no change down the group	decreases and then increases down the group	decreases down the group	increases down the group
Halogens are	highly electronegative	low electronegative	low electropositive	highly electropositive	highly electronegative
Halogens are	highly reactive	highly non reactive	high electropositivity	low electronegative	highly reactive
Halogens are	coloured	non-coloured	some are coloured and others are non coloured	block	coloured
All halogens exist as covalent	monoatomic molecules	mono and diatomic molecules	triatomic molecules.	diatomic molecules.	diatomic molecules.
Argon is used for filling electric bulbs because of its	inert nature	oxidation state	nobel gas	non inert nature	inert nature
White phosphorus reacts with caustic soda. The products are PH_3 and NaH_2PO_2. This reaction is an example of :	Oxidation	Reduction	Neutralization	Oxidation and reduction	Oxidation and reduction
PH_3 produces smoky rings when it comes in content with air. This is because:	It is inflammable	It combines with water vapour	It combines with nitrogen	It contains impurity of P_2H_4	It contains impurity of P_2H_4
One mole of calcium phosphide on reaction with excess of water gives:	Two mole of phosphine	Two mole of phosphorus pentaoxide	One mole of phosphine	Two mole of phosphoric acid	Two mole of phosphine
By the action of concentration H_2SO_4 phosphorus change to	Phosphorus acid	Metaphosphoric acid	Orthophosphoric acid	Dyrophosphoric acid	Orthophosphoric acid
IN white phosphorus (P_4) molecule which one is not correct ?	Six P – P single bond are present	Four P – P single bond are present	Four lone pair of electron are present	P – P – P bond angle is 60	Four P – P single bond are present
Which statement is not correct?	White and red phosphorus reach with chlorine at room temperature	White phosphorus is metastable, while red phosphorus is stable	White phosphorus is lighter than red phosphorus	White phosphorus is highly poisonous while red phosphorus is not.	White and red phosphorus reach with chlorine at room temperature
The bonds in the interhalogens compounds are	metallic	covalent	ionic	vanderwals bonded compounds	covalent

Halogens acts as a strong oxidizing agents due to their tendency to	accept electrons	accept protons	accept neutrons	donate electrons	accept electrons
The atoms of Group 16 elements have	6 valence electrons	5 valence electrons	4 valence electrons	3 electrons	6 electrons
Group 16 hydride molecules have a	bent shape	tetrahedral	square pyramidal	see saw	bent shape
Elemental fluorine was first discovered in 1886 by isolating it from	hydrofluoric acid	hydrochloric acid	sulphuric acid	nitric acid	hydrofluoric acid
Astatine is a radioactive element with an atomic number	85	86	87	88	85
Group 14 hydrides are chemical compounds composed of	hydrogen atoms and carbon group atoms	sulphur atoms	oxygen atoms	hydrogen and chlorine atoms	hydrogen atoms and carbon group atoms
The elements of group 14 form covalent hydrides of the type	MH$_4$.	MH1.	MH2.	MH3.	MH$_4$.
symbol of astatine is	At	As	Ag	Au	At
Hydrides of group 15 elements are strong	reducing agents	oxidising agents	reducing and oxidising agents	reductant	reducing agents
The stability of group 15 hydrides	decreases from ammonia to bismuthine	decreases and then increases from ammonia to bismuthine	no change from ammonia to bismuthine	increases from ammonia to bismuthine	decreases from ammonia to bismuthine
Chlorine also has two isotopes	^{35}Cl and ^{37}Cl	^{33}Cl and ^{37}Cl	^{34}Cl and ^{37}Cl	^{35}Cl and ^{36}Cl	^{35}Cl and ^{37}Cl
Elemental fluorine was first discovered in	1886	1896	1897	1895	1886
The low melting point of Ga is due to	diatomic	mono and diatomic	triatomic	monoatomic	diatomic
Heat of sublimation and boiling points of Ga show a steady	decrease	increase	decrease and increase	increase and decrease	decrease
Melting points decreases from Barium to gallium and then	increases up to Tl.	increases and sudden decrease up to Tl.	no change up to Tl.	decreases up to Tl.	increases up to Tl.

Helium is used for filling air ships and weather balloons because they are	light and non-inflammable.	light	non-inflammable.	light and inflammable.	light and non-inflammable.
Neon is used as	Beacon lights	CFL	incandascent bulbs	light	Beacon lights
peroxymonoshulphuric acid is used to	detoxify cyanide	detoxify chlorine	detoxify oxygen	detoxify sulphur	detoxify cyanide
A peroxy acid sometimes known as	per acid	sulphuric acid	hydrochloric acid	nitric acid	per acid
peroxy acids are strong	oxidizers	reducing agents	oxidising agents	reducers	oxidizers

UNIT V

SYLLABUS

Preparation, properties, structure and uses of the following compounds:

- ✓ Borazine
- ✓ Silicates, silicones,
- ✓ Phosphonitrilic halides {$(PNCl_2)_n$ where n = 3 and 4}
- ✓ Interhalogen and pseudohalogen compounds
- ✓ Clathrate compounds of noble gases, xenon fluorides (MO treatment of XeF_2).

Preparation, properties, structure and uses of the following compounds:

BORAZINE

Synthesis

The compound was reported in 1926 by the chemists Alfred Stock and Erich Pohland by a reaction of diborane with ammonia

Borazine is synthesized from diborane and ammonia in a 1:2 ratio at 250–300 °C with a conversion of 50%.

$$3\ B_2H_6 + 6\ NH_3 \rightarrow 2\ B_3H_6N_3 + 12\ H_2$$

An alternative more efficient route begins with lithium borohydride and ammonium chloride:

$$3\ LiBH_4 + 3\ NH_4Cl \rightarrow B_3H_6N_3 + 3\ LiCl + 9\ H_2$$

In a two-step process to borazine, boron trichloride is first converted to trichloroborazine:

$$3\ BCl_3 + 3\ NH_4Cl \rightarrow Cl_3B_3H_3N_3 + 9\ HCl$$

The B-Cl bonds are subsequently converted to B-H bonds:

$$2\ Cl_3B_3H_3N_3 + 6\ NaBH_4 \rightarrow 2\ B_3H_6N_3 + 3\ B_2H_6 + 6\ NaCl$$

Properties

Borazine is a colourless liquid with an aromatic smell. In water it hydrolyzes to boric acid, ammonia, and hydrogen. Borazine, with a standard enthalpy change of formation ΔH_f of −531 kJ/mol, is thermally very stable.

Structure and bonding

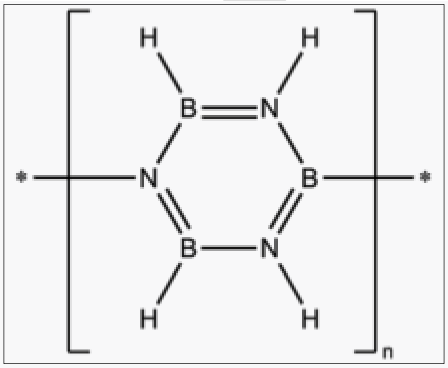
Borazine is isostructural with benzene. The six B-N bonds have length of 1.436 Å. The carbon–carbon bond in benzene is shorter length at 1.397 Å. The boron–nitrogen bond length is between that of the boron–nitrogen single bond with 0.151 nm and the boron–nitrogen double bond which is 0.131 nm. This suggests partial delocalisation of nitrogen lone-pair electrons.

The electronegativity of boron (2.04 on the Pauling scale) compared to that of nitrogen (3.04) and alsothe electron deficiency on the boron atom and the lone pair on nitrogen favor alternative mesomer structures for borazine.

Boron is the Lewis acid and nitrogen is the Lewis base.

Reactions

Although often compared with benzene, borazine is far more reactive. With hydrogen chloride it forms an adduct, whereas benzene is unreactive toward HCl.



Polyborazylene

$B_3N_3H_6 + 3\ HCl \rightarrow B_3N_3H_9Cl_3$
Addition reaction of borazine with hydrogen chloride
$B_3N_3H_9Cl_3 + NaBH_4 \rightarrow (BH_4N)_3$
Reduction with sodium borohydride

The addition reaction with bromine does not require a catalyst. Borazines undergo nucleophilic attack at boron and electrophilic attack at nitrogen. Heating borazine at 70 °C expels hydrogen with formation of a *borazinyl* polymer or *polyborazylene*, in which the monomer units are coupled in a para fashion by new boron-nitrogen bonds. Boron nitride can be prepared by heating polyborazylene to 1000 °C. Borazines are also starting materials for other potential ceramics such as *boron carbonitrides*. Borazine can also be used as a precursor to grow boron nitride thin films on surfaces, such as the nanomesh structure which is formed on rhodium.

Polyborazylene has been proposed as a recycled hydrogen storage medium for hydrogen fuel cell vehicle applications, using a "single pot" process for digestion and reduction to recreate ammonia borane.

