CHAPTER 13
STUDY OF GROUP CHEMISTRY OF ELEMENTS

(General Remarks)

The study of the chemistry of elements in a group may appear to be rather cumbersome and difficult particularly when the student is required to enumerate the points of comparison and contrast between two elements or sets of elements in the same group or of different groups. But the vast informations of the descriptive chemistry of groups of elements can easily be grasped if it is remembered that the physical and chemical properties of elements depend mostly on the electronic configurations. This is more readily understood by the elementary students who can easily correlate the facts with the electronic arrangements in the atoms of the group of elements under study. However, a knowledge of the important facts regarding the group chemistry of the elements is also necessary for correlation. This can be gathered from a general idea.

For instance, the mode of occurrence in nature of a particular element or group of elements may be easily understood from the point of view of electronic structures. The alkali metals cannot exist in nature in the free state, so also halogens. A student who is familiar with the chemical reactivity of these groups of elements can easily understand why these elements do not occur in nature in the free state. It is to be remembered that elements can occur in nature (in the atmosphere, in the earth and in the sea). On earth, the animal kingdom, the plant kingdom and the minerals are the possible sources of elements. Which element is found in what sources is governed mainly by its chemical reactivity which in turn is governed by the electronic structure. Water soluble salts, such as sodium chloride, magnesium chloride etc.are abundantly available in the sea water because these might have been washed down by water and ultimately have

become concentrated in the sea water. Most of the transition metals occur in the mineral kingdom because these are stabilised in combinations as oxides, sulphides, silicates etc. Carbon compounds obviously will be found in the plants and the animals. Thus the mode of occurrence can be correlated from the properties of the elements and their electronic structures.

The study of group chemistry of elements can be simplified by keeping in view the following points of discussion :—

I   Grouping of the elements in the Periodic Table and the electronic structures.

II   Discussions of the physical properties.

III   Discussions of the chemical properties.

IV   Extraction processes.

V   Some important compounds.

VI   Uses and industrial applications.

The descriptive chemistry of an individual element also follows a similar method of study comprising the above mentioned points. A short discussion of the important points are given below.

I Grouping in the Periodic Table and the Electronic Structure

The set of given elements belong to a particular group in the Periodic Table and this must be mentioned at the very outset in the descriptive chemistry. Their electronic structure will make it easier to give a description of the main features of the properties of the elements and hence this must be illustrated at this stage.

II Physical Properties

(1) The main points to be touched regarding the physical properties may have some obvious bearing with the electronic structure. The physical state or the state of aggregation has to be mentioned. The element or elements may be solid or liquid or gaseous, or some may be solid, some may be liquid or gaseous at the ordinary temperature, and there may be some apparent reasons for the same. If possible, an explanation may be given as to why the element or elements exist in one of the three states at the ordinary temperature. Mention here must be made regarding their metallic, non-metallic or metalloidic characters

if the elements are solid at ordinary temperatures. Colour, odour, hardness and density, may also be mentioned, if necessary ; otherwise, may be omitted.

It must be remembered that it is not necessary to give values for the physical properties and constants. But the gradation and a rough idea regarding the variations in physical properties may be illustrated in a qualitative manner. This again follows from the electronic structures to a great extent as given in Chapter 4.

(2) Atomic sizes, ionic radii and ionization potential can be discussed in relation to the electronic arrangements. As mentioned before, these considerations have great influence on the chemical behaviour of the elements in a group and the overall structures of the molecules.

(3) The melting and the boiling points of the elements and their compounds depend on the bonding characteristics and if they are explained from this point, it will give better understanding. For instance, alkali metals from Li to Cs have gradually low melting points whereas halogens from F_2 to I_2 exhibit the reverse phenomena and pass from gaseous state to solid at ordinary temperature.

(4) Solubility or insolubility in water and other well-known solvents, if necessary, may be mentioned. If there is a chemical reaction with water it should be mentioned in the discussions under the chemical properties. The solubility, apart from other characteristics, gives some idea about the bonding system in the element and their compounds.

(5) In the case of metals, conduction of heat and electricity may be mentioned in relation to the electronic configuration. Metals generally conduct electricity whereas non-metals are non-conductor. The presence of mobile electrons in metals arising out of the valence electrons gives an idea about the electrical condictivity.

(6) If the elements have characteristic spectra with striking features involving particular electronic arrangements, a mention of this point will be justified. For instance, the importance of spectral studies in the case of inert gases and other familiar group of elements are to be discussed.

(7) Special physical properties, such as allotropic forms, polymorphism, specific heat, crystal structures may be mentioned where necessary. As in the case of carbon, phosphorus, sulphur groups these features are of importance.

III Chemical Properties

The description of chemical properties of element in a group may deal with the following points :—

(1) *Valence state:* (Oxidation states) and the bonding system of the elements can be discussed with examples. Here again, the complete understanding of the electronic structure is a great help to develop this point which must be illustrated with examples. The oxidation state of alkali metals is +1, whereas in the case of the nitrogen group a number of oxidation states are possible. Similarly transition metals show variable oxidation states. These can be readily explained if the electronic structures of the elements are known.

(2) *Action of air* : A discussion regarding the stability or instability of the elements in air is quite interesting. Since air contains oxygen, nitrogen, moisture and carbondioxide etc., a description of the action of air on the elements naturally entail the effect of these agents at the ordinary condition and other conditions. For instance, burning of alkali metals and phosphorus in presence of air due to the combination with oxygen, formation of an oxide or carbonate films on the surface of metals or rusting of iron in moist air, are some of the examples. Everlasting brightness of gold and platinum indicates their inactivity with air. These facts are interesting and invoke inquisitiveness in the minds of students when the explanation of these facts are correlated with atomic structure.

(3) *Action of water* : Some elements react vigorously with water and some are attacked very slowly. The chemical reaction with water can be discussed from the point of view of the electronic structure. Water may give various types of reactions with elements. Hydrolysis may occur in which case the elements can combine both with H and OH parts of H_2O forming a hydride and a hydroxide of the element as in the case of chlorine :

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl$$
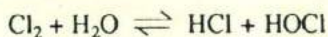
The water molecule may be reduced by an element thereby liberating free hydrogen gas if the reduction potential favours displacement reaction :

$$2 \, Na + 2 \, H_2O \quad = \quad 2 \, NaOH + H_2$$

Some elements decompose water at red heat. Why do such phenomena occur ?

(4) Action of acids : In this connection, actions of more well-known acids, such as HCl, HNO_3 and H_2SO_4 may be mentioned. Only the cases which require reference to special acids, may be included. In some cases the concentration of the acids and the temperature of reactions may be discussed. The special case of nitric acid being an acid and also an oxidising agent may be touched particularly in the case of its reaction with metals.

(5) Action of alkalis : The reactions of both the caustic alkalis and ammonium hydroxide may be discussed if applicable. Here also the state and concentrations of alkali solutions produce different results with different elements. For instance, some metals may not react with alkali at all (Au and Pt) either in the solid or in solutions at any temperature. Metals like zinc and aluminium dissolve in alkali solution evolving hydrogen. The halogens produce various oxidising products in alkali solutions depending upon the concentration.

(6) Action of halogens : Halogens (particularly F, Cl, Br) being a group of most reactive substances provide an opportunity to discuss the formation of halides of the given group of elements by direct reactions. The reactions with halogens throw a great deal of light on the reactivity of the elements under discussion and their normal oxidation states. The formation of halides of the elements having a general formula MX, MX_2, MX_3, M_2X_3, MX_4 etc. represent reactions between groups of elements which are either very uniform as in the case of alkali and alkaline earth metals or show different oxidation states as in the case of transition metals.

(7) Action of hydrogen : The activity of an element or a group of elements presents an interesting study because of the state in which hydrogen enters into combination. In the case of alkali and alkaline earth metals, the product known as hydrides, contain hydrogen as H^- ions and are crystalline solids. With group III elements, particularly boron, a very large number of complex polymer hydrides are generally formed. With transition metals they form interstitial types of compounds and in some cases hydrogen is absorbed in considerable quantity as in the case of Pd, Pt etc. With halogens it forms the

well-known hydracids in which hydrogen may be regarded as H^+ ions particularly in aqueous solutions as H_3O+.

(8) Special properties : Under this discussion other interesting reactions or formations of particular compounds peculiar to the group of elements may be mentioned. This may include formation of complex compounds as in the case of transition metals, departure from the general behaviour as in the case of similarity of Li and Mg, Be and Al etc.

IV Extraction Processes

The extraction processes and isolation of an element or group of elements in the Periodic Table naturally depend upon the mode of occurrence. It must be remembered that the extraction process from the naturally occuring materials require the understanding of the electronic structure of the element under consideration. Some of the metals, such as silver, gold, mercury, platinum and also the inert gases, occur free in nature. Others are found in the combined state generally known as minerals. A mineral which contains sufficient quantity of an element from which it can be readily and profitably extracted is known as an ore. The ore of an element has the element in combination with other elements in which it is most stable. Alkali metals are stable as halides and occur in nature as halide. Most metals occur as sulphides or oxides as well as carbonates, silicates and phosphates. These may be simple or complexed with other ores and minerals. The geological factor such as aging under pressure markedly decreases the chemical reactivity of minerals and ores and requires chemical treatment for *opening up* of the ores for the extraction of the particular element. Hence a short discussion of the principle involved in the process of extraction gives a good point in the description of the chemistry of an element or a group of elements.

V Compounds

Some important and well-known compounds may be briefly described giving special features as regards their formation, properties, structures and applications.

VI Uses and Industrial Applications

The study of chemistry as a science embodies the knowledge of elements and their compounds for useful purposes. This is the very basis of our civilization.

Hence a mention regarding some useful applications makes an interesting description.

THE MOST BASIC METALS : THE ALKALI METALS

(The Elements of Group IA)

Li—Lithium,	Na—Sodium,	K—Potassium
Rb—Rubidium,	Cs—Cesium,	Fr—Francium.

Of all the elements, the elements of Group IA, generally known as the alkali metals, have the simplest chemistry because these elements have a single electron in the outermost energy level. The inner electrons in the alkali metals screen the bulk of the positive charge on the nucleus so effectively that the single electron moves under the influence of a positive electric field resembling that of a hydrogen atom. The chemistry of the alkali elements is, thus, largely dependent upon this single electron.

The electronic structure : The electronic structures of the alkali metals are given in Table 14.1.

Table 14.1. Electronic structures of alkali metals.

At No.	Element	Electronic structures	Valence electron
3	Li	He core, $2s^1$	$2s^1$
11	Na	Ne core, $3s^1$	$3s^1$
19	K	Ar core, $4s^1$	$4s^1$
37	Rb	Kr core, $5s^1$	$5s^1$
55	Cs	Xe core, $6s^1$	$6s^1$
87	Fr	Rn core, $7s^1$	$7s^1$

It is to be remembered that an s electron having $n=1$ has one spherical zone of maximum charge density in the electron cloud and $n=2$ has two spherical zones and so on. Each horizontal row gives symmetry of the electron cloud corresponding to $l = 0, 1, 2, 3$ or s, p, d and f electrons.

It can be seen from the electron structure diagram in Table 14.1 that each alkali element has a solitary unpaired electron in the outermost shell. As the atomic number increases from Li (3) to Fr (87) thereby building the positive charges on the nucleus, the electrons of the inner completed shells are pulled very close to the nucleus. The completed shells of negative electricity are very effective in neutralizing the attraction of the positive nucleus on the solitary electron in the outermost energy level. The outermost shell is, therefore, very diffuse and the electron can be easily removed from the atom.. It is this factor which is largely responsible for the chemistry of alkali metals.

General Characteristics

Physical properties : Some of the physical properties of the alkali metals are given in Table 14.2 which are explained from the point of view of the electronic structure.

Table 14.2. Physical characteristics of alkali metals.

Physical properties	Li	Na	K	Rb	Cs	Fr
At. No.	3	11	19	37	55	87
At. Wt.	6.94	22.997	39.009	85.48	132.91	223
Atomic radius (Å)	1.5	1.86	2.27	2.43	2.62	2.7
Ionic radius (Å)	0.60	0.95	1.33	1.48	1.69	—
Ionization potential (ev)	5.4	5.1	4.3	4.2	3.9	—
Electronegativity	1.0	0.9	0.8	0.8	0.7	—
Density at 20°C(g./cm.^{3})	0.534	0.97	0.86	1.53	1.90	—
Melting point (°C)	186	97.6	62.3	38.5	28.5	—
Boiling point (°C)	1336	880	760	696	670	—
Electrode potentials M/M$^+$ (volts)	3.02	2.71	2.92	2.99	3.02	—

The above physical properties may be linked with the loose bonding of the single valence electron in the alkali metals. The values of ionization potentials indicate that it requires only 5.4 ev to remove $2s^1$ electron from Li (as compared to 13.6 ev required to remove $1s^1$ electron from H). The ionization energy decreases from Li to Cs because of the increasing shielding effect of the inner core of completed shell on the nuclear charge of the atoms. Thus, the ease with

which the valence electron is lost, increases with the increasing atomic radius since the valence electron occupies greater volume as the atomic number increases.

The electronegativity values give a similar measure of this tendency and reflect the same trend. Alkali metals are, therefore, the most electropositive elements having very low electronegativities. It is to be remembered that the loss or removal of the outer electron leaves the atoms in the form of alkali metal ions. The sizes of the ions indicate that the reduction from the neutral atomic radii is quite considerable because of the looseness of the solitary outermost electron. As a group, the alkali metals have greater atomic radii and lower ionization potentials than any other group of elements.

In metals it is the valence electrons that hold the individual atoms together in the solid. The combined neutral atoms have the outer electron clouds merged with that of the neighbours. In fact, the metals present a picture of ions as a close-packed arrangement immersed in a sea of valence electrons. In the alkali metals this sea of valence electrons is very diffuse and the merged electron clouds constitute a weak binding in the solid. The valence electrons move freely from one atom to the other. The relatively weaker binding in the solid alkali metals gives rise to the low melting and boiling points, softness of the metals and makes it easy to compress. The free motions of the valence electrons give rise to the high electrical conductivity (low electrical resistance) and high lustre of the metal surface is due to easy excitation of the electrons by ordinary light which is reflected (photoelectric effect). The alkali metals also give characteristic visible colouration to the flame.

Chemical properties : Because of easy removal of the single valence electron, the alkali metals invariably exhibit oxidation number of +1 in their compounds. Removal of a second electron from the completed shell is exceedingly difficult. This factor is responsible for the strongly developed ionic character of alkali metal compounds.

Because the alkali metals give up electrons so readily, these function as excellent reducing agents.

(a) **Action of air** : All the alkali metals except Li readily react with the oxygen of the air and tarnish quickly. There is gradation in the reactivity and the products of reaction have different composition.

Lithium reacts with oxygen of air in heated condition forming Li_2O. Sodium reacts slowly at room temperature and vigorously on heating to form peroxide, Na_2O_2. Potassium reacts vigorously at room temperature to give superoxide, KO_2, having O_2^- anion.

Rubidium and cesium react so rapidly with oxygen at room temperature that they are inflamed and yield superoxides, RbO_2 and CsO_2. Freshly prepared or cut surfaces of alkali metals are silvery white, but on exposure to the air they are coated with oxide film and the metallic lustre is destroyed (tarnished).

(b) **Reaction with water** : It is a well-known fact that alkali metals, such as sodium, react very vigorously with water forming hydrogen gas and an alkaline solution. The outermost single loose electron in the alkali metals is responsible for this vigorous reduction of water. Apparently, lithium appears to react with water less vigorously, but it is due merely to a physical condition although the energy released during the reaction with water is far greater than any other alkali metal. The physical factor for less vigorous reaction of lithium is the high melting point, above 100°C (186°C). The low melting points of other alkali metals actually make them melt due to the heat of reaction with water and hence the reaction is very vigorous.

But the case of lithium is different and lithium is actually the best reducing agent although cesium is the best electron donor. This is because of the fact that the standard electrode potential (E°) of lithium is as effective as that of cesium although the ionization potential of lithium is higher than any other alkali metals.

In order to understand the significance of the above statement the values for the ionization potential (energy needed to remove a single outer electron from the atom to form an ion) and the standard electrode potential (energy involved in removing an electron and forming a hydrated metal ion) of alkali metals are given in Table 14.3

Table 14. 3. Ionization potentials and standard electrode potentials of alkali metals.

Ionization potentials	(ev)	Standard electrode potential	(volts)
Li	5.4	Li/Li^+	3.05
Na	5.1	Na/Na^+	2.71
K	4.3	K/K^+	2.92
Rb	4.2	Rb/Rb^+	2.93
Cs	3.9	Cs/Cs^+	2.92

The standard electrode potentials of alkali metals show no gradation in values and is not gradually decreased as in the case of the ionization potential. As has been mentioned, the standard electrode potential is related to the amount of energy involved in removing an electron from a metal and forming a hydrated metal ion and hence this is a composite property and takes into account several factors.

Born-Haber Treatment : The factors which are involved in the formation of a hydrated metal ion from a solid metal are given by the well-known Born-Haber Treatment. A simplified version of the Born-Haber cycle in the case of energy involved in forming hydrated metal ion takes into account the following factors.

(1) Energy required for the breaking up of the solid (metal crystal structure) into individual atoms designated as sublimation energy (S).

(2) Energy-required for the atoms to become ions designated as ionization energy (I).

(3) Energy released when the ions become hydrated and designated as hydration energy (-H).

(4) Energy involved in randomness of the reaction for hydration of the metal ions since the water molecules tend to surround each metal ion and the freedom of motion of the ion is reduced. This is designated as entropy effect (Δ S) and is negligible in the case of alkali metals.

$$M \xrightarrow{S} M \xrightarrow{I} M^+ \xrightarrow{-H} M^+ (H_2O)_n$$

crystal   Free   Free   hydrated
(solid)   atoms   ions   ion
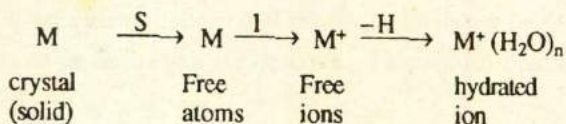
The electron lost during the ionization is responsible for the very exothermic reaction represented by,

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2$$

Hence the total reaction is actually,

$$2M + 2H_2O \longrightarrow H_2 + 2M^+ + 2OH^-$$
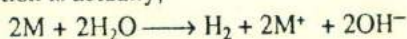
The total energy required by Li, Na and Cs for conversion from metal to hydrated ions are given in Table 14.4.

Table 14.4. Energy of hydration of some alkali metals for $M^+ (H_2O)_n$.

Metals	S Kcal	I Kcal	$-H$ Kcal	Net energy Kcal
Li	38	124	−123	39
Na	26	119	−97	48
Cs	19	90	−63	46

S = Sublimation energy, I = ionization energy, $-H$ = Hydration energy.

Thus a small ion, such as lithium, attracts the dipole of water more strongly and is more readily hydrated as compared to cesium. Hence the very high energy of hydration of the tiny lithium makes lithium a better reducing agent than cesium.

(c) Reaction with acids : The alkali metals react violently with dilute acids.

$$2Na + 2H^+ = 2Na^+ + H_2$$
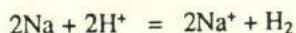
(d) Reaction with hydrogen : The alkali metals combine directly with hydrogen on gentle heating forming crystalline colourless compounds known as alkali metal hydrides. These are ionic compounds composed of alkali metal positive ion (M^+) and negative hydride ion (H^-). Thus in general,

$$2M + H_2 = 2 MH$$

$$2Na + H_2 = 2 NaH$$
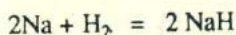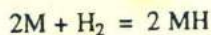
Lithium hydride and sodium hydride are well-defined compounds and have high melting points. The presence of a negative hydrogen ion is proved by

electrolysis of molten alkali metal hydrides, when hydrogen is released at the anode. These hydrides are easily decomposed by water producing hydrogen which is double the quantity contained in the hydride.

$$NaH + H_2O = H_2 + NaOH$$
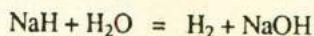
These alkali metal hydrides are of great practical importance as hydrogenating agents, deoxidizing agents in the manufacture of steel and as possible rocket fuels.

(e) **Reaction with halogens** : All the alkali metals react violently with the halogens to form the important compounds known as alkali halides. The reaction takes place with almost explosive violence which is the result of the rapid transfer of an electron from alkali metals to the halogen atom. The reaction follows the equation :

$$2M + X_2 = 2MX \qquad\qquad X = F, Cl, Br, I$$

But it has been noted that during the reaction free halogen atoms are also formed. Thus,

$$Na + Br_2 = NaBr + Br$$
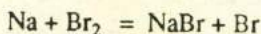
Due to the explosive nature of the reaction, alkali halides are never prepared by the above direct reactions. However, the reaction between the alkali metal hydroxide and halogen acids may be used for the formation of alkali metal halides in aqueous solutions.

The alkali halides are colourless solids, readily soluble in water and are of important applications.

(f) **Reaction with nitrogen** : The alkali metals form nitrides, M_3N, when gently heated in presence of nitrogen particularly in an electric discharge tube :

$$6Na + N_2 = 2Na_3N$$
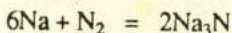
The nitrides are readily decomposed in presence of water giving off ammonia:

$$Na_3N + 3H_2O = 3NaOH + NH_3$$
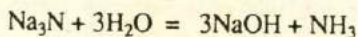
The azides of alkali metals are also formed having general formula MN_3. These detonate very easily and are decomposed in vacuum when gently heated giving off nitrogen :

$$NaN_3 \xrightarrow{200°C} Na_3N + N_2$$
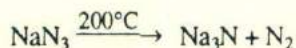
It is to be noted that the alkali metals show a much closer similarity to each other than the elements of any other group which is attributed to the presence of single valence electron which mainly determines the chemical characteristics of these elements.

Occurrence of the Alkali metals

The alkali metals always occur in nature as compounds having ions with a single positive charge. Because the compounds are generally soluble in water, they are found in solution, in the ocean, in the lakes and in underground water. They are found in the solid state in dried-up lakes or ocean beds and in underground deposits. Lithium, potassium and cesium also occur in silicate minerals, such as orthoclase, $K_2Al_2Si_6O_{16}$, spodumene, $LiAl((SiO_3)_2$, pollucite, $H_2Cs_4Al_4(SiO_3)_9$ etc. Lithium also occurs in mineral water and plants such as tea and tobacco leaves. Potassium is found in plants, and water-hyacinth also contains quite appreciable amount of K.

Metallurgy of Alkali Metals (Extraction)

Because of the great reactivity and reducing properties of alkali metals they cannot be prepared by chemical reaction from their compounds in large quantity. The pure alkali metals are obtained by electrolysis of their molten salts or hydroxides. Sodium is produced in commercial scale while lithium metal has shown marked increase in production in recent years.

SODIUM : Sodium is produced by electrolysis of fused sodium chloride mixed with sodium carbonate or calcium chloride to lower the melting point of the salt from 801° to 600°C. The cell used now-a-days for the electro-metallurgy of sodium is the Down's cell, shown in Fig. 14—1.

The electrolyte is a mixture of sodium chloride and calcium chloride. The graphite anode is encircled by an iron or copper cathode and the two are separated by an iron screen partition. This arrangement allows the electric current to pass,

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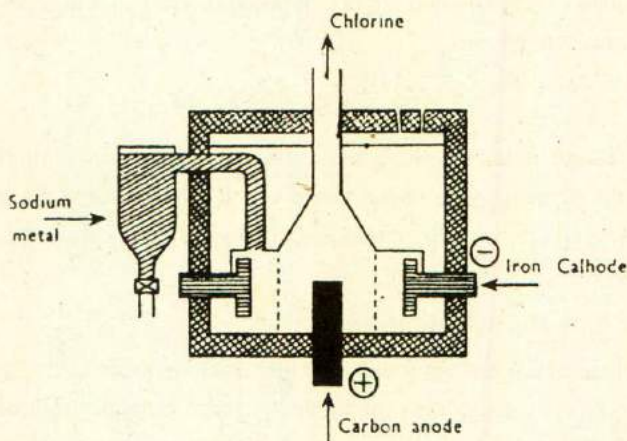
Fig. 14—1. Down's cell for sodium production.

but keeps the sodium and chlorine from coming in contact after they have been set free at the cathode and anode respectively. The fused sodium rises in a special compartment from which it may be drawn off, and dry chlorine is collected in the dome above the anode. Because of low consumption of energy the Down's process has largely replaced the Castner process using fused sodium hydroxide as the starting electrolyte.

LITHIUM : The silicate or phosphate minerals of lithium require chemical processing in order to convert it into lithium chloride which is then used for the extraction of lithium. The chemical processes of the minerals involve several techniques such as digestion with H_2SO_4 or K_2SO_4 to produce Li_2SO_4 which is converted to LiCl.

The extraction of lithium is carried out from fused lithium chloride in a similar manner as in the case of sodium.

POTASSIUM, RUBIDIUM AND CESIUM : Potassium is produced only in small scale from carnallite. In the case of potassium, the potassium hydroxide is a more convenient electrolyte than potassium chloride, because it has a low melting point of 360°C as compared to KCl, 776°C.

Metallic rubidium and cesium are not produced for commercial purposes.

FRANCIUM, element 87,is radioactive and has been isolated from the disintegration of an actinium isotope Ac^{227}. Francium is very unstable with a half-life of only 21 minutes and has the same chemistry as that of cesium and is the heaviest alkali metal. Actinium 227 decays with the emission of β–particles forming Th^{227}. But 1% of Ac^{227} disintegrates with the emission of α–particles forming element Fr(87) :

$$_{89}Ac^{227} \longrightarrow \beta^- + {}_{90}Th^{227.}$$
$$_{89}Ac^{227} \longrightarrow {}_2He^4 + {}_{87}Fr^{223}$$
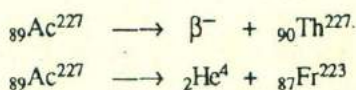
Uses of the alkali metals

Lithium is the lightest of all solid elements. In recent years considerable advance has been made in the applications of lithium. Lithium is extensively used for the purification of inert gases and in refining of metals, such as Cu and Ni, which are purified of impurities, such as oxides, sulphides etc. Lithium acts as a deoxidizer. Lithium is used in organic synthesis, e. g., preparation of ketones. Alloys of lithium have unusual properties. Pb-Li alloy is used as a bearing material. Li-Mg and Li-Zn alloys have high tensile strength and resistance to atmospheric corrosion. Scleron (Li-Zn alloy) compares with mild steel in tensile strength and elasticity.

Sodium is extensively used in industries and as reducing agents in the production of metals, such as titanium and zirconium from their chlorides and oxides. It is used in the production of Na-Pb alloys which are in turn used in the production of tetraethyl lead, a gasoline additive, from ethyle chloride. Sodium metal is used as catalyst in the production of organic compounds and also for organic analysis. It is also used for heat conduction in atomic reactors and aircraft engines. Sodium is used in sodium-vapour lamps which gives characteristic yellow light for lighting highways. The largest uses of sodium are in manufacture of compounds, such as sodium peroxides, sodium cyanide, amide etc. which cannot be made directly from sodium chloride. Sodium and other alkali metals are used in photoelectric tubes.

Potassium has limited use. a sodium-potassium alloy provides a convenient way of handling Na or K and is used in organic reactions and for heat transfer medium in industry. A 50—50 parts Na—K alloy is liquid at ordinary temperatures. Cesium is also used in photoelectric cells.

Alkali metals dissolve in liquid ammonia giving blue solutions containing ammoniated electrons. These solutions are good reducing agents.

Some Important Compounds of Alkali Metals

Alkali metals form well-defined compounds. Almost all of them are colourless and soluble in water except in some cases. The coloured anions, such as dichromate, permanganate, cobaltinitrite, nitroprusside etc., produce coloured salts of alkali metals. Some alkali metal salts, particularly those of lithium, such as Li_2CO_3 and Li_3PO_4, are insoluble in water.

Compounds of Lithium

All lithium salts are obtained from the lithium minerals in various ways. The minerals are processed to obtain Li_2CO_3 or LiCl. These are converted into other lithium compounds by chemical reactions.

Lithium fluoride, LiF : This is obtained by treating a soluble lithium salt, such as LiCl, with ammonium fluoride. LiF being sparingly soluble is precipitated out :

$$LiCl + NH_4F = LiF + NH_4Cl$$
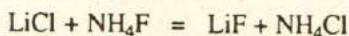
LiF is not hygroscopic. This is used as a flux in electrometallurgy and as opacifying agent in ceramic and enamel industries.

Lithium chloride, LiCl : This is produced when lithium carbonate or oxide is treated with HCl. LiCl is one of the most hygroscopic substances and it is soluble in organic solvents, such as alcohols, ether and pyridine. Due to its bygroscopic nature LiCl is extensively used as dehumidifier in air-conditioning plants. Lithium bromide LiBr is also used as dehumidifier and air conditioning.

Lithium sulphate, Li_2SO_4 : Tihis is formed from Li_2CO_3 dissolved in H_2SO_4. It is readily soluble in water and also in alcohol unlike other alkali metal sulphates.

Lithium oxide, Li_2O : This is obtained by heating Li_2CO_3, $LiNO_3$ or LiOH in presence of hydrogen.

Lithium hydroxide, $LiOH$: This is obtained by dissolving Li_2O in H_2O when LiOH is formed, LiOH is also obtained when Li_2SO_4 is treated with a solution of $Ba(OH)_2$:

$$Li_2SO_4 + Ba(OH)_2 = 2LiOH + BaSO_4$$
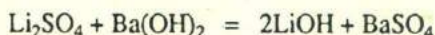
LiOH crystallises from solutions as $LiOH.H_2O$ and has strong basic character.

Lithium peroxide, Li_2O_2 : Lithium peroxide is formed by drying the precipitate of Li_2O_2. $H_2O_2.3H_2O$ which is obtained by adding H_2O_2 and alcohol to a solution of LiOH. The drying is done over P_2O_5.