Among other B-N type compounds mixed amino-nitro substituted borazines have been predicted to outperform carbon based explosives such as CL-20.

SILICATES

A **silicate** is a compound containing an anionic silicon compound. The great majority of the silicates are oxides, but hexafluorosilicate ($[SiF_6]^{2-}$) and other anions are also included.

"Orthosilicate" is the anion SiO4−
4 or its compounds. Related to orthosilicate are families of anions (and their compounds) with the formula $[SiO_{2+n}]^{2n-}$. Important members are the cyclic and single chain silicates $\{[SiO_3]^{2-}\}_n$ and the sheet-forming silicates $\{[SiO_{2.5}]^{-}\}_n$.

Silicates constitute the majority of Earth's crust, as well as the other terrestrial planets, rocky moons, and asteroids. Sand, Portland cement, and thousands of minerals are examples of silicates. Silicate compounds, including the minerals, consist of silicate anions whose charge is balanced by various cations. Myriad silicate anions can exist, and each can form compounds with many different cations. Hence this class of compounds is very large. Both minerals and synthetic materials fit in this class.

Structural principles

In the vast majority of silicates, including silicate minerals, the Si occupies a tetrahedral environment, being surrounded by 4 oxygen centres. In these structures, the chemical bonds to silicon conform to the octet rule. These tetrahedra sometimes occur as isolated SiO4−
4 centres, but most commonly, the tetrahedra are joined together in various ways, such as pairs. Commonly the silicate anions are chains, double chains, sheets, and three-dimensional frameworks. All these such species have negligible solubility in water at normal conditions.

Occurrence in solution

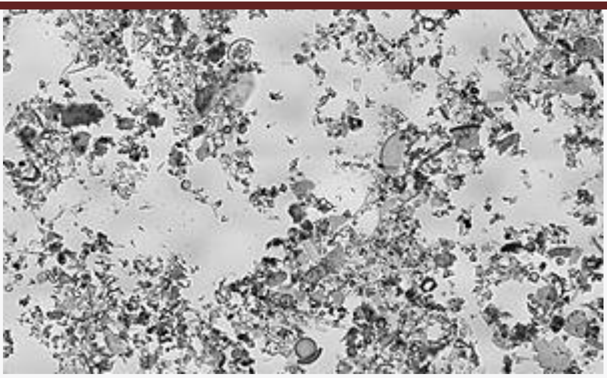
Sodium silicate

Silicates are well characterized as solids, but are less commonly observed in solution. The anion SiO4−
4 is the conjugate base of silicic acid, $Si(OH)_4$, and both are elusive as are all of the intermediate species. Instead, solutions of silicates are usually observed as mixtures of condensed and partially protonated silicate clusters. The nature of soluble silicates is relevant to understanding biomineralization and the synthesis of aluminosilicates, such as the industrially important catalysts called zeolites.

Silicates with non-tetrahedral silicon

Although the tetrahedron is the common coordination geometry for silicon compounds, silicon is well known to also adopt higher coordination numbers. A well-known example of such a high coordination number is hexafluorosilicate (SiF2−
6). Octahedral coordination by 6 oxygen centres is observed. At very high pressure, even SiO_2 adopts this geometry in the mineral stishovite, a dense polymorph of silica found in the lower mantle of the Earth. This structure is also formed by shock during meteorite impacts. Octahedral Si in the form of hexahydroxysilicate ($[Si(OH)_6]^{2-}$) is observed in thaumasite[*citation needed*] a mineral occurring rarely in nature but sometimes observed amongst other calcium silicate hydrate artificially formed in cement and concrete submitted to a severe sulfate attack.

Silicate rock and minerals



Diatomaceous earth, as viewed under a microscope, is a soft, siliceous, sedimentary rock made up of the frustules (shells) of single cell diatoms. Diatom cell walls are made up of biogenic silica; silica synthesised in the diatom cell by the polymerisation of silicic acid. This image of diatomaceous earth particles in water is at a scale of 6.236 pixels/μm, the entire image covers a region of approximately 1.13 by 0.69 mm.

Silicate minerals

In geology and astronomy, the term **silicate** is used to denote types of rock that consist predominantly of silicate minerals. On Earth, a wide variety of silicate minerals occur in an even wider range of combinations as a result of the processes that form and re-work the crust. These processes include partial melting, crystallization, fractionation, metamorphism, weathering and diagenesis. Living things also contribute to the silicate cycle near the Earth's surface. A type of plankton known as diatoms construct their exoskeletons, known as tests, from silica. The tests of dead diatoms are a major constituent of deep ocean sediment.

Silica, or silicon dioxide, SiO_2, is sometimes considered a silicate, although it is the special case with no negative charge and no need for counter-ions. Silica is found in nature as the mineral quartz, and its polymorphs.

Portland cement

Portland cement is produced by hydration of clinker, which consists of various calcium silicates, including tricalcium silicate (Ca_3SiO_5, also written $CaO{\cdot}Ca_2SiO_4$) and dicalcium silicate (Ca_2SiO_4). These components are often generated in situ by heating various clays and limestone.

Mineralogy

Mineralogically, silicate minerals are divided according to structure of their silicate anion into the following groups

- Nesosilicates (lone tetrahedron) – $[SiO_4]^{4-}$, e.g. olivine.
- Sorosilicates (double tetrahedra) – $[Si_2O_7]^{6-}$, e.g. epidote, melilite group.
- Cyclosilicates (rings) – $[Si_nO_{3n}]^{2n-}$, e.g. tourmaline group.
- Inosilicates (single chain) – $[Si_nO_{3n}]^{2n-}$, e.g. pyroxene group.
- Inosilicates (double chain) – $[Si_{4n}O_{11n}]^{6n-}$, e.g. amphibole group.
- Phyllosilicates (sheets) – $[Si_{2n}O_{5n}]^{2n-}$, e.g. micas and clays.

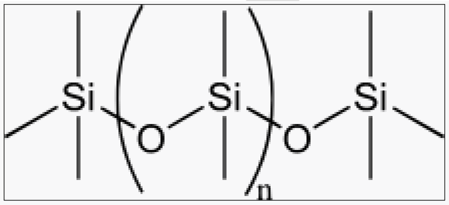
- Tectosilicates (3D framework) – $[Al_xSi_yO_{2x+2y)}]^{x-}$, e.g. quartz, feldspars, zeolites.

Note that tectosilicates can only have additional cations if some of the silicon is replaced by a lower-charge cation such as aluminium. Al for Si substitution is common.

SILICONES

Silicones, also known as **polysiloxanes**, are polymers that include any inert, synthetic compound made up of repeating units of siloxane, which is a chain of alternating silicon atoms and oxygen atoms, frequently combined with carbon and/or hydrogen. They are typically heat-resistant and rubber-like, and are used in sealants, adhesives, lubricants, medicine, cooking utensils, and thermal and electrical insulation. Some common forms include silicone oil, silicone grease, silicone rubber, silicone resin, and silicone caulk.

Chemistry



Chemical structure of the silicone polydimethylsiloxane (PDMS).

More precisely called polymerized siloxanes or polysiloxanes, silicones consist of an inorganic silicon-oxygen backbone chain (⋯-Si-O-Si-O-Si-O-⋯) with organic side groups attached to the silicon atoms. These silicon atoms are tetravalent. So, silicones are polymers constructed from inorganic-organic monomers. Silicones have in general the chemical formula $[R_2SiO]_n$, where R is an organic group such as methyl, ethyl, or phenyl.

In some cases, organic side groups can be used to link two or more of these -Si-O- backbones together. By varying the -Si-O- chain lengths, side groups, and crosslinking, silicones can be synthesized with a wide variety of properties and compositions. They can vary in consistency from liquid to gel to rubber to hard plastic. The most common siloxane is linear polydimethylsiloxane (PDMS), a silicone oil. The second largest group of silicone materials is based on silicone resins, which are formed by branched and cage-like oligosiloxanes.

Terminology and history

F. S. Kipping and Matt Saunders coined the word *silicone* in 1901 to describe polydiphenylsiloxane by analogy of its formula, Ph_2SiO (Ph stands for phenyl, C_6H_5), with the formula of the ketone benzophenone, Ph_2CO (his term was originally *silicoketone*). Kipping was well aware that polydiphenylsiloxane is polymeric whereas benzophenone is monomeric and noted that Ph_2SiO and Ph_2CO had very different chemistry. The discovery of the structural differences between Kippings' molecules and the ketones means that *silicone* is no longer the correct term (though it remains in common usage) and that the term *siloxanes* is correct according to the nomenclature of modern chemistry.

Silicone is sometimes mistakenly referred to as silicon. The chemical element silicon is a crystalline metalloid widely used in computers and other electronic equipment. Although silicones contain silicon atoms, they also include carbon, hydrogen, oxygen, and perhaps other kinds of atoms as well, and have physical and chemical properties that are very different from elemental silicon.