Lithium nitride, Li_3N : Metallic Li combines slowly with N_2 at room temperature but burns brightly when heated in N_2 forming Li_3N. It is the only alkali metal which combines with nitrogen directly. It resembles with Mg in forming Mg_3N_2. Li_3N is decomposed by H_2O. —

$$2Li_3N + 6H_2O = 6LiOH + 2NH_3$$
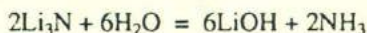
Li_3N is used as a catalyst in the manufacture of synthetic ammonia.

Lithium phosphate, Li_3PO_4 : This is obtained as precipitate when Na_3PO_4 is added to a soluble lithium salt, e.g., LiCl. This is also obtained by the reaction of H_3PO_4 with Li_2CO_3 :

$$3LiCl + Na_3PO_4 = Li_3PO_4 + 3NaCl$$

$$3Li_2CO_3 + 2H_3PO_4 = 2Li_3PO_4 + 3CO_2 + 3H_2O$$
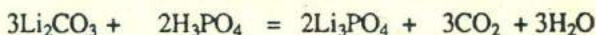
Li_3PO_4 is almost insoluble in water and, therefore, differs from the corresponding compounds of other alkali metals which are soluble. In this way, it resembles alkaline earth phosphate.

Lithium carbonate, Li_2CO_3 : This is also almost insoluble in water and thus differs from other alkali carbonates and resembles alkaline earth carbonates. Li_2CO_3 is obtained by the addition of ammonium carbonate to any soluble lithium salt in presence of ammonia :

$$2LiCl + (NH_4)_2CO_3 = Li_2CO_3 + 2NH_4Cl$$

Lithium carbonate is used in glass industry.

Li_2CO_3 dissolves in a solution of CO_2 giving lithium bicarbonate, $LiHCO_3$, which is more soluble in water than Li_2CO_3 like $Ca(HCO_3)_2$:

$$Li_2CO_3 + CO_2 + H_2O = 2LiHCO_3$$
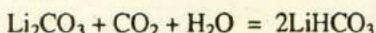
The solution of $LiHCO_3$ is known as Lithia water, and is used in medicine as a remedy for gout because lithium urate formed in the body is fairly soluble in water and is excreted with urine (for expelling uric acid from human system).

Lithium hydride, LiH : This is formed by direct combination of the elements. It is a white crystalline substance and is the lightest of all solid compounds. LiH is an ionic compound, Li^+H^-. It is decomposed with water to evolve hydrogen and is a ready source of the gas :

$$LiH + H_2O = LiOH + H_2$$

4.5 lbs. of LiH will furnish as much H_2 as contained in a steel cylinder of 200 cubic feet capacity when charged under 120 atmospheres. It is used for removing oxide scale from steel and as hydrogenating agent.

Lithium-aluminium hydride, LiAlH₄ : This is obtained when anhydrous $AlCl_3$ is added to LiH in ether :

$$4 LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + LiCl$$
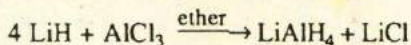
$LiAlH_4$ is readily decomposed by water :

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2$$
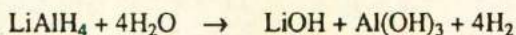
$LiAlH_4$ is a strong reducing agent and is used in organic chemistry with great advantages. $LiBH_4$ also has similar properties. Although $LiAlH_4$ is soluble in organic solvents, it is regarded as composed of Li^+ and AlH_4^- ions. AlH_4^- ion has tetrahedral structure.

The Anomaly of Lithium

The alkali metals as a group have a remarkable similarity in their chemistry but it is noticed that Li has certain unique physical and chemical properties different from other alkali metals. It is harder and has a higher melting point. It forms peroxide with great difficulty and reacts with nitrogen readily. The fluorides, carbonates and phosphates of lithium are insoluble in water as is the

case with the corresponding compounds of magnesium in group II. The organic derivatives of lithium are almost covalent.

The anomaly in the properties of Li is in accordance with the diagonal relationship in the Periodic Table of elements as discussed in Chapter 4.

As mentioned earlier, the relationship is due to the charge and the size of the elements and their ions. Li atom is the smallest of all the alkali metals and has only 2 electrons in the penultimate energy level, whereas all other alkali metals have 8 electrons. The ionic radii of Li^+ and Mg^{+2} are quite nearly the same (0.65—0.60Å). The ionic size is an important factor in determining the behaviour of elements in some aspects, and it is for this reason that Li and Mg have some similar properties.

Compounds of Sodium

Some of the important compounds of sodium are described here.

Sodium peroxide, Na_2O_2 : This is manufactured by passing small pieces of Na in aluminium trays through a furnace at 300°C while a current of dry and CO_2-free air is moving in the opposite direction. This is an application of the "counter current principle" and is widely used in industrial processes. The sodium metal moves in one direction while the air moves in the opposite direction.

Sodium peroxide is a yellow powder and absorbs moisture and CO_2 from atmosphere forming NaOH and Na_2CO_3. It evolves oxygen on strong heating. Oxygen can be readily prepared from Na_2O_2 by the action of hot water.

$$Na_2O_2 + 2H_2O = 4NaOH + O_2$$
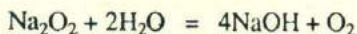
Dilute acids in the cold liberate hydrogen peroxide but on heating with acids oxygen is evolved :

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2 \text{ (cold and dilute)}$$

$$2Na_2O_2 + 2H_2SO_4 = 2Na_2SO_4 + 2H_2O + O_2 \text{ (heating)}$$
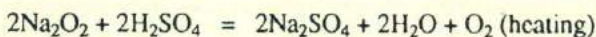
Carbondioxide also decomposes Na_2O_2 evolving O_2. This has been used for purifying air in closed spaces, such as submarines.

Sodium peroxide is a powerful oxidising agent. For instance, it converts $Cr(OH)_2$ into Na_2CrO_4 and also chromite, $FeCr_2O_4$ into ferric oxide and sodium

chromate. Sulphur dioxide is converted into SO_3. When Na_2O_2 is treated with absolute alcohol at $0°C$, it gives sodium hydrogen peroxide, NaO,OH :

$$Na_2O_2 + EtOH = NaOEt + NaO,OH$$
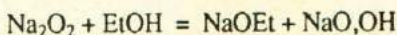
Benzoyl peroxide is obtained by the action of Na_2O_2 on benzoyl chloride. This is a very good bleaching agent :

$$2C_6H_5COCl + Na_2O_2 = (C_6H_5CO)_2O_2 + 2NaCl$$
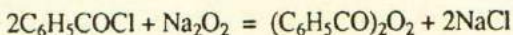
Na_2O_2 is used as an oxidising agent and as a bleaching agent. Na_2O_2 mixed with a little copper oxide is sold under the trade name "Oxone" for the preparation of oxygen. "Soda bleach", a mixture of Na_2O_2 and dilute HCl, is used for bleaching of fibres.

Sodium peroxide contains O_2^{-2} ions which consist of a chian of —O—O— in the molecular structure : Na—O—O—Na

$$\left[\begin{array}{cc} \ddot{\underset{..}{O}} & \ddot{\underset{..}{O}} \end{array} \right]^{-2}$$
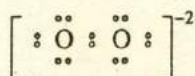
Sodium hydroxide, NaOH : It is an important industrial chemical and is manufactured in large scale known as caustic soda. The principles of some of the methods are given below :

1. Causticisation of soda ash : Soda ash (Na_2CO_3) solution is heated with slaked lime, $Ca(OH)_2$, in calculated amount at a temperature of about $85°C$, while steam is blown into the mixture. The process is known as *"causticisation"* or *"lime soda process"* :

$$Na_2CO_2 + Ca(OH)_2 = 2NaOH + CaCO_3$$
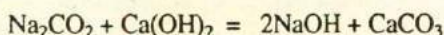
The precipitate of calcium carbonate is filtered off. The solution containing only 20% NaOH is evaporated to solid mass and then cast into sticks or cylinder.

2. The Löwig process : In this process a mixture of sodium carbonate and ferric oxide is strongly heated in a furnace to give sodium ferrite, $NaFeO_2$:

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2$$
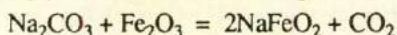
Sodium ferrite on treatment with hot water gives NaOH :

$$NaFeO_2 + 2H_2O = NaOH + Fe(OH)_3$$
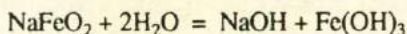
3. The electrolytic method : A number of electrolytic cells have been developed for the production of caustic soda from NaCl solution. The principles of the method involved are : (i) electrolytic dissociation of NaCl, (ii) electrolysis of NaCl forming metallic sodium at the cathode and chlorine gas, Cl_2, at the anode, (iii) the instantaneous reaction of metallic sodium with water in the cell to give NaOH and H_2.

In the Castner-Kelner cell, mercury is used at the cathode in order to form sodium amalgam (Na–Hg) when metallic sodium is liberated. Sodium amalgam is unreactive towards strong brine. Sodium amalgam is made to react with water to form NaOH. The Castner-Kelner cell produces almost pure caustic soda :

$$Na\text{-}Hg + H_2O \rightarrow NaOH + H_2 + Hg$$
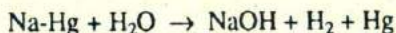
In the Solvay mercury cell which is a modification of Castner-Kelner cell, flowing mercury cathode is used. The sodium amalgam formed at the cathode is drawn out and is decomposed by water in a separated iron vessel. The solution of caustic soda is evaporated in iron pots to give solid product in the form of sticks or pellets. In all the cells, the graphite rods are used as anode because of evolution of Cl_2 gas from NaCl solution during electrolysis (Fig. 14—2).
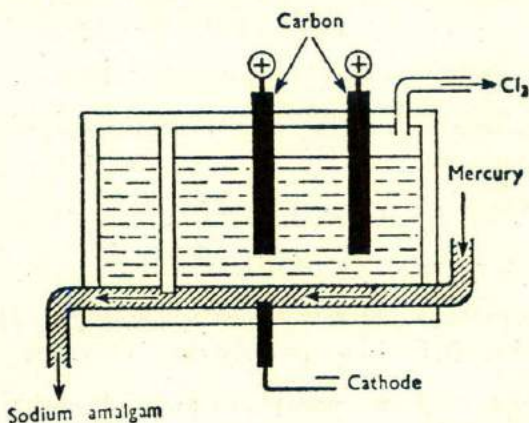
Fig. 14—2. Solvay's electrolytic cell for NaOH.

Properties : Caustic soda is a white crystalline solid, very hygroscopic and absorbs moisture and a little CO_2 forming a saturated solution. The solution slowly resolidifies by absorption of CO_2 when Na_2CO_3 is formed which is

sparingly soluble in NaOH solution. A strong solution of caustic soda is known as "*lye*" or "*soda lye*". NaOH is an ionic compound and melts and boils without decomposition. When dissolved in water, it evolves a great deal of heat due to the formation of a number of hydrates. NaOH liberates ammonia from ammonium salts and precipitates hydroxides from appropriate salt solution :

$$NH_4Cl + NaOH = NaCl + H_2O + NH_3$$
$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl$$
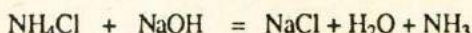
Uses : Caustic soda is extensively used in the production of chemicals, rayons, soaps, textile, paper and pulp, dye stuff and petrolium refining. It is an item of the heavy chemical industries.

Sodium carbonate, Na_2CO_3 : It occurs in the natural salt deposit from dried-up lakes in many parts of the world. Na_2CO_3 is produced in commercial scale by several methods.

1. Le Blanch Process : This is an old method and Na_2CO_3 is produced by a series of chemical reactions. The starting materials are NaCl, H_2SO_4, $CaCO_3$ and coke. The following reactions take place :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl \ (150°C)$$
$$NaCl + NaHSO_4 = Na_2SO_4 + HCl \ (400°C)$$
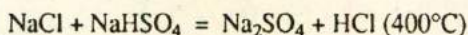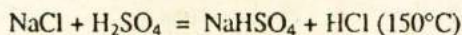
Sodium sulphate is known as *salt-cake* and this is heated with coke and limestone, $CaCO_3$:

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$
$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$
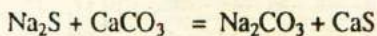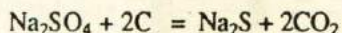
The solid mass (black ash) on lixiviation with water gives a solution of Na_2CO_3. Crude Na_2CO_3 is obtained on evaporating the solution.

2. Ammonia soda or Solvay process : Although both sodium carbonate, Na_2CO_3 and bicarbonate, $NaHCO_3$, can be made by the reaction of NaOH and CO_2 the use of NaOH is uneconomic :

$$NaOH + CO_2 = NaHCO_3$$
$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$
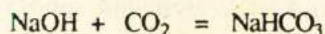
The Solvay process is a model of economy in chemical industries and both Na_2CO_3 and $NaHCO_3$ are produced in very large scale, using brine and limestone as starting materials. Brine saturated with ammonia and carbondioxide, obtained from limestone or burning of natural gas, is passed through the carbonation tower :

$$CaCO_3 \xrightarrow{\text{heat}} CaO + \overset{\cdot}{CO_2}$$

$$CO_2 + H_2O + NH_3 = NH_4HCO_3$$

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$
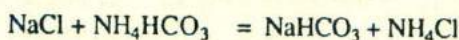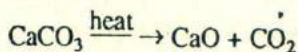
$NaHCO_3$ separates out as crystallie mass and NH_4Cl remains in solution. $NaHCO_3$ on heating gives Na_2CO_3 and CO_2 which is recycled to ammonical brine.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$
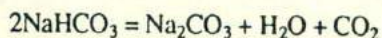
The lime, CaO, formed during the roasting of $CaCO_3$, is added to NH_4Cl in solution to regenerate NH_3 gas and recycled to the brine :

$$CaO + 2NH_4Cl = CaCl_2 + H_2O + 2NH_3$$
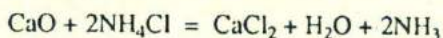
In effect, the overall reaction in the Solvay process is,

$$2NaCl + CaCO_3 \rightleftharpoons CaCl_2 + Na_2CO_3$$
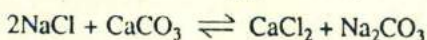
Due to extreme insolubility of $CaCO_3$, the reaction goes towards the left, but with the help of ammonia which is recovered, both $NaHCO_3$ and Na_2CO_3 are manufactured. An schematic representation of the process is given in Fig. 14—3.
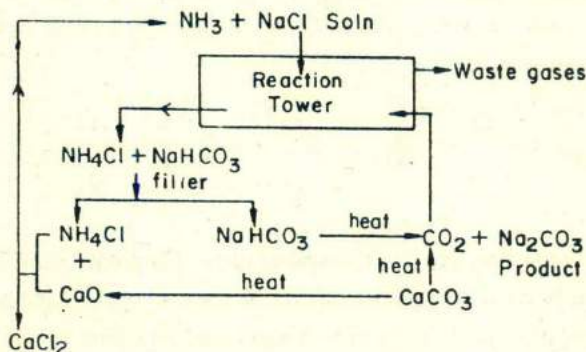
Fig. 14—3. Flow sheet of Solvay process for Na_2CO_3.

Since alkali carbonates are salts of strong bases and weak acid, they undergo extensive hydrolysis in H_2O forming MOH (M is an alkali metal) :

$$Na_2CO_3 + H_2O = NaOH + NaHCO_3$$

Na_2CO_3 crystallises with $10H_2O$ forming $Na_2CO_3.10H_2O$ (washing soda). But the vapour pressure of water at room temperature in equilibrium with $Na_2CO_3.10H_2O$ being greater than partial pressure of water in the atmosphere, it loses water when exposed to the air, a phenomenon known as *efflorescence*.

Na_2CO_3 is used in the manufacture of glass. Washing soda, $Na_2CO_3.10H_2O$, is used for laundering. Large amounts of Na_2CO_3 are used for making soap, paper and pulp, textiles and in petroleum refinery and water softening.

Baking soda, $NaHCO_3$, is used in baking powder and in alkali mixtures of doctors. In baking powder, $NaHCO_3$ liberates CO_2 either by heat or by reactions with $KHC_4H_4O_6$ (potassium hydrogen tartrate) etc. causing the dough to rise and give the desired lightness of bread.

The CO_3^{-2} ion has the structure :

The arrangement is such that all the atoms in CO_3^{-2} lie in the same plane and all the O—C—O angles are equal (120°). Also all the three O—C bonds are equal. Thus each oxygen atom in CO_3^{-2} ion is identical in every respect, suggesting resonance structure :

Sodium chloride, NaCl (Common salt) : Sodium chloride is one of the most abundant and important minerals. Sea-water contains about 2.5 per cent of NaCl. There are vast deposits of rock salt in the Strassfurt region of Germany and in the U. S. A. During the dry season Rann of Ketch (India) has large areas

as bed of salt. The salt is obtained from underground deposits by mining and from sea-water by evaporation during the dry season in salt beds near sea coasts as in Chittagong district of Bangladesh. The salt obtained in this way is called *solar salt* and the mother liquor containing magnesium bromide is called *bittern*. NaCl obtained from sea-water or mines is impure.

Purification of NaCl : Salt is purified by dissolving it in water, concentrating the solution by evaporation and crystallising the salt. Impurities which are more soluble are retained in the solution. Salt obtained in this way is not very pure and contains, among others, $MgCl_2$ and $CaCl_2$, the presence of which makes the commercial salt moist during humid weather.

Pure NaCl is obtained by passing HCl gas to a saturated solution of the commercial salt. The solid NaCl is deposited in cubic crystals in the pure form due to common ion effect :

$$Na^+ + Cl^- + H^+ + Cl^- = NaCl \text{ (precipitate)} + HCl$$
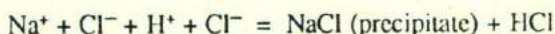
Pure NaCl is generally called table salt. Sodium chloride is the usual source of a host of chemicals of great importance. Salt is the essential constituent of the foods of animals and human beings.

Sodium nitrate, NaNO₃ : This is formed in nature by the interaction of organic matters with compounds of the soil. There are large deposits of $NaNO_3$ in Chile known as Chile Nitre or *"Caliche"*. Pure $NaNO_3$ is obtained from the *Chile Nitre* by lixiviating it with water, evaporating the solution and recrystallising. $NaNO_3$ is deliquescent whereas KNO_3 is not. KNO_3 is obtained from $NaNO_3$ by addition of KCl.

$$KCl + NaNO_3 = KNO_3 + NaCl$$

NaCl is removed as solid when the solution is evaporated. $NaNO_3$ is hygroscopic. $NaNO_3$ requires higher temperature (380°C) for decomposition to $NaNO_2$ and O_2 as compared to other nitrates.

Sodium nitrite, NaNO₂ : Sodium nitrite is now-a-days an important commercial compound. This is obtained by various methods. For instance, N_2

and O_2 of air may be combined to form NO under electric spark and subsequently NO_2 is formed which dissolves in NaOH to give $NaNO_2$. This is also obtained when $NaNO_3$ is heated with Pb :

$$NaNO_3 + Pb = PbO + NaNO_2$$
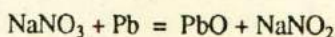
$NaNO_2$ is extensively used for the manufacture of azo dyes and in organic synthesis. It has both oxidizing and reducing properties. It reduces $KMnO_4$ and liberates iodine from KI.

Sodium silicate, Na_2SiO_3 (Soluble glass or water glass) : This is obtained by melting together Na_2CO_3 and pure sand :

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$
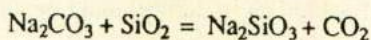
The product is a greenish blue glass. When this is heated with water under pressure, it slowly dissolves to give a thick heavy solution known as Water Glass. This is used as additive in soap, as a mordant, adhesive etc. $Na_2SiO_3.5H_2O$ crystals are readily soluble in cold water.

Sodamide, $NaNH_2$: When ammonia gas is passed over heated Na at about 300°C, $NaNH_2$ is produced :

$$2Na + 2NH_2 = 2NaNH_2 + H_2$$
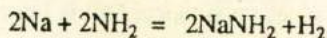
$NaNH_2$ is decomposed by water to give NH_3 and with CO_2, forms cyanamide, $CNNH_2$:

$$NaNH_2 + H_2O = NaOH + NH_3$$
$$2NaNH_2 + 2CO_2 = Na_2CO_3 + H_2O + CNNH_2$$
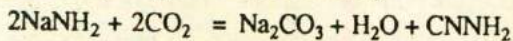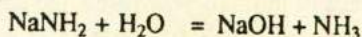
Sodium azide is formed when $NaNH_2$ is heated with N_2O gas :

$$NaNH_2 + N_2O = NaN_3 + H_2O$$
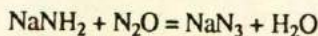
Sodium azide is also obtained when liquid ammonia solution of $NaNO_3$ and $NaNH_2$ are warmed.

$$NaNO_3 + 3NaNH_2 = NaN_3 + 3NaOH + NH_2$$
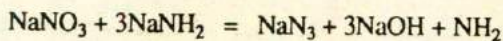
All other alkali amides and azides are obtained in a similar manner.

Azidodithio carbonates are obtained when NaN_3 reacts with CS_2 in aqueous solutions :

$$NaN_3 + CS_2 = NaS.CSN_3$$
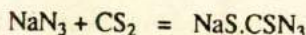
Sodium cyanide, NaCN : This is formed when $NaNH_2$ is heated with red-hot charcoal :

$$Na \xrightarrow{NH_3} \underset{\substack{\text{sodium} \\ \text{amide}}}{NaNH_2} \xrightarrow[\text{heat}]{+C} Na_2CN_2 \text{ (sodium cyanamide)}$$

$$+ C \downarrow heat$$

$$NaCN$$
(sodium cyanide)
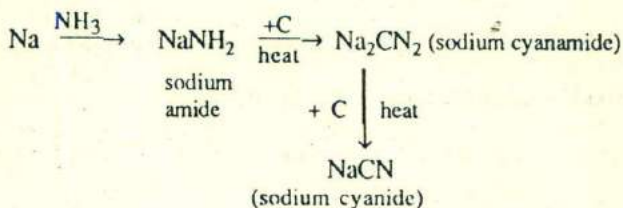
NaCN is also obtained from coal gas which contains HCN and NH_3 :

$$HCN + NH_3 \xrightarrow[\text{Soln.}]{CuSO_4} (NH_4)_2Cu(CN)_3 \text{ (ammonium cuprocyanide)}$$

$$dil \downarrow H_2SO$$

$$H_2O + NaCN \xleftarrow{NaOH} HCN \text{ (gas)} + [CuCN + (NH_4)_2SO_4]$$
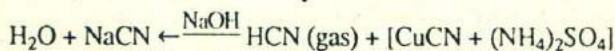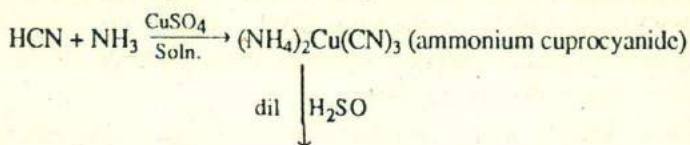
Sodium cyanide is used in electroplating and in the extraction of gold and silver. It is also used in organic synthesis and as a reducing agent.

Sodium sulphite, Na_2SO_3 : This is prepared from NaOH and SO_2 :

$$NaOH + SO_2 = NaHSO_3$$

$$2NaOH + SO_2 = Na_2SO_3 + H_2O$$
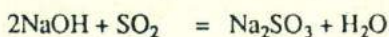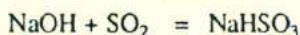
Both SO_2 and SO_3^{-2} ion are strong reducing agents. Na_2SO_3 is used in the manufacture of wood pulp. It is also used to remove excess chlorine in bleaching industry.

Compounds of Potassium

Most of the compounds of potassium are obtained in the like manner as described in the case of sodium. Only some of these which have properties peculiar to potassium will be described here.

Potassium oxides : K_2O, K_2O_2 and KO_2 are formed by direct union of K with oxygen at various conditions. Only the larger alkali metals K. Rb, give the superoxides, such as KO_2. The superoxides contain O_2^- ion as compared to the peroxides which has O_2^{-2} ions. Thus KO_2 is actually $K^+O_2^-$ and has crystal lattice similar to Na^+Cl^- in which Na is replaced by K^+ and Cl^- by O_2^-. KO_2 is decomposed in aqueous solution to give KOH and O_2 :

$$2KO_2 + 2H_2O = 2KOH + 2HO_2$$
$$\downarrow$$
$$H_2O_2 + O_2$$
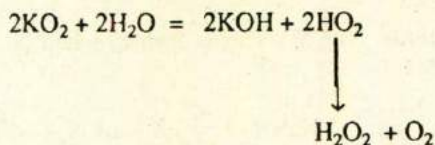
Superoxide ion has the following structures :

$$\left[\ _{\substack{\bullet\bullet}}\overset{\bullet\bullet}{O}\ _{\substack{\bullet\bullet}}\ _{\substack{\bullet\bullet}}\overset{\bullet\bullet}{O}\ _{\substack{\bullet\bullet}}\right]^{-}\qquad\text{or}\qquad\left[\ _{\substack{\bullet\bullet}}\overset{\bullet\bullet}{O}\ _{\substack{\bullet\bullet}}\ _{\substack{\bullet\bullet}}\overset{\bullet\bullet}{\underset{\bullet}{O}}\ _{\substack{\bullet\bullet}}\right]^{-}$$
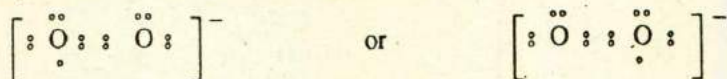
Potassium hydroxide, KOH : Caustic potash is obtained in a similar manner as NaOH by electrolysis of KCl solution. It is used in the manufacture of soft soap and in organic reactions. Alcoholic caustic potash is used as a reagent. KOH is more soluble than NaOH.

Potassium chloride, KCl : This occurs in nature as *sylvine*. It is more soluble in water than NaCl, KCl is used in fertiliser.

Potassium bromide, KBr :This is obtained by the reaction of KOH and HBr :

$$KOH + HBr = KBr + H_2O$$
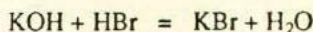
It is manufactured from iron bromide, a by-product of bromine manufacture :

$$FeBr_2.2FeBr_3 + 4K_2CO_3 \xrightarrow{4H_2O} Fe(OH)_2.2Fe(OH)_3 + 8KBr + 4CO_2$$
$$\left.\begin{array}{c}\\\\\end{array}\right| \text{filtered and}$$
$$\text{crystallised}$$
$$\downarrow$$
$$KBr$$
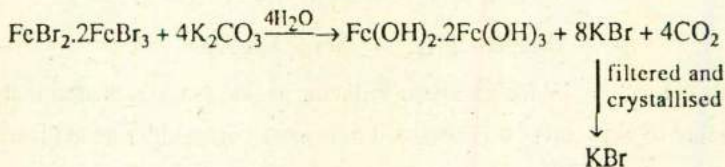
It is a white crystalline solid and is used in photography and in medicine as sedative.

Potassium iodide, KI : This is obtained in a similar manner as KBr. Iron iodide is first obtained by the reaction of iron filings and iodine :

$$Fe + I_2 \xrightarrow{H_2O} FeI_2. 2FeI_3$$
$$\text{boiled}\left|\ K_2CO_3 + H_2O\right.$$
$$\downarrow$$
$$KI$$
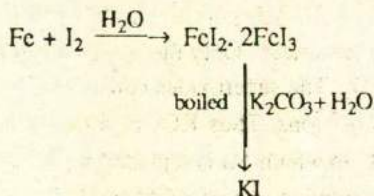
This is also obtained from KOH, I_2 and carbon :

$$6 KOH + 3I_2 + 3C = 6KI + 3H_2O + 3 CO$$

Potassium iodide is a white solid, dissolves in water and alcohol. It is a reducing agent. An oxidising agent liberates iodine from KI.

Potassium fluoride, KF : This is obtained by evaporating a neutral mixture of HF and KOH in a platinum dish. When the neutral mixture is treated with more HF and recrystallised, the product is potassium hydrogen fluoride, KHF_2, known as *Fremy's salt*.

Potassium cyanide, KCN : This is obtained from potassium ferrocyanide when it is heated strongly alone or with metallic potassium :

$$K_4Fe(CN)_6 = 4 KCN + Fe + 2C + N_2$$

$$K_4Fe(CN)_6 + 2K = 6 KCN + Fe$$
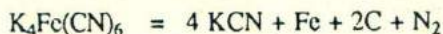
Potassium cyanide, KCN, is also formed when calcium cyanamide is heated with KCl and carbon in an electric furnace :

$$CaCN_2 + C + 2KCl = CaCl_2 + 2KCN$$
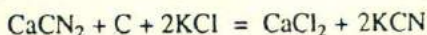
High temperature reaction between Na_2CO_3 or K_2CO_3, C and N_2 produces NaCN or KCN as the case may be :

$$Na_2CO_3 + 4C + N_2 = 3CO + 2NaCN$$
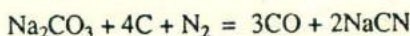
KCN is a deadly "poison" soluble in water and alcohols. It is used in the extraction of gold and as an analytical reagent. Cyanides are extremely important as a metal complexing agent. The extreme poisonous nature is due to complexing of metal atoms present in the enzyme of the animal system. Cyanide complexes are only slightly dissociated as in the case of $K_4Fe(CN)_6$ so that both Fe and CN^- cannot be detected. Cyanide ions stabilizes the various valence states of metal ions which are otherwise unstable in simple salts. For example, Mn^{+1}, Mn^{+3}, Ni^{+1}, Cu^{+1} etc. form stable compounds with CN^- ion.