A true *silicone group* with a double bond between oxygen and silicon does not commonly exist in nature; chemists find that the silicon atom usually forms single bonds with each of two oxygen atoms, rather than a double bond to a single atom. Polysiloxanes are among the many substances commonly known as "silicones".

Molecules containing silicon-oxygen double bonds do exist and are called silanones but they are very reactive. Despite this, silanones are important as intermediates in gas-phase processes such as chemical vapor deposition in microelectronics production, and in the formation of ceramics by combustion.

Synthesis

Most common are materials based on polydimethylsiloxane, which is derived by hydrolysis of dimethyldichlorosilane. This dichloride reacts with water as follows:

$$n\ \mathrm{Si(CH_3)_2Cl_2} + n\ \mathrm{H_2O} \rightarrow [\mathrm{Si(CH_3)_2O}]_n + 2n\ \mathrm{HCl}$$

The polymerization typically produces linear chains capped with Si-Cl or Si-OH (silanol) groups. Under different conditions the polymer is a cyclic, not a chain.

For consumer applications such as caulks silyl acetates are used instead of silyl chloridesThe hydrolysis of the acetates produce the less dangerous acetic acid (the acid found in vinegar) as the reaction product of a much slower curing process. This chemistry is used in many consumer applications, such as silicone caulk and adhesives.

Branches or cross-links in the polymer chain can be introduced by using organosilicon precursors with fewer methyl groups, such as methyltrichlorosilane and methyltrimethoxysilane. Ideally, each molecule of such a compound becomes a branch point. This process can be used to produce hard silicone resins. Similarly, precursors with three methyl groups can be used to limit molecular weight, since each such molecule has only one reactive site and so forms the end of a siloxane chain.

Combustio

When silicone is burned in air or oxygen, it forms solid silica (silicon dioxide) as a white powder, char, and various gases. The readily dispersed powder is sometimes called silica fume.

Properties

Silicones exhibit many useful characteristics, including:[1]

- Low thermal conductivity
- Low chemical reactivity
- Low toxicity
- Thermal stability (constancy of properties over a wide temperature range of −100 to 250 °C).
- The ability to repel water and form watertight seals.
- Does not stick to many substrates, but adheres very well to others, e.g. glass.
- Does not support microbiological growth.

- Resistance to oxygen, ozone, and ultraviolet (UV) light. This property has led to widespread use of silicones in the construction industry (e.g. coatings, fire protection, glazing seals) and the automotive industry (external gaskets, external trim).
- Electrical insulation properties. Because silicone can be formulated to be electrically insulative or conductive, it is suitable for a wide range of electrical applications.
- High gas permeability: at room temperature (25 °C), the permeability of silicone rubber for such gases as oxygen is approximately 400 times that of butyl rubber, making silicone useful for medical applications in which increased aeration is desired. Conversely, silicone rubbers cannot be used where gas-tight seals are necessary.

Uses

Silicones are used in many products. Ullmann's Encyclopedia of Industrial Chemistry lists the following major categories of application: Electrical (e.g., insulation), electronics (e.g., coatings), household (e.g., sealants for cooking apparatus), automobile (e.g., gaskets), aeroplane (e.g., seals), office machines (e.g., keyboard pads), medicine/dentistry (e.g., teeth impression molds), textiles/paper (e.g., coatings). For these applications, an estimated 400,000 tons of silicones were produced in 1991. Specific examples, both large and small are presented below.

Automotive

In the automotive field, silicone grease is typically used as a lubricant for brake components since it is stable at high temperatures, is not water-soluble, and is far less likely than other lubricants to foul. It is also used as DOT 5 brake fluid.

Automotive spark plug wires are insulated by multiple layers of silicone to prevent sparks from jumping to adjacent wires, causing misfires. Silicone tubing is sometimes used in automotive intake systems (especially for engines with forced induction).

Sheet silicone is used to manufacture gaskets used in automotive engines, transmissions, and other applications.

Automotive body manufacturing plants and paint shops avoid silicones, as they may cause "fish eyes", small, circular craters in the finish.

Additionally, silicone compounds such as silicone rubber are used as coatings and sealants for airbags; the high strength of silicone rubber makes it an optimal adhesive/sealant for high impact airbags. Recent technological advancements allow convenient use of silicone in combination with thermoplastics to provide improvements in scratch and mar resistance and lowered coefficient of friction.

Coatings

Silicone films can be applied to such silica-based substrates as glass to form a covalently bonded hydrophobic coating.

Many fabrics can be coated or impregnated with silicone to form a strong, waterproof composite such as silnylon.

Cookware

- As a low-taint, non-toxic material, silicone can be used where contact with food is required. Silicone is becoming an important product in the cookware industry, particularly bakeware and kitchen utensils.
- Silicone is used as an insulator in heat-resistant potholders and similar items; however, it is more conductive of heat than similar less dense fiber-based products. Silicone oven mitts are able to withstand temperatures up to 260 °C (500 °F), allowing reaching into boiling water.
- Molds for chocolate, ice, cookies, muffins and various other foods.
- Non-stick bakeware and reusable mats used on baking sheets.
- Other products such as steamers, egg boilers or poachers, cookware lids, pot holders, trivets, and kitchen mats.

Defoaming

Silicones are used as active compound in defoamers due to their low water solubility and good spreading properties.

Dry cleaning

Liquid silicone can be used as a dry cleaning solvent, providing an alternative to the traditional chlorine-containing perchloroethylene (perc) solvent. Use of silicones in dry cleaning reduces the environmental impact of a typically high-polluting industry.

Electronics

Electronic components are sometimes encased in silicone to increase stability against mechanical and electrical shock, radiation and vibration, a process called "potting".

Silicones are used where durability and high performance are demanded of components under hard conditions, such as in space (satellite technology). They are selected over polyurethane or epoxy encapsulation when a wide operating temperature range is required (−65 to 315 °C). Silicones also have the advantage of little exothermic heat rise during cure, low toxicity, good electrical properties and high purity.

The use of silicones in electronics is not without problems, however. Silicones are relatively expensive and can be attacked by solvents. Silicone easily migrates as either a liquid or vapor onto other components.

Silicone contamination of electrical switch contacts can lead to failures by causing an increase in contact resistance, often late in the life of the contact, well after any testing is completedUse of silicone-based spray products in electronic devices during maintenance or repairs can cause later failures.

Firestops

Silicone foam has been used in North American buildings in an attempt to firestop openings within fire-resistance-rated wall and floor assemblies to prevent the spread of flames and smoke from one room to another. When properly installed, silicone-foam firestops can be fabricated for building code compliance. Advantages include flexibility and high dielectric strength. Disadvantages include combustibility (hard to extinguish) and significant smoke development.

Silicone-foam firestops have been the subject of controversy and press attention due to smoke development from pyrolysis of combustible components within the foam, hydrogen gas escape, shrinkage, and cracking. These problems have led to reportable events among licensees (operators of nuclear power plants) of the Nuclear Regulatory Commission (NRC).

Silicone firestops are also used in aircraft.

PHOSPHONITRILIC HALIDES

Inorganic polymers, and more speci?cally to a stable inor ganic polymer which possesses a phosphonitrilic back bone. In recent years considerable interest has ‘developed in the production of so called inorganic polymers which possess‘ structural skeletons of “backbones” comprised of elements other than carbon. It is often foundthat in organic polymers exhibit desirable characteristics such as heat resistance‘ which make them particularly applicable for use in modern technology. Polymeric phosphonitrilic halides.

Chemically, the phosphonitrilic halides are known to undergo hydrolysis and ammonolysis reactions due to the reactive nature of the attached halogen atoms. Conse quently, while the phosphonitrilic polymers have excellent heat resistance characteristics, in that they do not tend to depolymerize at temperatures much below about, 350° C., their tendency to undergo chemical degradation has limited their general usefulness. It is, therefore, an object- of the present invention to provide a novel phosphonitrilic polymer which possesses a superior degree of chemical inertness. It is an object of the invention to provide a method by which a high molecular weight phosphonitrilic polymer may be produced from inexpensive and readily available raw materials. A further object of the present invention is to provide a series of novel intermediate compounds from which the presently intended phosphonitrilic polymers may be read ily obtained. These and still further objects of the present invention will become readily apparent to one skilled. in the art form the following detailed description and specific exam ples. _ Broadly, the present invention contemplates a novel phosphonitrilic polymer which is believed to possess the repeating structural unit / I / I it wherein ¢ represents phenyl radicals. (In the body of the present disclosure the symbol ¢ will be used to rep resent the phenyl (C6I-I5-—) radical.) More speci?cally, the invention involves a high molecu lar weight phosphonitrilic polymer which is prepared by the rfollowing three general steps: (1) Reacting monophenyl phosphorus tetrahalide ($C_6H_5PX_4$) with ammonium halide .