Potassium carbonate, K_2CO_3 : It is extracted from wood ash. It is obtained by the reaction if KCl with H_2SO_4 and then by heating the product with coke and limestone :

—22

$$2KCl + H_2SO_4 = K_2SO_4 + 2HCl$$
$$K_2SO_4 + 2C = K_2S + 2CO_2$$
$$K_2S + CaCO_3 = K_2CO_3 + CaS$$
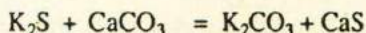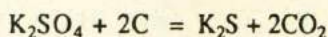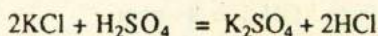
K_2CO_3 is now usually made by the reaction of KCl and $MgCO_3.3H_2O$ in presence of CO_2 :

<center>KCl + $MgCO_3.3H_2O$ (in water)</center>

<center>| CO_2 passed</center>

<center>↓   ↓</center>

$KHCO_3.MgCO_3.4H_2O$ $MgCl_2$
Solid   (in solution)

     | $H_2O + MgO$, 40°C filter

↓   ↓

$MgCO_3.3H_2O$ K_2CO_3 (in solution)
residue

                                  | evaporated
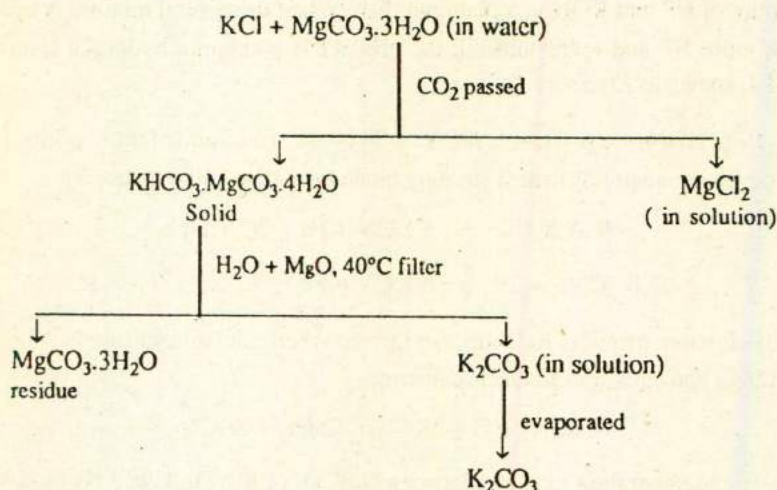
                                 K_2CO_3

K_2CO_3 is a very hygroscopic solid and is readily soluble in water forming a strong alkaline solution due to hydrolysis. When CO_2 is passed in a saturated solution of K_2CO_3, potassium bicarbonate, $KHCO_3$, is formed :

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_2$$
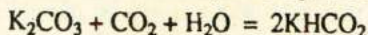
Potassium bicarbonate, $KHCO_3$, is much more soluble than $NaHCO_3$ and hence cannot be made by Solvay's process since crystals of $KHCO_3$ are not deposited. K_2CO_3 is easily fusible and is used as fusion mixture with Na_2CO_3.

Rubidium and cesium compounds : These are rare metals and occur in minerals from which these compounds are isolated for chemical investigations and research. Cs is the most electropositive of all elements and CsOH is the strongest base obtained by double decomposition between cesium sulphate and barium hydroxide. Rubidium hydroxide, RbOH, is similarly prepared. Rubidium and cesium salts are more soluble than the corresponding potassium salts. They easily form superoxides, RbO_2 and CO_2 besides other oxides.

Spectra of Alkali Metals and Their Compounds

When salts of the alkali metals are heated at a moderate temperature, as in the Bunsen Flame, characteristic colours are produced. These colours serve as a means for identification of the alkali metals. The emission of visible light is due to the low value of the ionization constant. The following flame colourations are produced :—

   Li—Brilliant crimson
   Na—Golden yellow
   K—Violet (Lavender)
   Rb—Lilac red
   Cs—Bright blue,

QUESTIONS AND PROBLEMS

1. Give a brief account of the properties of the alkali metals, emphasizing the gradation of properties with increasing atomic number. How would you explain these properties on the basis of the atomic structure of the alkali metals ?

2. Describe preparation, properties and some of the uses of sodium bicarbonate.

3. Explain why alkali metals are highly reactive elements,

4. (a) Discuss briefly the general chemistry of the alkali metals with special reference to the gradation of the properties with increasing atomic number. (b) Discuss the anomalies in the chemistry of lithium and compare it with that of magnesium.

5. Describe the preparation, properties and uses of sodium cyanide.

6. Outline, with the help of a diagram, the manufacture of washing soda from sodium chloride by the Solvay process. Explain the chemistry of this process, drawing attention to physio-chemical principles involved.

7. Discuss the properties of lithium with special reference to its position in the Periodic Table. Compare and contrast its properties with those of sodium.

8. Explain :—

  (a) Why metallic sodium does not occur free in nature ?

  (b) Why is sodium carbonate or calcium chloride added to the electrolyte in the electrolysis of sodium chloride ?

(c) How will you prove that NaH contains the negative hydride ion ?

(d) Why are alkali metals electropositive ?

9.   Outline the chemistry of the Solvay process for the production of sodium carbonate. Can you manufacture $KHCO_3$ by the Solvay process ?

10.   Discuss the relative stabilities of alkali metal carbonates.

11.   Explain the apparent anomalous properties of lithium in relation to other alkali metals.

12.   Explain the reducing actions of alkali metals.

13.   Give the method of preparation of lithium aluminium hydride.

14.   Explain why alkali metals are highly reactive.

15.   Write note on preparation, properties and uses of $NaHCO_3$.

16.   Of the alkali metals, which has the lowest ionization potential and greatest oxidation potential.

17.   Which alkali metal forms the most highly ionic compound ?

18.   Which alkali metals form superoxides when burnt in air ?

19.   What would happen if you keep sodium metal immerged in kerosene, ethanol, linseed oil and water ?

20.   Alloys of lithium and sodium are used as heat transfer media in nuclear reactors. Explain.

21.   Explain why Li is a better reducing agent than Cs.

CHAPTER 15
THE COINAGE METALS
(Elements of Group IB)

Copper, silver and gold are elements of sub-group IB in the Periodic Table. They occur in nature in the free state and are also easily extracted from their minerals. For this reason, they are known from ancient time and have been used for the purpose of making coins and are, therefore, known as the *coinage metals*. Because of their stability and non-reactive nature, particularly of silver and gold, they are also known as noble metals which include Ir and Pt also. These metals can withstand wear and exposure to the air and moisture and maintain their lustre without tarnishing. The single electron in the outermost orbital of the coinage metals is very firmly held by the positive nucleus.

The Electronic Structure

The metals of group IB follow a completely filled d level of transition elements. They have a single s electron in their outermost level and are, therefore, expected to show similar properties as the alkali metals, i.e. group IA. The electronic structures of the coinage metals may be written as follows :

Cu (29)—$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$ (Ar core, $3d^{10}\,4s^1$)

Ag(47)—$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,5s^1$ (Kr core, $4d^{10}\,5s^1$)

Au(79)—$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,4d^{10}\,4f^{14}5s^2\,5p^6\,5d^{10}\,6s^1$

                                (Xe core, $4f^{14}\,5d^{10}\,6s^1$)
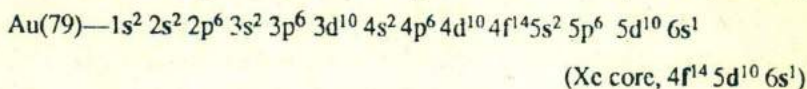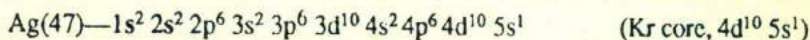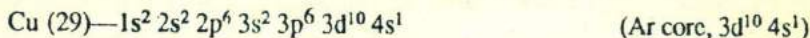
The chemistry of copper, silver and gold is dependent upon the outermost s^1 electron and also the adjacent d electron which is different from that of the group IA metals. These metals, therefore, show characteristics of the transition elements.

Physical properties : Some of the physical properties of copper, silver and gold are listed in Table 15·1.

Table 15·1. Physical properties of copper, silver and gold.

Properties	Cu	Ag	Au
At. No.	29	47	79
At. Wt.	63.57	107.88	197.2
Outer electron orbitals	$3d^{10}4s^1$	$4d^{10}5s^1$	$5d^{10}6s^1$
Colour of metal	Red	Shining white	Yellow
Atomic radius (Å)	1.28	1.44	1.44
Ionic radius (Å)	Cu^+ 0.96	Ag^+ 1.26	Au^+ 1·37
	Cu^{+2} 0.69		
Ionization potential (ev)	7.71	7.54	9.18
Oxidation states	+1, +2	+1	+1,+3
Density at 20°C (g/cm³)	8.92	10.5	19.3
Melting point (°C)	1083	960	1063
Boiling point (°C)	2310	1950	2600
Electronegativity	1.75	1.42	1.42
Oxidation potential	−0.52	−0.8	−1.68
$M = M^+(aq.) + e-$ Standard electrode potential (v)	Cu/Cu^{+2}−0.34	Ag/Ag^+ −0.8	Au/Au^{+3}−1.5

It is interesting to note that copper and gold are coloured metals whereas silver is white. Whenever we find a colour in a chemical substance it is due to the excitation of low-lying energy level produced by a low-energy photon of visible light corresponding to an energy of about 1 to 3 ev. If we examine the electronic structures of copper, silver and gold, we find that all the three metals undergo the transition $d^{10}{\rightarrow}d^9s^1$. The energy needed for this transition is 2·7 ev for copper, 4·8 ev for silver, and 1·9 ev for gold. Thus copper and gold absorb visible light and are coloured. Whereas silver absorbs in the invisible ultraviolet and, hence, is a white silvery metal. The variable oxidation states of the coinage metals is also due to the presence of d electrons which undergo transition.

The gradation in the physical properties is not very well-marked in many cases. Copper, silver and gold have melting points near about 1000°C. The

atomic radii of Ag and Au are almost the same due to the lanthanide contraction. The ionization potentials for removing the s^1 electron are near about the same but it is easy to remove electrons from the inner 2—6—10 core and requires less energy. Moreover, the d electrons participate in covalent bonding. Thus, we have Cu^{+2} and Au^{+3}, very common ions.

The values of oxidation-reduction potential provide a clue to the inertness of the elements of group IB in the metallic state as compared with that of alkali metals which have much greater values. The resistance to oxidation as expressed in terms of the values of oxidation potential results from the following factors or a combination of these :—

(i) High heat of sublimation to the atoms.

(ii) High ionization potential.

(iii) Low energy of hydration for the positive ion.

In the coinage metals the s^1 electron (valence electron) is incompletely shielded by the inner d orbitals. Hence the ionization potentials for these metals are high. Due to incomplete shielding, the nuclear charge of the adjacent atoms are appreciably attracted by the neighbouring electron clouds and the break-up of the metallic structure to isolated atoms of the metals is extremely difficult resulting in greater heat of sublimation. Although the hydration energies of the coinage metals are high and they are expected to undergo easy oxidation, their effects are reduced to a great extent by the high sublimation energies and high ionization potentials.

Although the fairly high ionization potential would not suggest high electrical conductivity, Cu, Ag and Au are fairly good conductors of electricity because of the unpaired valence electron.

Chemical properties :

An idea of the chemical properties can be had from the electronic structures and the physical constants discussed before. The variable oxidation states and stable oxidation states do not follow any set pattern, although all the three metals can have oxidation states, +1, +2 and +3. Cu is more stable in +2 state, Ag in +1 state and Au in +3 state.

The reactions of various agents are given below :—

(a) *Action of air* : The oxygen of the air combines only with Cu on heating forming Cu_2O and CuO. Ag and Au do not combine with oxygen at all. Ag becomes tarnished in air on long exposure due to the presence of other gases, such as H_2S, SO_2, CO_2 etc. In pure dry air, Cu remains bright, but the surface of Cu becomes covered with green film of basic sulphate, $CuSO_4$, $3Cu(OH)_2$, in humid air containing SO_2 wrongly attributed to basic carbonate, although occasionally some basic carbonates are formed in presence of CO_2.

(b) *Action of water* : Water has practically no action on these metals at ordinary temperature.

(c) *Reaction of acids* : Dilute HCl has also no action on Cu, Ag and Au. Copper readily dissolves in dilute nitric acid with the evolution of nitric oxide :

$$3Cu + 8HNO_2 \text{ (dil.)} = 4H_2O + 2NO + 3Cu(NO_3)_2$$
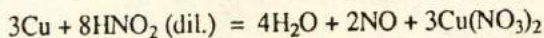
Copper dissolves slowly in hot concentrated HCl with evolution of hydrogen but more rapidly in hot conc HBr and HI forming cuprous compounds. Ag is dissolved in hot dil HNO_3 and in hot conc. HI with evolution of hydrogen. Silver is also attacked by boiling conc. H_2SO_4 as in copper :

$$2Cu + 2HI = Cu_2I_2 + H_2$$
$$Ag + 2HNO_3 = AgNO_3 + H_2O + NO_2$$
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$
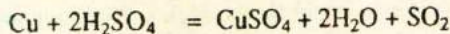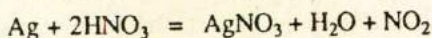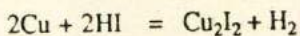
Gold is not attacked by any single acid except selenic and iodic acid. It is dissolved by chlorine water or by aqua regia which is a mixture of HNO_3 and HCl.

(d) *Reaction of alkali* : Even a strong alkali has practically no action on these metals. Silver and gold resist action of alkalies even in the fused states and hence are used for crucibles for fusion with caustic alkalies. Aqueous ammonia in the presence of air dissolves copper and gives a blue solution containing $Cu(NH_3)_4^{+2}$ ion.

(e) *Reaction of hydrogen* : Copper, silver and gold do not react with hydrogen directly. However, CuH and AgH have been reported to be formed but appear to be doubtful.

(f) Reaction of halogen : Cuprous halides of the general formula CuX, are formed with all the halogens. Similarly, Ag gives AgX but also forms Ag_2F with flourine. With chlorine and bromine gold forms $AuCl_2$ and $AuBr_3$. AgF_2 is formed by the action of fluorine on silver powder.

(g) Reaction of sulphur : Cu_2S is one of the main ores of copper. It is also formed when Cu is heated in excess of sulphur :

$$2Cu + S = Cu_2S$$
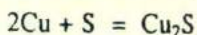
Cupric sulphide, CuS, is not formed because it is decomposed to cuprous sulphide, Cu_2S, at 300°C :

$$2\ CuS = Cu_2S + S$$
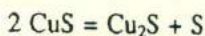
Comparison of the Alkali Metals and the Coinage Metals

Because of the fact that alkali metals of group IA and the coinage metals of group IB each has one unpaired electron, s^1, in the outermost level, the elements of these two groups might be expected to behave in a similar manner. The elements in both groups are good conductors of electricity and show oxidation state of +1. The univalent compounds are formed with analogous formulas and posses similar crystal structures. For instance.

Na_2O	Ag_2O
NaCl	AgCl
Na_2SO_4	Ag_2SO_4
$K_2SO_4,Al_2(SO_4)_3,24H_2O$	$Ag_2SO_4,Al_2(SO_4)_3,24H_2O$
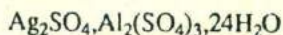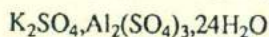
But the similarities do not extend beyond this and there are a great deal of dissimilarities both in physical and in chemical properties of the elements of the two sub-groups. The dissimilarities in the properties of alkali metals and coinage metals are due to the fact that the outermost s^1 electron in the alkali metals is situated after an inert gas s^2p^6 electrons whereas in the coinage metals the outermost s^1 electron comes after the d^{10} electrons. The dissimilarities are listed below.

(1) Electronic structures are different although they have s^1 electron in the outermost level.

Z		Alkali metal		Z		Coinage metal	
3	Li	(2),	$2s^1$	29	Cu	(18),	$3d^{10}4s^1$
11	Na	(10),	$3s^1$	47	Ag	(36),	$4d^{10}5s^1$
19	K	(18),	$4s^1$	79	Au	(68),	$5d^{10}6s^1$
37	Rb	(36),	$5s^1$				
55	Cs	(54),	$6s^1$				
87	Fr	(86),	$7s^1$				

(2) The alkali metals are most reactive elements while the coinage metals are unreactive and difficult to oxidise.

(3) The alkali metals never occur in nature in free state, but always in combination, whereas the coinage metals are found abundantly in free state.

(4) The alkali metals have only one oxidation state, +1, whereas the coinage metals may lose one or more than one electron per atom to give +1, + 2 and + 3 oxidation states particularly in gold.

(5) The alkali metals have melting points ranging from 180°C for lithium to 28·4°C for cesium. The coinage metals have melting points near about 1000°C.

(6) The alkali metals form strong bases because of their small charge (+) and large sizes. Their hydroxides are strongly ionized and their halides are not hydrolysed. The coinage metals do not give strongly basic oxides or hydroxides. Silver oxides when moist is only feebly basic and $Au(OH)_3$ is amphoteric.

(7) The coinage metals can be worked and used as metals because these are heavy, ductile and malleable. The alkali metals cannot be handled easily and are kept in kerosene.

(8) The alkali metals are never found in anions and practically have no complex cations. The coinage metals form large number of stable complexes, both as cations and anions, such as,

$K[Ag(CN)_2]$,   , $KAuO_2$

$[Ag(NH_3)_2]Cl$, $[Cu(NH_3)_4](NO_3)_2$

$K[Au(CN)_2]$, $[Cu(NH_3)_4]Cl$, $K_2[Cu(CN)_4]$
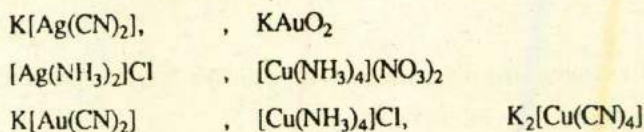
(9) Most compounds of the alkali metals are soluble in water ; this is not the case with the coinage metal compounds. Oxides, sulphides and chlorides of the alkali metals are soluble in water while the corresponding salts of Cu, Ag and Au are insoluble (excepting $AuCl_3$ and $CuCl_2$).

(10) Many of the ions and compounds of the coinage metals are coloured, whereas those of the alkali metals are colourless. The alkali metals form coloured compounds only when the anions are coloured as in $K_2Cr_2O_7$, $KMnO_4$ etc.

(11) The alkali metals are of recent discovery and their uses are only scientific and technological. The coinage metals were among the first to be used by primitive men from time immemorial for ornaments and for coinage purposes.

Extraction of Coinage Metals

Extraction of copper : Copper is generally extracted from its ores.

Ores of copper : The important ores of copper are,

Copper pyrite—	$CuFeS_2$ or Cu_2S, Fe_2S_3
Chalcocite (copper glance)—	Cu_2S
Malachite—	$CuCO_3, Cu(OH)_2$
Cuprite—	Cu_2O

The principle of extraction : The metallurgical operation involving the extraction of copper from its ores is of technological importance. Since the most important ores contain also iron and sulphur, any procedure for extracting pure copper from such an ore require a number of operations. Both dry and wet methods are used for the extraction of copper which is purified by electrolytic method.

Large amount of copper is obtained from copper pyrites, $CuFeS_2$, by smelting. The separation of Fe and S from Cu is the main task and is difficult since bonds between Cu and S are stronger than those between Fe and S. But Fe is removed by oxidation as ferrous silicate which dissolves in the slag leaving Cu_2S. Partial roasting of Cu_2S in air converts it to Cu_2O which reacts with Cu_2S to form metallic copper. The reactions involved are,

$$2CuFeS_2 + 4O_2 = Cu_2S + 2FeO + 3SO_2$$

$$FeO + SiO_2 = FeSiO_3$$

$$Fe_2O_3 + 3SiO_2 = Fe_2(SiO_3)_3$$

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$Cu_2S + 2CuO = 4Cu + SO_2$$
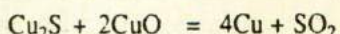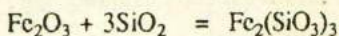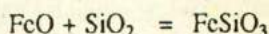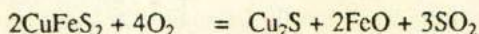
The process of extraction from the copper pyrites.

(1) Concentration of the ore : Copper pyrite ore is first concentrated by froth floatation process.

(2) Roasting : The concentrated ore is then roasted in furnace. This drives off moisture, removes part of sulphur as sulphur dioxide and also arsenic and antimony are removed. The roasted ore is called "calcine" which consists of Cu_2S, FeS, FeO and SiO_2.

$$2CuFeS_2 + O_2 = Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$2FeS + 3O_2 = 2FeO + 2SO_2$$
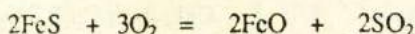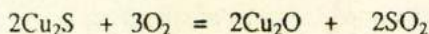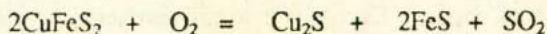
(3) Smelting : The roasted ore is smelted in a blast furnace with limestone and sand for the formation of slag. Limestone serves as a flux :

$$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$$

$$FeO + SiO_2 = FeSiO_3$$
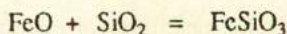
The impure Cu_2S containing FeS obtained after smelting is called "matte".

(4) Bessemerisation : The matte is reduced in a Bessemer convertor by blowing air through the molten material. The air first oxidises FeS to FeO and SO_2. Sand is added to form a slag of $FeSiO_3$. The air blast converts some Cu_2S to Cu_2O which instantaneously reacts with Cu_2S to give metallic copper :

$$2Cu_2S + 3O_2 = 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S = 6Cu + SO_2$$
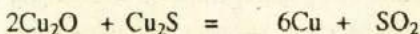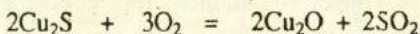
Some CuO is also produced by the air blast. This is removed by stirring the metal with poles of green wood, the resulting gases acting as reducing agent. The copper obtained has a characteristic appearance and is called "blister copper".

Refining of blister copper : The impure copper is cast into large plates which are used as anodes in the electrolytic purification of copper. Thin sheets of pure copper serve as the cathodes and $CuSO_4$ solution acidified with H_2SO_4 serves as the electrolyte. A schematic diagram of the electrolytic cell is given in Fig. 15—1. The impure copper passes into solution from the anodes
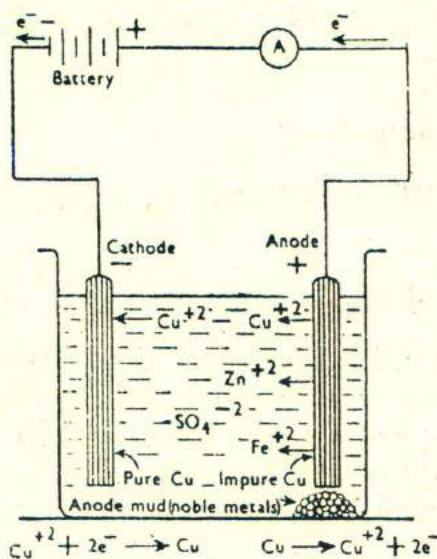
Fig. 15—1. Refining of copper by electrolytic method

and pure copper is deposited on the cathodes as the electrolysis proceeds. The principal impurities are silver and iron. The voltage applied to the electrolytic cell is just kept below the voltage necessary for silver deposition. Silver does not go into solution but along with gold it falls to the bottom as "anode mud" which also contains bits of slag and Cu_2O. Silver, gold and platinum group metals are recovered from the anode mud as valuable by-products. Fe and Zn pass into solution and are not deposited. The copper deposited is in extremely pure form when the voltage is controlled at precisely the right value. The cost of electro-refining of copper is generally met from the precious metals recovered from the "anode mud."

The entire process for the extraction of copper may be given schematically as :

Crushed and
ground ore $\xrightarrow[\text{floatation}]{\text{forth}}$ Concentrated ore
(CuFeS$_2$)

                             ⏐ roasted
                             (reverberatory
                           ↓ furnace)

"Matte" $\xleftarrow[\text{(blast furnace)}]{\text{smelting}}$ "Calcine" (Cu$_2$S, FeS, FeO, SiO$_2$)
Cu$_2$S,FeS

    ⏐   Bessemerised
    ↓

"Blister copper" $\xrightarrow{\text{electro-refined}}$ Pure copper
(impure)
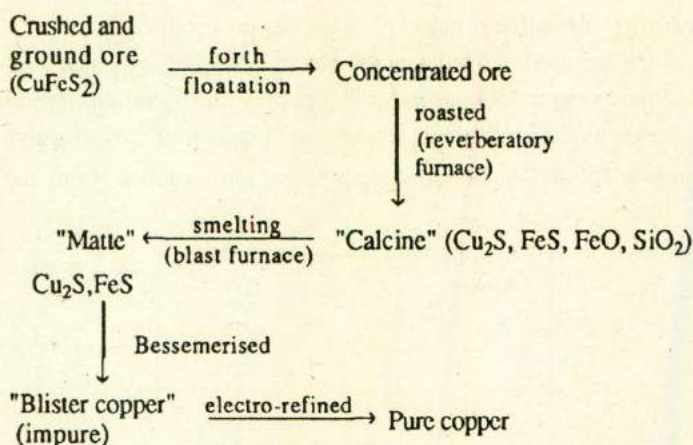
Hydrometallurgy of Copper

In this process Cu$_2$S,FeS$_2$ is converted to CuSO$_4$. This is based on the fact that CuS or Cu$_2$S is more easily oxidized to CuSO$_4$ than FeS or Fe$_2$S$_3$. The ore is exposed to the weathering action of air and rain for a long time. Copper sulphate and iron sulphate are formed which are leached by water. Metallic copper is then precipitated by adding iron filings.

In order to hasten the conversion of the ore to CuSO$_4$ and FeSO$_4$, the ore is first roasted at a controlled temperature in a reverberatory furnace. Both CuSO$_4$ and FeSO$_4$ are formed. Some of the FeSO$_4$ is converted to Fe$_2$O$_3$, but CuSO$_4$ remains unaffected because it requires higher temperature to decompose to CuO. Even if some CuO is formed it is converted to CuSO$_4$ by SO$_2$ gas liberated during roasting. Copper sulphate is leached with water along with some FeSO$_4$. Copper is precipitated from the solution by adding scraps of iron or by electrolytic process :

$$CuFeS_2 + O_2 \longrightarrow CuSO_4 + FeSO_4 + SO_2$$

$$FeSO_4 + O_2 \longrightarrow Fe_2O_3 + SO_2$$

$$CuO + SO_2 \longrightarrow CuSO_4$$

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4$$
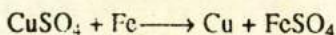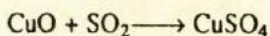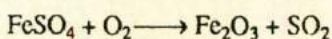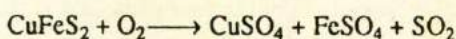
Extraction of Silver

Ores of silver : Almost pure silver is found in nature mixed with copper and gold. Important ores of silver are :

Argentite (silver glance)—Ag_2S

Haloargyrite—$AgCl, AgBr, AgI$

(AgCl is also known as horn-blende)

Pyroargyrite—Ag_5SbS_4

Some silver is found in galena, PbS.

A large part of silver produced in the world comes from the residues (anode mud) obtained from the electrolytic refining of copper.

The extraction of silver is carried out by various techniques. The principles of these techniques are described here.

1. The cupellation process : When silver and lead ores are smelted together, they form an alloy of lead and silver which on heating forms lead monoxide, PbO, and metallic silver. The lead monoxide forms a scum on the surface and is blown off giving the metallic silver. The alloy is heated on a 'cupel' or oval-shaped wrought-iron vessel filled with bone-ash and hence the process is known as *cupellation process.*

2. The amalgamation process : This process has become now almost out of use. This is based upon the fact that silver ores mixed with some salt and roasted pyrites and ground to a mud with water form silver chloride, AgCl. When mercury is thoroughly mixed with the slime, AgCl reacts with mercury to produce silver. The liberated silver forms amalgam with excess of mercury. The amalgam on distillation gives metallic silver while mercury is distilled off :

$2Cu_2Cl_2 + Ag_2S \rightarrow Cu_2S + 2AgCl$ $2AgCl + 2Hg = 2Ag + Hg_2Cl_2$
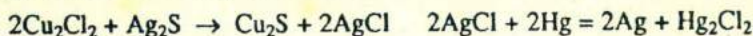
3. The Parke's process : This is based upon the fact that molten lead dissolves about 1% of zinc and molten zinc about 1% of lead. But silver is completely soluble in molten zinc. Hence, when molten zinc is added to fused lead-silver alloy. silver goes into solution in zinc forming zinc-silver alloy which solidifies and floats on the surface of molten lead. The process is called desilverisation of lead and depends upon the parting of silver from lead to zinc.

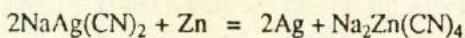Silver can be obtained from zinc-silver alloy by distillation when zinc is distilled off.

4. The cyanide process : Most of the silver is now obtained by the cyanide process. This is dependent upon the formation of the complex dicyanoargentate ion, $Ag(CN)_2^-$, with cyanide, CN^- ion. Silver metal and all its compounds are easily soluble in alkali cyanides in presence of air. The hydrometallurgy of silver is based upon the fact that the metallic silver is deposited from the cyanide solution upon the addition of zinc or aluminium. The air blast serves to stir up the solution and brings about the oxidation of the sulphide present in Ag_2S.

$$4Ag + 8NaCN + 2H_2O + O_2 \ = \ 4NaAg(CN)_2 + 4NaOH$$

$$Ag_2S + 4NaCN \ = \ 2NaAg(CN)_2 + Na_2S$$
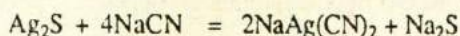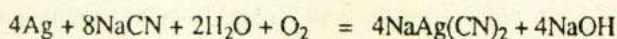
The sodium sulphide is oxidised to sulphate in presence of air :

$$4Na_2S + 2H_2O + 5O_2 \ = \ 2Na_2SO_4 + 4NaOH + 2S$$
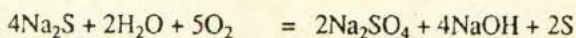
The silver is deposited from the solution by zinc :

$$2NaAg(CN)_2 + Zn \ = \ 2Ag + Na_2Zn(CN)_4$$

The process of extraction of silver may be given schematically as :

Grinded
ore of Ag $\xrightarrow[\text{floatation}]{\text{forth}}$ Concentrated
(Ag_2S) ore

$\Big\downarrow$ dil. NaCN soln.