Interhalogen compounds

Interhalogen compounds are compounds formed when halogen group elements react with each other. In other words it is a molecule which consists of two or more different elements of group 17. There are four types of interhalogen compounds:

- Diatomic interhalogens (AX)
- Tetratomic interhalogens (AX_3)
- Hexatomic interhalogens (AX_5)
- Octatomic interhalogens (AX_7)
- A halogen with large size and high electropositivity reacts with an element of group 17 with small size and lower electropositivity. As the ratio of radius of larger and smaller halogen increases, the number of atoms in a molecule also increases.

Preparation of Interhalogen compounds:

These molecules are formed due to the direct combination or by the action of a group 17 element with a lower interhalogen compound under specific conditions. For example: At 437K, chlorine reacts with fluorine of equal volume to form ClF. This method is widely used in the production of group 17 fluorides.

INTERHALOGEN COMPOUNDS

$Cl_2 + F_2 \rightarrow 2ClF$ (473K)
$I_2 + Cl_2 \rightarrow 2ICl$

Properties of Interhalogen Compounds:

- These molecules are covalent and diamagnetic in nature.
- The bonds formed between these compounds are more reactive than diatomic halogen bonds.
- The physical properties of these molecules are transitional between its constituents.
- The molecular structure of AX_3 molecules is bent T shaped, an AX_5 molecule is square or pyramidal and the structure of AX_7 is bipyramidal or pentagonal.
- The bond length depends upon the size of the constituent halogens.
- The molecule which consists of lighter group 17 elements is fairly colourless but one which is made up of higher halogens is deeper in colour which is due to the rise in the molecular weight.

Uses of Interhalogen Compounds:

- These are used as non-aqueous solvents.
- They are used as a catalyst in few reactions.
- UF_6 which is used in the enrichment of ^{235}U is produced by using ClF_3 and BrF_3.

$U (s) + 3ClF_3 (l) \rightarrow UF_6 (g) + 3ClF (g)$

- These are used as fluorinating compounds.

Psedohalogen compounds

The **pseudohalogens** are polyatomic analogues of halogens, whose chemistry, resembling that of the true halogens, allows them to substitute for halogens in several classes of chemical compounds.[1] Pseudohalogens occur in **pseudohalogen molecules**, inorganicmolecules of the general forms *Ps*–*Ps* or *Ps*–X (where *Ps* is a **pseudohalogen group**), such as cyanogen; **pseudohalide** anions, such as cyanide ion; inorganic acids, such as hydrogen cyanide; as ligands in coordination complexes, such as ferricyanide; and as functional groups in organic molecules, such as the nitrile group. Well-known pseudohalogen functional groups include cyanide, cyanate, thiocyanate, and azide.

Examples of pseudohalogen molecules

Examples of symmetrical pseudohalogens (*Ps*–*Ps*) include cyanogen $(CN)_2$, thiocyanogen $(SCN)_2$, selenorhodane $(SeCN)_2$, azidodithiocarbonate $(N_3CS_2)_2$. Another complex symmetrical pseudohalogen is dicobalt octacarbonyl, $Co_2(CO)_8$. This substance can be considered as a dimer of the hypothetical cobalt tetracarbonyl, $Co(CO)_4$.

Examples of non-symmetrical pseudohalogens (*Ps*–X), analogous to the binary interhalogen compounds, are cyanogen halides (ICN, ClCN, BrCN), and other compounds. Sometimes nitrosyl chloride NOCl also is considered as pseudohalogen.

Not all combinations are known to be stable.

PSEUDOHALIDES

Pseudohalides are the anions (or functional groups) of corresponding pseudohalogen groups such as cyanides, cyanates, isocyanates, rhodanides (i.e. thiocyanates and isothiocyanates), selenocyanogens, tellurorhodanides and azides.

A common complex pseudohalide is tetracarbonylcobaltate ($Co(CO)_4^-$). The acid $HCo(CO)_4$ is in fact quite a strong acid, though its low solubility renders it not as strong as the true hydrohalic acids.

The behavior and chemical properties of the above pseudohalides are identical to that of the true halide ions. The presence of the internal double bonds or triple bonds do not appear to affect their chemical behavior. For example, they can form strong acids of the type HX (compare HCl to $HCo(CO)_4$), and they can react with metals to form compounds like MX (compare NaCl to NaN_3).

Nanoclusters of aluminium (often referred to as superatoms) are sometimes considered to be pseudohalides since they, too, behave chemically as halide ions, forming $Al_{13}I_2^-$ (analogous to I_3^-) and similar compounds. This is due to the effects of metallic bonding on small scales.

Clathrate compounds of noble gases

Noble gas compounds are chemical compounds that include an element from the noble gases, group 18 of the periodic table. Although the noble gases are generally unreactive elements, many such compounds have been observed, particularly involving the element xenon. From the standpoint of chemistry, the noble gases may be divided into two groups: the relatively reactive krypton (ionisation energy 14.0 eV), xenon (12.1 eV), and radon (10.7 eV) on one side, and the very unreactive argon (15.8 eV), neon (21.6 eV), and helium (24.6 eV) on the other.

History and background

It was initially believed that the noble gases could not form compounds due to their full valence shell of electrons that rendered them very chemically stable and nonreactive.

All noble gases have full *s* and *p* outer electron shells (except helium, which has no *p* sublevel), and so do not form chemical compounds easily. Because of their high ionization energy and almost zero electron affinity, they were not expected to be reactive.

In 1933, Linus Pauling predicted that the heavier noble gases would be able to form compounds with fluorine and oxygen. Specifically, he predicted the existence of krypton hexafluoride (KrF_6) and xenon hexafluoride (XeF_6), speculated that XeF_8 might exist as an unstable compound, and suggested that xenic acid would form perxenate salts.These predictions proved quite accurate, although subsequent predictions for XeF_8 indicated that it would be not only thermodynamically unstable, but kinematically unstable.As of 2013, XeF_8 has not been made, although the octafluoroxenate(VI) anion has been observed.

The heavier noble gases have more electron shells than the lighter ones. Hence, the outermost electrons are subject to a shielding effect from the inner electrons that makes them more easily ionized, since they are less strongly attracted to the positively charged nucleus. This results in an ionization energy low enough to form stable compounds with the most electronegative elements, fluorine and oxygen, and even with less electronegative elements such as nitrogen and carbon under certain circumstances.

True noble gas compounds

These compounds are listed in order of decreasing order of the atomic weight of the noble gas, which generally reflects the priority of their discovery, and the breadth of available information for these compounds, with the exception of radon due to its radioactivity.

Radon compounds

Radon is not chemically inert, but its short half-life and the high energy of its radioactivity make it difficult to investigate its sole described fluoride (RnF_2), its sole described oxide (RnO_3), and their reaction products.

XENON COMPOUNDS

The first published report, in June 1962, of a noble gas compound was by Neil Bartlett, who noticed that the highly oxidising compound platinum hexafluoride ionised O_2 to O+
2. As the ionisation energy of O_2 to O+
2 (1165 kJ mol^{-1}) is nearly equal to the ionisation energy of Xe to Xe^+ (1170 kJ mol^{-1}), he tried the reaction of Xe with PtF_6. This yielded a crystalline product, xenon hexafluoroplatinate, whose formula was proposed to be Xe+[PtF6]−. It was later shown that the compound is actually more complex, containing both $XeFPtF_5$ and $XeFPt_2F_{11}$. Nonetheless, this was the first real compound of any noble gas.

The first binary noble gas compounds were reported in 1962. Neil Bartlett synthesized Xenon tetrafluoride (XeF_4) by subjecting a mixture of xenon and fluorine to high temperature.Rudolf Hoppe, among other groups, synthesized xenon difluoride (XeF_2) by the reaction of the elements. Since these initial studies, other xenon compounds that have been synthesized include other fluorides (XeF_6), oxyfluorides ($XeOF_2$, $XeOF_4$, XeO_2F_2, XeO_3F_2, XeO_2F_4) and oxides (XeO
2, XeO_3 and XeO_4). Xenon difluoride has been produced by the exposure of Xe and F_2 gases to sunlight, a result which eluded observation for 50 years. Xenon fluorides react with several other fluorides to form fluoroxenates, such as sodium octafluoroxenate (Na+
2XeF2− halide reactivity, short-lived excimers of noble gas halides such as $XeCl_2$ are prepared in situ, and are used in the function of excimer lasers.

Recently,xenon has been shown to produce a wide variety of compounds of the type XeO_nX_2 where *n* is 1,2 or 3 and X is any electronegative group, such as CF_3, $C(SO_2CF_3)_3$, $N(SO_2F)_2$, $N(SO_2CF_3)_2$, $OTeF_5$, $O(IO_2F_2)$, etc.; the range of compounds is impressive, similar to that seen with the neighbouring element iodine, running into the thousands and involving bonds between xenon and oxygen, nitrogen, carbon, boron and even gold, as well as perxenic acid, several halides, and complex ions.