$NaAg(CN)_2$ solution $\xleftarrow[\text{blown}]{\text{air}}$ Suspension

filtered & $\Big|$ Zn added

Precipitated Ag $\xrightarrow[\text{dried \& fused}]{\text{filtered,}}$ Metallic silver
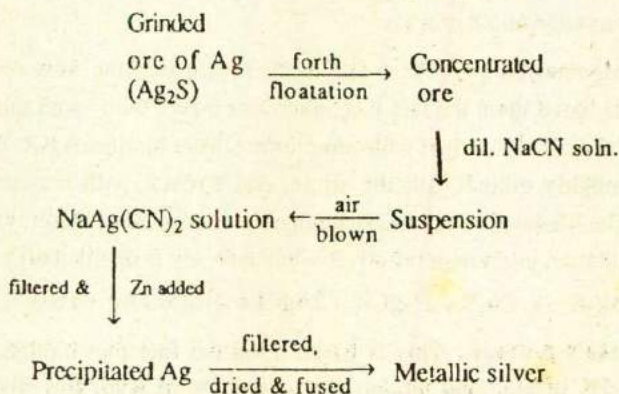
Purification of silver : Silver is refined by electrolysis of silver nitrate solution in presence of about 1% HNO_3. The cathode is a thin plate of silver and the impure blocks of silver serve as anode. Silver is deposited on thin silver

cathode, copper dissolves and gold collects as a mud. The process is also known as parting of silver from gold.

Extraction of Gold

Sources of gold : (1) Gold is found chiefly in the form of metal. The nuggets of gold are found scattered through gravel and in small particles in the veins of rocks or sands. Alluvial sands of river beds contain some gold particles in certain places. (2) In the combined state it is found as gold telluride, $AuTe_2$, and double telluride, $AuAgTe_4$, known as silvanite. (3) Au is obtained as a by-product from the extraction of Ni, Cu and Ag by the process of electrometallurgy.

Metallurgy of Gold

(1) Process depending on the specific gravity of gold : From ancient times gold has been obtained by several physical processes, such as "panning", "sluicing" etc. In these methods gold-bearing sands and gravels are washed with water to separate the lighter particles from the heavy particles of gold.

Hydraulic mining of gold has been developed to separate gold from rocks with powerful streams of water. The gold is washed into sluices which are long troughs and deposited free from sand and clay.

(2) Process depending on the amalgamation with mercury : Amalgamation process has also been in use. Finely powdered rocks are washed over plates of copper coated with mercury. Gold contained in the slime dissolve in the mercury. The gold amalgam is removed and distilled. Mercury is distilled off and the gold residues known as "taillings" are refined.

(3) The cyanide process : The process of extraction of gold by cyanide process is based on the same principle as described in the case of silver. In fact, the two metals are extracted simultaneously. The gold-bearing rocks are first crushed and pulverised in stamp mills. The pulverised ore is washed with water and treated with a dilute solution of NaCN through which air is blown. In presence of air (oxygen) gold dissolves in a solution of NaCN or KCN when finely powdered ore is treated with the reagent :

$$4Au + 8KCN + 2H_2O + O_2 = 4KAu(CN)_2 + 4KOH$$
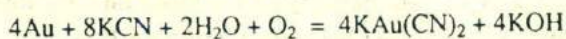
The gold is precipitated from the solution by displacement reaction with Zn or Al :

$$Zn + 2KAu(CN)_2 = 2Au + K_2Zn(CN)_4$$
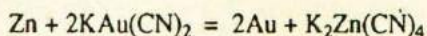
Refining of gold : Gold obtained by any of the process is impure and contains silver and also lead, copper, zinc etc. The refining or 'parting' of gold is done by—(i) electrolysis or (ii) by dissolving the impurities in a chemical reagent.

(i) The impure gold is made the anode and a thin sheet of pure gold is the cathode. The electrolytic solution is chlorauric acid. The gold deposits on the cathode and silver is precipitated as silver chloride, AgCl.

(ii) The chemical process of the parting of gold is based on the treatment of impure gold with nitric acid or sulphuric acid in which silver dissolves and gold remains unaffected.

Uses of Coinage Metals

Uses of copper : Copper is second in importance to iron because of its wide range of uses.

The most important use of copper is in the production of electrical wiring.

It is also used for making utensils in the fermentation industries and for making coins. Since copper is electrically deposited in thin sheets which are smooth and tough, it is used in electrotyping for printing books and integrated circuits in electronics.

A large number of useful alloys of copper are made. Some of the important alloys of copper are :

(i) Brass : Cu : 60—80% and Zn : 20—40%. It has yellow colour and can be made into any desired shape.

(ii) German silver : Cu : 50—60% : Zn : 20%; Ni : 20—25%. It is white in colour and largely used in making utensils and table wares and also ornaments.

(iii) Bronze : Cu : 70—95% ; Zn : 1—25% ; Sn : 1—18%. It is a tough alloy and is used in making machinery parts and propellers.

(iv) Phosphor bronze : Bronze containing P—1% is hard, elastic and tough.

(v) Monel metal : Cu—30% ; Ni—67% and Fe or Mn—3%. This alloy is resistant to chemical action and has great strength. It is used in chemical industries.

(vi) Nickel coin : Cu—75%. Ni—25%. It is used for making coins.

Uses of silver : Silver is largely used for making coins, silver wares and ornaments. Silver is too soft and is, therefore, hardened by alloying with copper and other metals. Silver is also used in making dental alloys and mirrors. Silver salts are used in photography.

Recently silver alloys have been used as bearing metals in automobiles, aeroplanes and locomotives. High grade stainless steel containing about 0.3% silver has been made.

Uses of gold : Gold is a precious metal and has a permanent bright lustre. It is used in making ornaments and jewellery.

The unit of fineness of gold : Pure gold is a soft metal and it is generally alloyed with copper to make it hard. The fineness of gold is expressed in *carats*. Pure gold is 24 carats.

Gold is used for gold plating and gilding.

Colloidal gold is made by reducing gold chloride solution with hydrazine etc.

Purple of Cassius : This is a combination of gold with colloidal stannic acid. This is used as pigment in making red glass and high class pottery. This is made by mixing gold chloride with stannous chloride solution.

Compounds of Coinage Metals

Some important and well-known compounds of copper, silver and gold are described here.

Compounds of copper : Copper forms two series of compounds having copper atoms in two oxidation states of + 1 and + 2. This can be easily visualized from the electronic structures of Cu, Cu^{+1} and Cu^{+2} states :

$$Cu\ (29) - 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$$

$$Cu^+ - 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$$

$$Cu^{+2} - 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9$$
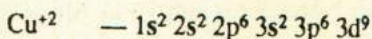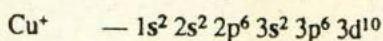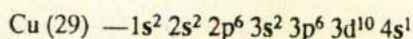
Thus when one electron in the outermost level of the copper atom is used in bond formation, we get cuprous compounds. With two electrons removed, one from 4s and another from 3d level, we get cupric compounds.

There are marked differences in the stabilities of cuprous and cupric compounds. Binary compounds of cuprous $Cu(1)$, are quite stable, such as halides, oxides, but the oxyacid salts of Cu^{+1} are readily decomposed by water. Cu^{+2} forms quite stable oxycompounds while its binary salts are unstable and are decomposed spontaneously. $CuSO_4$ is stable whereas CuI_2 is not. The electronegative character of the anions has a bearing on the properties of Cu^{+1} and Cu^{+2} compounds since the power to draw electrons from the 4s and 3d levels are involved. Thus in water Cu^{+1} ion normally undergoes disproportionation reaction giving Cu^{+2} ion and metallic Cu :

$$2Cu^+ \longrightarrow Cu^{+2} + Cu(solid)$$
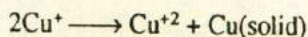
The stable compounds of Cu^{+1} are insoluble in water, such as CuI, CuCl, CuBr, CuSCN. These are generally white and the chemistry of Cu^{+1} thus resembles that of Ag^{+1} in this respect.

However, unstable Cu^{+1} and Cu^{+2} compounds are made stable by complexing agents. Thus stable Cu^{+2} compounds, such as,

$$[Cu(NH_3)_4]I_2 \qquad \text{or} \qquad [Cu(NH_2-CH_2-CH_2-NH_2)_2]I_2$$
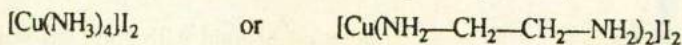
exist and are soluble in water. Even the oxyacid anions of cuprous salts which do not exist as such in water have been made stable by complexing agents. Thus cuprous nitrate,. $CuNO_3$, is stabilized by complexing with thiourea and ethylene thiourea giving

$$[Cu\ (ethylene\ thiourea)_4]NO_3 \qquad \text{or} \qquad [Cu(etu)_4]_2SO_4$$
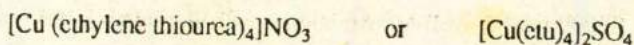
Monovalent copper forms complexes with NH_3, $Cu(NH_3)_2^+$ and also with halides CuX_2^-. KCN gives complexes $KCu(CN)_2$ and $K_3Cu(CN)_4$. Cu^{+1} complexes are generally colourless in contrast to Cu^{+2} complexes which are intensely coloured.

Compounds of Cu(I) or Cu⁺

Cuprous oxide, Cu_2O : This is obtained by boiling CuCl with NaOH in the form of a red precipitate. Heating of metallic copper in air also gives Cu_2O. When basic salts of Cu^{+2} e.g., the alkaline solution of $CuSO_4$ in Na-K tartrate (Fehling Solution) is heated with reducing agents such as glucose or an aldehyde, reddish brown precipitate of Cu_2O is obtained :

$$2CuCl + 2NaOH = Cu_2O + 2NaCl + H_2O$$

$$2Cu^{+2} + 2OH^- + 2e^- = Cu_2O + H_2O$$
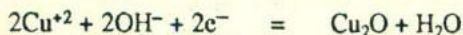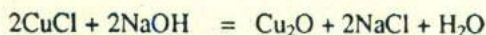
This reaction is used for testing reducing sugars in the urine of diabetic patients. Cu_2O is used for making red ruby glass. Cu_2O reacts with dilute sulphuric or nitric acids to give the corresponding cupric salts and metallic copper:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

$$Cu_2O + 2HNO_3 = Cu + Cu(NO_3)_2 + H_2O$$
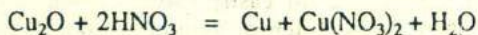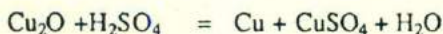
Cuprous chloride, CuCl : This is obtained in the form of a precipitate when copper metal is added to a solution of $CuCl_2$ in presence of HCl. The precipitate of CuCl is formed by oxidation-reduction reaction :

$$CuCl_2 + Cu = 2CuCl$$

Cuprous chloride is easily produced by dissolving Cu_2O in conc. HCl. CuCl is a white crystalline compound and soluble in conc. HCl giving $CuCl_2^-$:

$$CuCl + HCl = 2HCuCl_2$$
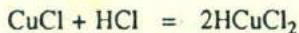
The solution of CuCl in HCl containing $CuCl_2^-$ ion has the two Cl linked to copper by covalent bonds :

$$\left[\overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}} \, \colon \, Cu \, \colon \, \overset{\bullet\bullet}{\underset{\bullet\bullet}{Cl}} \colon \right]$$
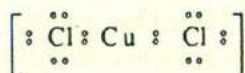
CuCl solution in HCl is used in gas analysis for the absorption of CO giving CuCl.CO.2H$_2$O :

$$
\begin{array}{ccc}
\text{OC} & \text{Cl} & \text{CO} \\
\searrow & \diagup \quad \searrow & \swarrow \\
 & \text{Cu} \qquad \text{Cu} & \\
\nearrow & \nwarrow \quad \diagup & \nwarrow \\
\text{H}_2\text{O} & \text{Cl} & \text{H}_2\text{O}
\end{array}
$$
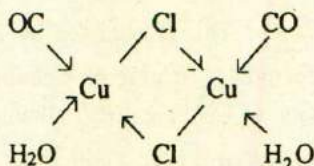
Cuprous chloride dissolves in ammonia forming a colourless solution known as *ammonical cuprous chloride*, Cu(NH$_3$)$_4$Cl. This solution absorbs oxygen and becomes blue due to the conversion of Cu^{+1} to Cu^{+2} and also absorbs CO. With acetylene this gives a bright-red precipitate of cuprous acetylide, Cu$_2$C$_2$:

$$2CuCl + C_2H_2 + 2NH_4OH \rightarrow Cu_2C_2 + 2NH_4Cl + 2H_2O$$
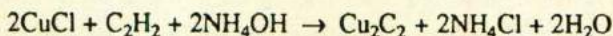
The structure of Cu$_2$C$_2$ is, $Cu \overset{\bullet}{\underset{\bullet}{}} C \overset{\bullet}{\underset{\bullet}{}} \overset{\bullet}{\underset{\bullet}{}} C \overset{\bullet}{\underset{\bullet}{}} Cu$

In the vapour state cuprous chloride has the formula Cu$_2$Cl$_2$ determined by the vapour density method.

Cuprous iodide, CuI : This is most easily formed when any soluble iodide, such as KI, reacts with copper sulphate solution. Cupric iodide, CuI$_2$, first formed, is unstable and decomposes into cuprous iodide and free iodine :

$$2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$$
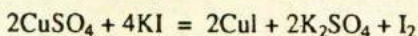
This reaction is used for the iodometric determination of copper in solutions by titration of the free iodine or the tri-iodide ion, I$_3^-$, with sodium thiosulphate according to the reaction :

$$2\,Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$
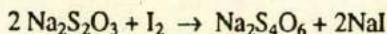
Cuprous thiocyanate, CuSCN : This is obtained in the form of a white precipitate when CuSO$_4$ solution is treated with NH$_4$CNS or KCNS in presence of SO$_2$. The green precipitate of Cu(CNS)$_2$ first formed is converted to CuCNS by reduction with sulphurous acid :

$$2Cu^{+2} + HSO_3^- + H_2O = 2\,Cu^+ + HSO_4^- + 2H^+$$

$$Cu^+ + SCN^- = CuSCN$$
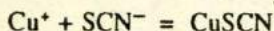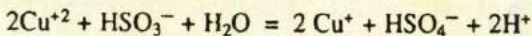
This white precipitate is filtered and washed. This is used for gravimetric method for copper determination and also for the separation of copper from zinc which does not form insoluble compound with CNS$^-$ ion.

Compounds of Divalent Copper (Cu^{+2})

As mentioned before the cupric ion has incomplete 3d orbital containing 9 electrons. All its compounds are coloured except anhydrous CuF_2 and $CuSO_4$. The deep coloured compounds or complexes of Cu^{+2} have copper in covalent bonding. Thus, the Cu—O bond in $CuSO_4$ is more ionic in the anhydrous $CuSO_4$ than in $CuSO_4.5H_2O$. In the solid state the divalent copper compounds may be of various colours but the dilute solutions have the blue colour due to the formation of $[Cu(H_2O)_4]^{+2}$ complex ion.

Cupric oxide, CuO : This is obtained when copper metal in finely divided form is heated in oxygen (air). CuO is also formed when cupric nitrate or carbonate is heated strongly as given by the following equations :

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$
$$CuCO_3 = CuO + CO_2$$
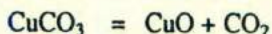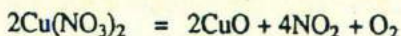
Cupric oxide is a good oxidising agent and is used to determine carbon in organic compounds.