A compound with an Xe-Xe bond has been reported, and is noteworthy: the compound $Xe_2Sb_2F_{11}$ contains a Xe–Xe bond, and it is the longest element-element bond known (308.71 pm = 3.0871 Å). Short-lived excimers of Xe_2 are reported to exist as a part of the function of excimer lasers.

Krypton compounds

Following the first successful synthesis of xenon compounds, synthesis of krypton difluoride (KrF_2) was reported in 1963.Krypton gas reacts with fluorine gas under extreme forcing conditions, forming KrF_2 according to the following equation:

$$Kr + F_2 \rightarrow KrF_2$$

KrF_2 reacts with strong Lewis acids to form salts of the KrF^+ and Kr $2F^{+3}$ cations. The preparation of KrF_4 reported by Grosse in 1963, using the Claasen method, was subsequently shown to be a mistaken identification.

Krypton compounds with other than Kr-F bonds (compounds with atoms other than fluorine) have also been described.

Argon compounds

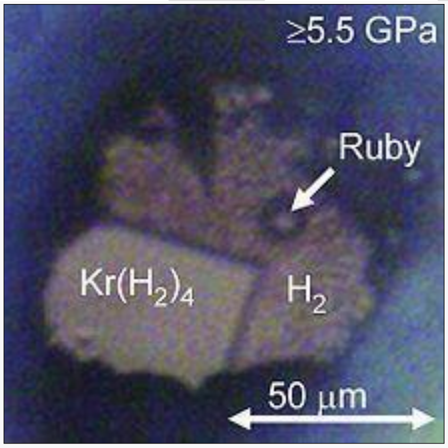
The discovery of HArF was announced in 2000.[15][16] The compound can exist in low temperature argon matrices for experimental studies, and has also been studied computationally. Argon hydride ion ArH+ was obtained in the 1970s. This molecular ion has also been identified in the Crab nebula, based on the frequency of its light emissions.

Neon and helium compounds

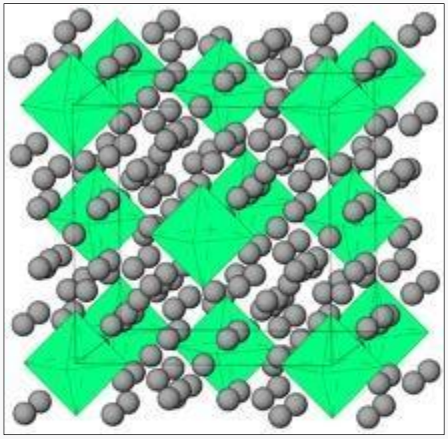
Helium compounds and Neon compounds

A neon compound has yet to be described. There is some empirical and theoretical evidence for a few metastable helium compounds which may exist at very low temperatures or extreme pressures. The stable cation HeH^+ was reported in 1925.

CLATHRATES



$Kr(H_2)_4$ and H_2 solids formed in a diamond anvil cell. Ruby was added for pressure measurement.



Structure of $Kr(H_2)_4$. Krypton octahedra (green) are surrounded by randomly oriented hydrogen molecules.

Prior to 1962, the only isolated compounds of noble gases were clathrates (including clathrate hydrates); other compounds such as coordination compounds were observed only by spectroscopic means. Clathrates (also known as cage compounds) are compounds of noble gases in which they are trapped within cavities of crystal lattices of certain organic and inorganic substances. The essential condition for their formation is that the guest (noble gas) atoms should be of appropriate size to fit in the cavities of the host crystal lattice; for instance, Ar, Kr, and Xe can form clathrates with crystalline β-quinol, but He and Ne cannot fit because they are too small. As well, Kr and Xe can appear as guests in crystals of melanophlogite.

Helium-nitrogen ($He(N_2)_{11}$) crystals have been grown at room temperature at pressures ca. 10 GPa in a diamond anvil cell.[21] Solid argon-hydrogen clathrate ($Ar(H_2)_2$) has the same crystal structure as the $MgZn_2$ Laves phase. It forms at pressures between 4.3 and 220 GPa, though Raman measurements suggest that the H_2 molecules in $Ar(H_2)_2$ dissociate above 175 GPa. A similar $Kr(H_2)_4$ solid forms at pressures above 5 GPa. It has a face-centered cubic structure where krypton octahedra are surrounded by randomly oriented hydrogen molecules. Meanwhile, in solid $Xe(H_2)_8$ xenon atoms form dimers inside solid hydrogen.

Coordination compounds

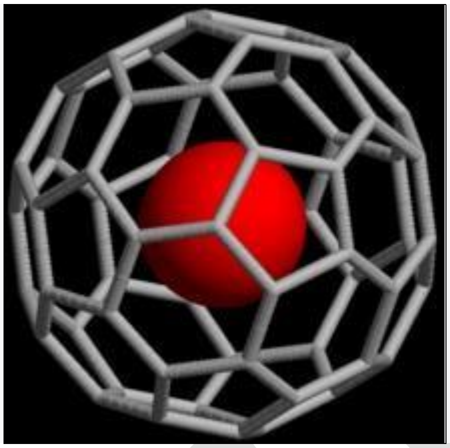
Coordination compounds such as $Ar·BF_3$ have been postulated to exist at low temperatures, but have never been confirmed.[a] Also, compounds such as WHe_2 and $HgHe_2$ were reported to have been formed by electron bombardment, but recent research has shown that these are probably the result of He being adsorbed on the surface of the metal; therefore, these compounds cannot truly be considered chemical compounds.

Hydrates

Hydrates are formed by compressing noble gases in water, where it is believed that the water molecule, a strong dipole, induces a weak dipole in the noble gas atoms, resulting in dipole-dipole interaction. Heavier atoms are more influenced than smaller ones, hence $Xe•5.75\ H_2O$ was reported to have been the most stable hydrate it has a melting point of 24 °C. The deuterated version of this hydrate has also been produced.

Fullerene adducts

Non-metal doped fullerenes



Noble gases can also form endohedral fullerene compounds where the noble gas atom is trapped inside a fullerene molecule. In 1993, it was discovered that when C_{60} is exposed to a pressure of around 3 bar of He or Ne, the complexes He@C_{60} and Ne@C_{60} are formed.Under these conditions, only about one out of every 650,000 C_{60} cages was doped with a helium atom; with higher pressures (3000 bar), it is possible to achieve a yield of up to 0.1%. Endohedral complexes with argon, krypton and xenon have also been obtained, as well as numerous adducts of Helium at C_{60}.

Text Books:

1. Lee, J.D. (2010). *Concise Inorganic Chemistry*. Pearson Education.
2. Shriver, D.F., Atkins P.W & Langford, C.H. (2010). *Inorganic Chemistry.* 5th Ed. Oxford University Press.

POSSIBLE QUESTIONS:

Part-A (1 Mark)

Multiple Choice Questions (Each Question Carry One Mark)

1. Valence shell configuration of Boron

(a) **$2s^2$ p^1** (b) $2s^2$ p^3 (c) $2s^2$ p^2 (d) $2s^1$ p^1

2. Valence shell configuration of gallium

(a) **$3s^2$ p^1** (b) $3s^2$ p^2 (c) $3s^2$ p^3 (d) $2s^2$ p^1

3. Nitrogen is …….

(a) **Lewis base** (b) Lewis acid (c) Base (d) Acid

4. Carborazine is a six-membered aromatic ring with two carbons,

(a) **Two borons** (b) Two oxygen (c) Two nitrogen (d) Two sulphur

5. Halogens are

(a) **Highly electronegative** (b) Low electronegative

(c) Low electropositive (d) Highly electropositive

6. All halogens exist as covalent

(a) Monoatomic molecules (b) Mono and diatomic molecules

(c) Triatomic molecules. (d) D**iatomic molecules.**

7. Argon is used for filling electric bulbs because of its

(a) **Inert nature** (b) Oxidation state (c) Nobel gas (d) Noninert nature

8. White phosphorus reacts with caustic soda.

(a) Oxidation (b) Reduction

(c) Neutralization (d) **Oxidation and reduction**

9. In water borazine hydrolyzes to

(a) Hydrogen (b) B**oric acid, ammonia, and hydrogen**

(c) Ammonia (d) Boric acid

10. Nitrogen is…..

(a) **Lewis base** (b) Lewis acid (c) Base (d) Acid

11. When silicone is burned in air or oxygen, it forms..

(a) **Silicon dioxide** (b) Silicates (c) Silicones (d) Silicon monoxide

12. BrF_3 has the…..

(a) **Highest thermal stability** (b) Low boiling point

(c) High boiling point (d) Lowest thermal stability

13. $B_3N_3H_6 + ? \rightarrow B_3N_3H_9Cl_3$

(a) 3HCl **(b)** 2HCl (c) HCl (d) 4HCl

14. Which of the following has the highest thermal stability

(a) **BrF_3** (b) ClF_3 (c) BH_3 (d) IF_3

15. Clathrates have been used for separation of He and Ne from

(a) Ar, Kr (b) Ar, and Xe, (c) Kr, and Xe, (d) **Ar, Kr, and Xe**,

16. Xenon tetrafluoride is used as a decomposition agent of

(a) Silicate rubber (b) Silica rubber **(c) Silicone rubber** (d) Rubber

17. Molecules containing silicon-oxygen double bonds do exist and are called

(a) silanones (b) **silicates** (c)silicones (d)silanes

18. Silicones, also known as polysiloxanes, are polymers that include any inert, synthetic compound made up of repeating units of

(a) **Siloxane** (b) Silicates (c) Silicones (d) Silcanes

19. Xenon difluoride is a powerful

(a) F**luorinating agent** (b) Reducing agent

(c) Brominating agent (d) Chlorinating agent

20. $? + NH_4Cl \rightarrow 1/n\ (NPCl_2)n + 4\ HCl$

(a) PCl_2 (b)**PCl_5** (c)PCl_3 (d)PCl_4

PART- B (Each Carry 2 Marks)

1. Write a note on silicates.
2. Give some uses of borazine
3. Give the preparation, properties of phosphonitrilic halides.
4. What is borazole? It is similar to which compound?
5. Explain the physical properties of borazine.
6. Give any four uses of Silicates?
7. What is the structure of Xenon Fluoride compounds?
8. Write any two properties of Interhalogen compounds?
9. Give any four applications of Silicones?

10. Define Pseudohalogen compounds?

Part-C (Each Carry 6 Marks)

1. Describe preparation,properties,structure and uses of borazine.
2. Describe preparation,properties , structure and uses of interhalogen compounds.
3. Explain the preparation, properties,structure of silicones.
4. Discuss the preparation, properties,structure of clathrate compounds of nobel gases.
5. Write the preparation, properties and structure of phosphonitrilic halides.
6. Explain the preparation, properties and uses of interhalogen compounds.
7. Describe the preparation, properties and uses of borazine.
8. Describe the preparation, properties and structure of silicones.
9. Explain the preparation, properties and structure of xenon fluorides.

18CHU202
Karpagam Academy of Higher Education
Coimbatore-21
(For the candidate admitted on 2017 onwards)
Department of Chemistry
II- semester
Inorganic Chemistry- II (Metallurgy and S,P-Block Elements

UNIT V- Objective Questions for online examination (Each carry 1 Marks)

Question	**Option 1**	**Option 2**	**Option 3**	**Option 4**	**Answer**
Borazine is an inorganic compound with the chemical formula	$(BH)_3(NH)_3$	$(BH)_4(NH)_4$	$(BH)_3(NH)_4$	$(BH)_3(NH)_2$	$(BH)_3(NH)_3$
Borazine is isoelectronic and isostructural with	benzene	ester	ether	phenol	benzene
Borazine is a	colourless liquid	coloured liquid	solvent	Yellow	colourless liquid
In water borazine hydrolyzes to	hydrogen	boric acid, ammonia, and hydrogen	ammonia	boric acid	boric acid, ammonia, and hydrogen
Borazine can be used as a precursor to grow boron nitride thin films on surfaces,such as	nanomesh	polymer	nanotube	nanoclusters	nanomesh
Heating borazine at 70 °C expels	hydrogen	oxygen	chlorine	sulphur	hydrogen
$B_3N_3H_6 + ? \rightarrow B_3N_3H_9Cl_3$	3HCl	2HCl	HCl	4HCl	3HCl
$? + 6\ NH_3 \rightarrow 2\ B_3H_6N_3 + 12\ H_2$	$3\ B_2H_6$	$2\ B_2H_6$	B_2H_6	$4\ B_2H_6$	$3\ B_2H_6$
Boron is	Lewis acid	Lewis base	acid	base	Lewis acid
Nitrogen is	Lewis base	Lewis acid	base	acid	Lewis base
Carborazine is a six-membered aromatic ring with two carbons, two nitrogens and	two borons	two oxygen	two nitrogen	two sulphur	two boron
A silicate is a compound containing	a cationic silicon compound	an anionic silicon compound	an anionic and cationic silicon compound	silicon compound	an anionic silicon compound

Sand, Portland cement, and thousands of minerals are examples of	silicates	silicones	silica	SiO2	silicates
Silicates are well characterized as	solids	liquids	gases	solids and gases	solids
Portland cement is produced by hydration of clinker, which consists of	calcium silicates	magnesium silicates	calcium sulphate	magnesium sulphate	calcium silicates
Silica is found in nature as the mineral quartz, and its	polymorphs	monomorphs	polymers	oligomers	polymorphs
Silicones, also known as polysiloxanes, are polymers that include any inert, synthetic compound made up of repeating units of	siloxane	silicates	silicones	silanes	siloxane
silicones consist of an inorganic	silicon-oxygen backbone chain	silicon-sulphur backbone chain	oxygen backbone chain	silicon backbone chain	silicon-oxygen backbone chain
Molecules containing silicon-oxygen double bonds do exist and are called	silanones	silicates	silicones	silanes	silanones
When silicone is burned in air or oxygen, it forms	silicon dioxide	silicates	silicones	silicon monoxide	silicon dioxide
Silicones have	low toxicity	high toxicity	no toxicity	toxicity	low toxicity
an inorganic compound with the formula (NPCl2)3	Hexachlorophosphazene	phosphazene	Hexaphosphazene	chlorophosphazene	Hexachlorophosphazene
Hexachlorophosphazene together with the related $(NPCl_2)_4$ are precursors to inorganic polymers called	Hexachlorophosphazene	polyphosphazenes.	Hexaphosphazene	chlorophosphazene	polyphosphazenes.
Hexachlorophosphazene is a precursor to poly(dichlorophosphazene) or	inorganic rubber	organic rubber	chlorophosphazene	Hexaphosphazene	inorganic rubber
$? + NH_4Cl \rightarrow 1/n\ (NPCl_2)_n + 4\ HCl$	PCl2	PCl5	PCl3	PCl4	PCl_5
An interhalogen compound is a molecule which contains two or more different	halogen atoms	chlorine atoms	oxygen atoms	sulphur atoms	halogen atoms
Most interhalogen compounds known are	binary elements	tertiary elemens	triply elements	elements	binary elements

Chlorine monofluoride is the	lightest interhalogen compound	interhalogen compound	halogen compound	heaviest interhalogen compound	lightest interhalogen compound
ClF is a colorless gas with a normal boiling point of	−100 ℃.	−400 ℃.	−300 ℃.	−200 ℃.	−100 ℃.
Iodine monofluoride unstable and decomposes at	0 ℃	−400 ℃.	−300 ℃.	−200 ℃.	0 ℃
ClF_3 is the	most reactive of the XY_3 interhalogens.	unreactive of the XY_3 interhalogens.	reactive of the XY_3 interhalogens.	most unreactive of the XY_3 interhalogens.	most reactive of the XY_3 interhalogens.
ICl_3 is the	least reactive	average reactive	most reactive	reactive	least reactive
BrF_3 has the	highest thermal stability	low boiling point	high boiling point	lowest thermal stability	highest thermal stability
Most interhalogens are	covalent gases	ionic gases	covalent solids	covalent liquids	covalent gases
All interhalogens are	diamagnetic	ferrimagnetic	ferromagnetic	paramagnetic	diamagnetic
Smaller interhalogens, such as ClF, can form by direct reaction with	pure halogens	pure sulphides	pure chlorides	pure oxides	pure halogens
BrF_5 is too reactive to generate	fluorine	iodine	bromine	chlorine	fluorine
A number of interhalogens, including IF_7, are used to form	polymorphs	polyiodides	polybromides	polyhydrides	polyhalides
F_2 reacts with Cl_2 at 250 ℃ to form two molecules of	ClF.	Cl	F.	ClBr.	ClF.
I_2 reacts with diatomic fluorine at only	35 ℃		25℃	55℃	35 ℃
Among the hexatomic interhalogens, IF_5 has a	higher boiling point	lower melting point	higher melting point	lower boiling point	higher boiling point
The interhalogen IF7 can be formed by reacting palladium iodide with	fluorine	bromine	iodine	chlorine	fluorine
The pseudohalogens are	polyatomic analogues of halogens	polyatomic analogues of sulphides	polyatomic analogues of hydrides	polyatomic analogues of oxides	polyatomic analogues of halogens
Examples of symmetrical pseudohalogens (*Ps*–*Ps*) include	cyanogen	iodide	bromide	cyanide	cyanogen

The word clathrate is derived from the Latinclatratus meaning with	bars or lattice	crystal	bars	lattice	bars or lattice
clathrates are	Inclusion compounds	organic compounds	inorganic compounds	exclusion compounds	Inclusion compounds
The natural silica clathrate mineral, chibaite was recently described from	japan	china	india	australia	japan
Many clathrates are derived from organic	hydrogen-bonded frameworks	chloride-bonded frameworks	oxygen-bonded frameworks	sulphur-bonded frameworks	hydrogen-bonded frameworks
Metal organic frame works forms	clathrates	ring compouns	ring compounds	sulphur compounds	clathrates
The most famous clathrates are	methane clathrates	ethane clathrates	butane clathrates	propane clathrates	methane clathrates
Clathrates are compounds of	noble gases in which they are trapped within cavities of crystal lattices of certain organic and inorganic substances	solids	gases	liquids	noble gases in which they are trapped within cavities of crystal lattices of certain organic and inorganic substances
Clathrates have been used for separation of He and Ne from	Ar, Kr, and Xe,	Ar, Kr	Ar, and Xe,	Kr, and Xe,	Ar, Kr, and Xe,
Xenon difluoride is a powerful	fluorinating agent	reducing agent	brominating agent	chlorinating agent	fluorinating agent
Xenon difluoride as	low vapor pressure	high vapor pressure	no vapor pressure	presssure	low vapor pressure
Xenon difluoride is a	linear molecule	square pyrimadal	see saw	tetrahedral	linear molecule
Xenon difluoride is a strong fluorinating and	oxidising agent	reductant	oxidant	reducing agent	oxidising agent
Xenon difluoride is also used as an isotropic gaseous etchant for	silicon	silicates	silica	Si	silicon
Fluorine is the main etchant in the	silicon etching process	silicate etching process	silica etching process	Si	silicon etching process
Xenon tetrafluoride is a colorless	crystalline substance	inorganic substance	deliquescent substance	amorphous substance	crystalline substance

Xenon tetrafluoride is used as a decomposition agent of	silcone rubber	silica rubber	silicate rubber	rubber	silicone rubber
Xenon hexafluoride the compound is	monomeric	polymers	polymorphs	dimeric	monomeric
XeF6 reacts with strong	fluoride acceptors	chloride acceptors	bromide acceptors	iodide acceptors	fluoride acceptors

Reg. No.: ----------------------------- [18CHU202]

KARPAGAM ACADEMY OF HIGHER EDUCATION
Deemed to be University
(Established Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

B.Sc., Degree Examination
(For the candidates admitted from 2018 & onwards)

I- B.Sc., Chemistry

Ist Internal Test

Inorganic Chemistry-II
Metallurgy and S-block & P-block elements

Time: 2 Hours Maximum: 50 marks

Date:

Section-A 20X1=20

Answer all the questions

1. Ellinghan diagrams can be used to predict the converion
   a. **Metals into their oxides** b. Metal oxide into metal c. Impure metal into pure metal
   d. Ore into metal

2. The ore of Ti is
   a. Tl_2O b**. TiO_2** c. $CaTiO_3$ d. $TiCl_4$

3. Which one of the following is used for the manufacture of surgical instruments
   a. WO_3 b. WO_2 c. W d. **W with Co and Cr**

4. The standard free energy change of the formation of metal oxides is
   a. Positive **b. Negative** c. One d. Zero

5. The following which one is rare earth element
   a. Ti b. Mn c. V **d. Tl**

6. For the dyeing of wool and silk which of the following is used
   a. **Mo compounds** b. W compounds c. V compounds d. Ti compounds

7. The art of winning the a metal from its ore is known as
   a. Minerals b. Ores **c. Metallurgy** d. Matrix

8. The ore which is mined is usually associated with rocky impurities called
   a. Flux b. Salt c. Slag **d. Gangue**

9. Which of the following metals can be obtained by the electrolytic reduction of its fused halide
   a. Fe b. Hg **c. Na** d. W

10. Germanium and gallium may be purified by
   a. Electrolysis b. Recrystallization c. Distillation **d. Zone refining**

11. DMG is used for the detection of
   a. Zn^{2+} b. Ca^{2+} c. Fe^{2+} **d. Ni^{2+}**

12. Pick out the neutral ligand?
   a. Chloride b. Cyanide c. Hydroxide **d. Carbon monoxide**

13. The metal ion largely responsible for hardness of water are
   a. Ca(II) and Mg(II) **b. Ca(II) and Zn(II)** c. Ca(II) and Cu(II) d. Mg(II) and Al(III)

14. Alkali metals are strong reducing agents due to
   a. **Low ionisation energy** b. Large ionic radii c. High enthalpy of hydration
   d. Potential value

15. Identify the process when an ore is heated in the absence of O2
   a. Smelting **b. Calcination** c. Roasting d. Carbonisation

16. Argentite is the ore of
   a. Gold b. Zinc **c. Silver** d. Mercury

17. In alumino thermic process which is used a s reducing agent
   a. Ca powder b. Mg powder **c. Al powder** d. Fe powder

18. Identify the process when an ore is heated in the presence of excess of air
   a. Smelting b. Calcination **c. Roasting** d. Carbonisation

19. In electrolytic refining method, the impurities are collected below the
   a. Cathode **b. Anode** c. Electrode d. Vessel

20. Zone refining method is also known as
   a. Electrolytic refining b. Vapour phase method **c. Fractional crystalisation**
   d. Chromatography method

Section B 3x2 = 6

Answer all the questions

21. Define Metallurgy

22. What is standard electrode potential?

23. Write a short note on flame colour of the ns^1 group elements?

Section C 3x8 = 24

Answer all the questions

24. a. Explain in brief characterization and uses of “Elligham Diagram”?

Or

b. Write a note on i) Van Arkel- De Bore process ii) Mond’s process

25. a. What is Hydrometallurgy? Compare with cyanide process of Au and Ag?

Or

b. Briefly explain melting point and boiling point, reducing nature of group-I metals?

26. a. What are the diagonal properties of Li compare with Mg?

Or

b. Explain the reaction of ns^2 metals with Hydrogen, Nitrogen, Oxygen and Water?

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Section B 3x2 = 6

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49. Write a short note on flame colour of the ns^1 group elements?

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Answer all the questions

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Or

b. Write a note on i) Van Arkel- De Bore process ii) Mond’s process

51. a. What is Hydrometallurgy? Compare with cyanide process of Au and Ag?

Or

d. Briefly explain melting point and boiling point, reducing nature of group-I metals?

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I- B.Sc., Chemistry
IInd Internal Test
Inorganic Chemistry-II
Metallurgy and S-block & P-block elements

Time: 2 Hours   Maximum: 50 marks
Date: 5.2.2019 (FN)

Section-A   20X1=20

Answer all the questions

1. Which is not true with EDTA?
a. Relatively low price   b. High water solubility   c. Good chelating agent   d. Denticity is four

2. A elements are named as alkali metals because
a. Their oxides are basic   b. Their oxide and hydroxides are water soluble
c. Hydroxides are water soluble   d. They are found in earth

3. The oxides of beryllium BeO is
a. Acidic   b. Basic   c. Amphoteric   d. Neutral

4. Carbonates of lithium are not stable like that of sodium due to
a. Low electronegativity   b. Low electropositivity   c. Low charge density   d. High charge density

5. Nitrates of which pair of elements give different products on thermal decomposition?
a. Na K   b. Mg Ca   c. Li Na   d. Li Ca

6. Which one of the following carbonate is water insoluble?
a. Na_2CO_3 b. K_2CO_3 c. $(NH_4)_2CO_3$ d. $CaCO_3$

7. Which one of the following alkali metals forms only normal oxide when it reacts with O2?
a. Lithium   b. Sodium   c. Potassium   d. Rubidium

8. NaOH is named as caustic soda because
a. It corrodes the organic tissues   b. It is used in soda water   c. It reacts with chlorine gas
d. It reacts with fats to form soap

9. Which ion will have maximum value of heat of hydration?
a. $A1^{+3}$ b. Cs^{+} c. Ba^{+} d. Mg^{+2}

10. The temporary hardness of water is due to calcium bicarbonate can be removed by adding
a. $CaCO_3$ b. $Ca(OH)_2$ c. $CaCl_2$ d. HCl

11. DMG is used for the detection of
a. Zn^{2+} b. Ca^{2+} c. Fe^{2+} d. Ni^{2+}

12. The metal ion in haemoglobin assumes
a. Square planar structure b. Tetrahedron structure c. Octahedron structure d. Linear structure

13. Alkali metals are strong reducing agents due to
a. Low ionisation energy b. Large ionic radii c. High enthalpy of hydration d. Potential value

14. Among the alkali metals, caesium should be
a. Least ionisable b. Lightest of all c. More electropositive than Fransium
d. Having low b.p and m.p

15. In beryllium acetate, the Be atoms are arranged in
a. Tetrahedrally b. Hexagonal c. Octahedrally d. Square Planar

16. How many number of oxalate ligand present in the basic beryllium acetate
a. 8 b. 7 c. 4 d. 6

17. EDTA is an
a. Mono dentate b. Bi dentate c. Chelating d. Tri dentate

18. Be compounds are more toxic due to
a. High boiling point b. Low solubility c. Complex formation with enzymes
d. Low Melting point

19. The compound crown-4 is highly suitable for
a. Li^{+} b. Ca^{2+} c. Na^{+} d. Mg^{2+}

20. Which one of the following fact is favours the complex formation
a. Large ions b. Low charged c. Lack of empty orbits d. Small size and High charge

Section B 3x2 = 6

Answer all the questions

21. Define Crown ethers
22. List out the elements present in Group-14?
23. Write any two uses of EDTA?

Section C 3x8 = 24

Answer all the questions

24. a. Explain in brief solubility and thermal stability of oxides of 1s group elements.

Or

b. Write a note on sulphates and nitrate salts of 2s group elements and its uses

25. a. Explain the structure of basic beryllium acetate and beryllium nitrate

Or

b. Write a note on solutions of alkali metals in liquid ammonia and their properties.

26. a. Give an account of EDTA complex of Ca^{2+} and Mg^{2+} ions and its biological application?

Or

b. Briefly explain the structure, properties and uses of Crown ethers and Cryptates of S-block elements?

Reg. No.: -----------------------------   [18CHU202]

KARPAGAM ACADEMY OF HIGHER EDUCATION
Deemed to be University
(Established Under Section 3 of UGC Act 1956)
COIMBATORE-641 021

B.Sc., Degree Examination
(For the candidates admitted from 2018 & onwards)

I- B.Sc., Chemistry
IInd Internal Test
Inorganic Chemistry-II
Metallurgy and S-block & P-block elements

Time: 2 Hours   Maximum: 50 marks
Date: 5.2.2019 (FN)

Section-A   **20X1=20**

Answer all the questions

27. Which is not true with EDTA?
a. Relatively low price   b. High water solubility   c. Good chelating agent   **d. Denticity is four**

28. A elements are named as alkali metals because
a. Their oxides are basic   b**. Their oxide and hydroxides are water soluble**
c. Hydroxides are water soluble   d. They are found in earth

29. The oxides of beryllium BeO is
a. Acidic   b. Basic   **c. Amphoteric**   d. Neutral

30. Carbonates of lithium are not stable like that of sodium due to
a. Low electronegativity   **b. Low electropositivity**   c. Low charge density   d. High charge density

31. Nitrates of which pair of elements give different products on thermal decomposition?
a. Na K   b. Mg Ca   **c. Li Na**   d. Li Ca

32. Which one of the following carbonate is water insoluble?
a. Na_2CO_3 b. K_2CO_3 c. $(NH_4)_2CO_3$ **d. $CaCO_3$**

33. Which one of the following alkali metals forms only normal oxide when it reacts with O2?
a. **Lithium**   b. Sodium   c. Potassium   d. Rubidium

34. NaOH is named as caustic soda because
a. **It corrodes the organic tissues**   b. It is used in soda water   c. It reacts with chlorine gas
d. It reacts with fats to form soap

35. Which ion will have maximum value of heat of hydration?
a. **$A1^{+3}$**   b. Cs^{+} c. Ba^{+} d. Mg^{+2}

36. The temporary hardness of water is due to calcium bicarbonate can be removed by adding
a. $CaCO_3$ **b. $Ca(OH)_2$** c. $CaCl_2$ d. HCl

37. DMG is used for the detection of
a. Zn^{2+} b. Ca^{2+} c. Fe^{2+} **d. Ni^{2+}**

38. The metal ion in haemoglobin assumes
a. Square planar structure b. Tetrahedron structure **c. Octahedron structure** d. Linear structure

39. Alkali metals are strong reducing agents due to
a. **Low ionisation energy** b. Large ionic radii c. High enthalpy of hydration d. Potential value

40. Among the alkali metals, caesium should be
a. Least ionisable b. Lightest of all c. More electropositive than Fransium
d. Having low b.p and m.p

41. In beryllium acetate, the Be atoms are arranged in
a. Tetrahedrally b. Hexagonal c. Octahedrally d. Square Planar

42. How many number of oxalate ligand present in the basic beryllium acetate
a. 8 b. 7 c. 4 **d. 6**

43. EDTA is an
a. Mono dentate b. Bi dentate **c. Chelating** d. Tri dentate

44. Be compounds are more toxic due to
a. High boiling point b. Low solubility **c. Complex formation with enzymes**
d. Low Melting point

45. The compound crown-4 is highly suitable for
a. **Li^+** b. Ca^{2+} c. Na^+ d. Mg^{2+}

46. Which one of the following fact is favours the complex formation
a. Large ions b. Low charged c. Lack of empty orbits **d. Small size and High charge**

Section B 3x2 = 6

Answer all the questions

47. Define Crown ethers

48. List out the elements present in Group-14?

49. Write any two uses of EDTA?

Section C 3x8 = 24

Answer all the questions

50. a. Explain in brief solubility and thermal stability of oxides of 1s group elements.

Or

b. Write a note on sulphates and nitrate salts of 2s group elements and its uses

51. a. Explain the structure of basic beryllium acetate and beryllium nitrate

Or

b. Write a note on solutions of alkali metals in liquid ammonia and their properties.

52. a. Give an account of EDTA complex of Ca^{2+} and Mg^{2+} ions and its biological application?

Or

b. Briefly explain the structure, properties and uses of Crown ethers and Cryptates of S-block elements?

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Section-A 20X1=20

Answer all the questions

1. Phosphorus exist in many forms like
a. **Red phosphorus, white phosphorus** b. Yellow phosphorus, white phosphorus
c. Blue phosphorus, white phosphorus d. Red phosphorus, violet phosphorus

2. an example of catenation
a. **S_8** b. S_7 c. S_6 d. S_5

3. Catenation is not shown among
a. Alkali and alkaline earth metals **b. Halogens and noble gases**
c. Alkaline earth metals and noble gases d. Alkali metals and noble gases.

4. Carbon compounds are the best example of a group of
a. **Covalently bonded compounds** b. Ionic bonded compounds
c. Metallic bonded compounds d. Vanderwals bonded compounds

5. Borazine is iso-electronic and iso-structural with
a. **Benzene** b. Ester c. Ether d. Phenol

6. Borazine can be used as a precursor to grow boron nitride thin films on surfaces,such as
a. **Nanomesh** b. Polymer c. Nanotube d. Nanoclusters

7. The general electronic configuration of nitrogen group is
a. **$ns^2 np^3$** (b)$ns^2 np^4$ (c)$ns^1 np^3$ (d)$ns^2 np^4$

8. Bismuth has a……
a. **+3 oxidation state** b. +2 oxidation state c. +1 oxidation state
d. +4 oxidation state

9. Chalcogens have…..
a. Two electrons in their outermost shell.
b. **Six electrons in their outermost shell**.
c. Five electrons in their outermost shell.
d. Three electrons in their outermostshell.

10. The metallic character of chalcogens elements
a. **Increases down the group** b. No change down the group
c. Decreases and then increases down the group d. Decreases down the group

11. Halogens are
a. **Highly electronegative** b. Low electronegative c. Low electropositive
d. Highly electropositive

12. Argon is used for filling electric bulbs because of its
a. **Inert nature** b. Oxidation state c. Nobel gas d. Noninert nature

13. White phosphorus reacts with caustic soda.
a. Oxidation b. Reduction c. Neutralization d. **Oxidation and reduction**

14. Al and Ga form
a. Acidic oxides **b. Amphoteric oxides** c. Basic oxides d. Carbonates

15. In and Tl forms
a. **Basic oxides** b. acidic oxides c. carbonates d. acidic and basic oxides

16. Boron trihalides are covalent in character due to their
a. **Smaller size** b. Larger size c. High electropositivity d. High nuclear charge

17. Electronic configuration of tin
a. $5s^2p^1s^2p^2$ **b. $5s^2p^1s^2p^1$** c. $6s^2p^1s^2p^1$ d. $4s^2p^1s^2p^1$

18. Chlorine atom is…..
a. **Lewis base** b. Lewis acid c. Base d. Acid

19. When silicone is burned in air or oxygen, it forms..
a. **Silicon dioxide** b. Silicates c. Silicones d. Silicon monoxide

20. BrF_3 has the…..
a. **Highest thermal stability** b. Low boiling point c. High boiling point
d. Lowest thermal stability

Section B 3x2 = 6

Answer all the questions

21. Define Electrogain enthalphy and ionization energy.
22. List out the uses of silicates.
23. What is Inter halogen and Pseudohalogen compounds?

Section C 3x8 = 24

Answer all the questions

24. a) Give an account of alltrophy forms of Carbon and Phosphours.

(OR)

b) Discuss the structure and properties of oxides of phosphorus and sulphur.

25. a) Explain the anomalous behaviour of Nitrogen and Oxygen?

(OR)

b) Describe preparation, properties, structure and uses of phosphonitrile compounds.

26. a) Why borazine is called as inorganic benzene and write their preparation, properties and uses?

(OR)

b) Briefly explain the diagonal relationship of B and Si