Copper hydroxide, $Cu(OH)_2$: This is obtained by adding alkali solution to cold solution of cupric salt. In hot condition, CuO is formed. The composition of this precipitate appears to be indefinite. It is somewhat amphoteric and dissolves in excess of concentrated alkali giving a deep blue solution containing cuprate ion, $Cu(OH)_4^{-2}$. The hydroxide precipitate is readily soluble in aqueous ammonia giving a deep blue solution known as "Schwezer's Reagent". This dissolves cellulose and is used for making rayon. The blue solution contains $Cu(NH_3)_4^{+2}$ ions.

Copper sulphate, $CuSO_4$: This is the most important common salt of copper. It is obtained by dissolving CuO or $CuCO_3$ in dil H_2SO_4 and crystallizing :

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

Anhydrous $CuSO_4$ is formed by heating metallic copper in conc. H_2SO_4 :

$$Cu + H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$
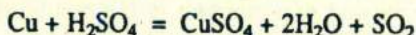
Copper sulphate is produced on a large scale by roasting copper pyrites at a controlled temperature. Iron is oxidised to insoluble Fe_2O_3 and $CuSO_4$ is leached

out with water. The leaching on evaporation and crystallization gives the crystals of $CuSO_4.5H_2O$. It is also produced by dissolving scrapes of copper in dil. H_2SO_4 in presence of air :

$$2Cu + 2H_2SO_4 + O_2 = 4CuSO_4 + 2H_2O$$
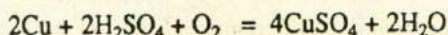
The oxidative leaching of oxide ore also gives $CuSO_4$:

$$2Cu_2O + 4H_2SO_4 + O_2 = 4CuSO_4 + 4H_2O$$
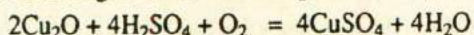
These reactions are now-a-days used for the extraction of copper from low-grade ores. $CuSO_4$ solution obtained is electrolysed as described before.

The anhydrous copper sulphate is white but when crystallized from aqueous solution, the blue pentahydrate, $CuSO_4.5H_2O$ commonly known as *blue vitriol*, is formed. $CuSO_4.5H_2O$ contains 4 molecules of water co-ordinated to copper and the fifth molecule is attached to the sulphate and also with 2 coordinated water molecules by hydrogen bonding as given in Fig. 15—2. $CuSO_4.5H_2O$, as most of the Cu^{+2} complexes, actually possess distorted octahedral structures containing 4 short and two long metal-to-ligand bonds (see chapter 24).
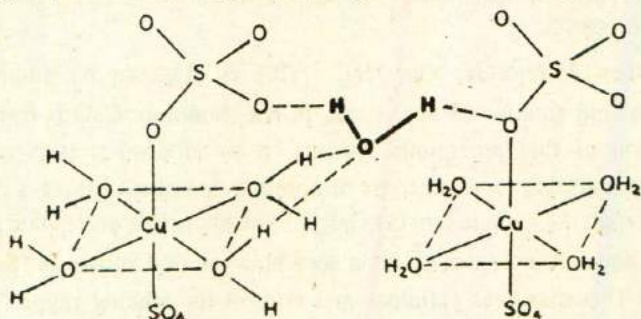
Fig. 15—2. Structure of $CuSO_4.5H_2O$ (two dimensions)

The dehydration of hydrated $CuSO_4$ proceeds in steps giving $CuSO_4.3H_2O$, $CuSO_4.H_2O$ and finally $CuSO_4$ at about 360°C. At high temperature it tends to decompose into CuO and SO_3.

$CuSO_4$ in ammonia solution gives the blue complex $Cu(NH_3)_4SO_4.H_2O$.

$CuSO_4$ is used in electrolytic refining of copper, in electroplating, in making green pigments and as a mordant in the textile industry. This is also used in making Bordeaux Mixture (a mixture of $CuSO_4$ solution and milk of lime) as a wash to kill fungi on plants. It is used to manufacture other compounds of copper. Anhydrous $CuSO_4$ readily takes up water and turns blue

and hence it is used for detecting water in alcohols and ether and also for removing water from these liquids since $CuSO_4.5H_2O$ is insoluble in alcohol and ether.

Copper carbonate, $CuCO_3$: Only basic $CuCO_3$ are formed having compositions $2CuCO_3.Cu(OH)_2$ (deep blue) and $CuCO_3.Cu(OH)_2$ (bright green). They occur in nature as minerals, *azurite* and *malachite* and basic $CuCO_3$ is made by adding limestone to copper nitrate solution.

Copper acetate : The basic copper acetate is made by exposing sheets of copper to vinegar and air :

$$2Cu + 2CH_3COOH + O_2 = (CH_3COO)_2Cu.Cu(OH)_2$$
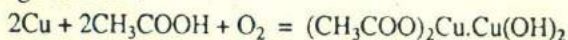
This is only a basic compound and the bright-green substance is known as 'verdigris' and is used as pigments.

Copper chloride : Cupric chloride may be obtained in the anhydrous state by the reaction of copper metal and chlorine. In the hydrated state copper chloride is formed when CuO is dissolved in HCl and the crystalline product is obtained in the form of blue green dihydrate $CuCl_2.2H_2O$.

The anhydrous $CuCl_2$ has chain structures :
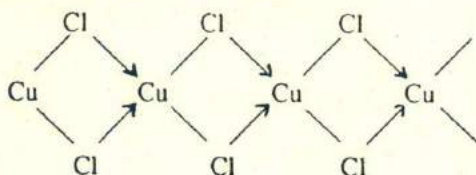
In aqueous solutions $CuCl_2$ behaves as strong electrolytes and exhibits tendency to form complex $[CuCl_4]^{-2}$ ions :

$$Cu^{+2} + 4Cl^- \rightleftharpoons [CuCl_4]^{-2}$$
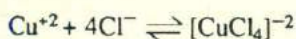
Copper cyanide, $Cu(CN)_2$: This is obtained when potassium cyanide is added to $CuSO_4$ solution as a red precipitate. On boiling, $Cu(CN)_2$ is decomposed forming cuprous cyanide and cyanogen :

$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2$$
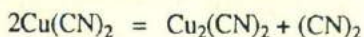
Both cuprous cyanide and cupric cyanide are dissolved in excess of KCN forming colourless complexes of composition $K_3Cu(CN)_4$ and $K_2Cu(CN)_4$ respectively. Cuprous compounds generally form $KCu(CN)_2$ complex with KCN, and cupric compounds also give the complex cyanides of cuprous ion

because $Cu(CN)_2$ first formed is readily decomposed to CuCN which actually forms the complex $KCu(CN)_2$ or $K_3Cu(CN)_4$. These cyanide complexes of copper are stable in solution and do not form precipitate of copper sulphide with H_2S whereas Cd complex, $K_2Cd(CN)_4$, is unstable and gives CdS with H_2S. This is the basis of the separation of Cu and Cd.

Copper nitrate, $Cu((NO_3)_2$: This is obtained when metallic copper or CuO is dissolved in dilute HNO_3. The solution on evaporation gives beautiful blue crystals of $Cu(NO_3)_2.3H_2O$ (or $6H_2O$). This is very hygroscopic and on heating decomposes to CuO and NO_2:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$
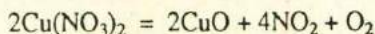
Copper thiosulphate, CuS_2O_3: On adding $Na_2S_2O_3$ solution to $CuSO_4$, a colourless solution is obtained due to the formation of $NaCuS_2O_3$ complex containing Cu^{+1}:
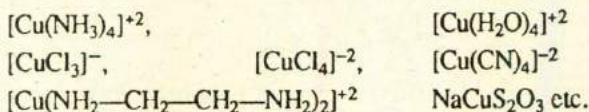
$$CuSO_4 + Na_2S_2O_3 = Na_2SO_4 + CuS_2O_3$$
$$2CuS_2O_3 + 2Na_2S_2O_3 = 2NaCuS_2O_3 + Na_2S_4O_6$$
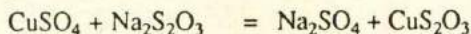
But the solution of $NaCuS_2O_3$ is unstable and is decomposed to give Cu_2S on warming:

$$2NaCuS_2O_3 + H_2O = Cu_2S + Na_2S_2O_3 + H_2SO_4$$
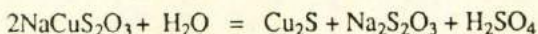
Complex Compounds of Copper

A large number of complex compounds of both Cu^+ and Cu^{+2} have been described above. The most common complexes are:

$[Cu(NH_3)_4]^{+2}$,		$[Cu(H_2O)_4]^{+2}$
$[CuCl_3]^-$,	$[CuCl_4]^{-2}$,	$[Cu(CN)_4]^{-2}$
$[Cu(NH_2-CH_2-CH_2-NH_2)_2]^{+2}$		$NaCuS_2O_3$ etc.

Organic acids form large number of complexes with Cu^{+2}. The complexes of Cu^{+1} are tetrahedral in structure but Cu^{+2} complexes are distorted octahedral although they appear to be square planar.

Fehling Solution :

In presence of tartrate ion, $C_4H_4O_6^{-2}$, copper sulphate forms an intense blue solution from which copper cannot be precipitated, as $Cu(OH)_2$ by alkali. The

alkaline solution of $CuSO_4$ with potassium hydrogen tartrate, $KHC_4H_4O_6$, is known as *Fehling Solution*. This is used to detect the presence of reducing sugars, such as glucose. The copper complex has probably the structure as shown in Fig. 15—3.
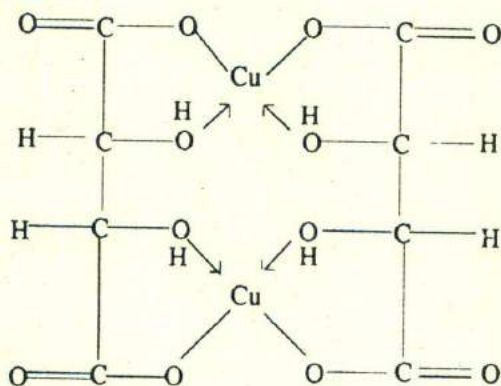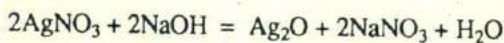

Fig. 15—3. Copper tartrate complex in Fehling Solution.

Compounds of Silver

Silver oxide, Ag_2O : This is formed in a number of ways. Usually it is made by the action of alkalies on silver nitrate solution. A dark brown precipitate of Ag_2O is formed :

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$$

Ag_2O is sparingly soluble in water; the solution is distinctly alkaline due to the reaction :

$$Ag_2O + H_2O \rightleftharpoons 2Ag^+ + 2OH^-$$
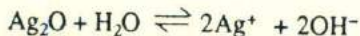
Silver oxide readily dissolves in aqueous ammonia to form a strong base which is a colourless complex, $Ag(NH_3)_2OH$. This solution behaves as a weak oxidizing agent. This reacts with aliphatic and aromatic aldehydes reducing $[Ag(NH_3)_2]^+$ ion to metallic silver which deposits in the form of mirror. $[Ag(NH_3)_2]OH$ is known as *Tollens' Reagent*.

$$2Ag(NH_3)_2OH + RCHO \longrightarrow RCOONH_4 + 3NH_3 + H_2O + 2 Ag$$
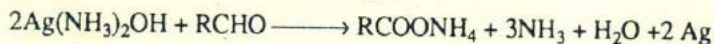
On heating, Ag_2O is readily decomposed to metallic silver in presence of air. Hence the case of extracting silver by roasing of its ores :

$$2Ag_2O = 4Ag + O_2$$
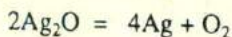
In presence of alkaline solution, Ag^{+1} is oxidised to Ag^{+2} and Ag^{+3} by strong oxidising agents forming AgO and Ag_2O_3.

Ag_2O is a good reagent for preparing soluble hydroxides from halides. It is used both in organic and inorganic chemistry. Thus, cesium chloride reacts with Ag_2O to form soluble $CsOH$ and $AgCl$ which is removed by filtration :

$$2CsCl + Ag_2O + H_2O = 2CsOH + 2AgCl$$
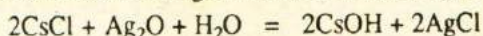
Silver halides, AgX : Silver fluoride, AgF, is extremely soluble in water whereas the chloride, bromide and iodide are insoluble. The curdy precipitates of silver halides are obtained when $AgNO_3$ is added to soluble halides. Thus,

$$AgNO_3 + NaX \rightarrow AgX + NaNO_3$$

AgF is obtained by dissolving Ag_2O in HF and by crystallization. The colour of the various silver halides are different.

Ag X	Colours	Solubility in H_2O	Solubility in NH_4OH
AgF	white	soluble	soluble
AgCl	white	insoluble	soluble
AgBr	pale yellow	insoluble	difficultly soluble
AgI	pale brown	insoluble	insoluble

Many of the silver salts are insoluble in water except $AgNO_3$, $AgClO_4$ and AgF. Most silver salts are also colourless but those containing polarizable anions are coloured as well as insoluble. AgI, Ag_3AsO_4, Ag_2CrO_4 Ag_3PO_4 are coloured. The small Ag^{+1} ion has great polarizing action on large I^- ion and, according to Fajan's rule, AgI is considered as a covalent compound.

The solution of AgX in ammonia gives complex $Ag(NH_3)_2X$.

Silver halides are affected by light and turn dark in colour because of the reduction into their elements :

$$2AgX + light\ (h\nu) = 2Ag + X_2$$
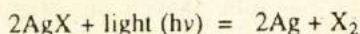
This fact has been used in large scale applications of silver halides in the production of photographic films.

Silver nitrate, AgNO₃ : This is obtained by dissolving silver metal in HNO_3 and crystallising $AgNO_3$ by evaporation :

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO$$
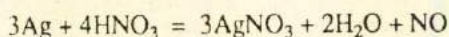
AgNO$_3$ is the only simple salt of Ag which is of great use in solution. The solution of AgNO$_3$ in water is neutral and not hydrolysed. This indicates that Ag$_2$O is a strong base.

AgNO$_3$ is produced on a commercial scale under the trade name "Lunar caustic". Organic substances readily reduce AgNO$_3$ to give free Ag. For instance, the black stains on skins and clothes are due to the deposition of silver from AgNO$_3$ by reduction. AgNO$_3$ is mostly used in producing photographic films and mirrors and as a laboratory reagent.

Complex Compounds of Silver

Silver forms a large number of complexes as in the case of copper. Silver salts dissolve in KCN and NH$_4$OH to form soluble colourless complexes :

Amino complexes of silver : Many insoluble silver compounds dissolve readily in aqueous ammonia forming amino-silver complexes. Thus Ag$_2$O which is formed by adding a base to a silver salt dissolves in NH$_4$OH solution to give [Ag(NH$_3$)$_2$]$^+$ ion :

$$Ag_2O \text{ (solid)} + 4\,NH_3 + H_2O \rightarrow 2\,[Ag(NH_3)_2]^+ + 2OH^-$$
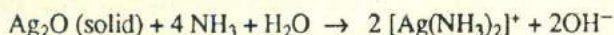
Solutions of silver salts in ammonia are used in silver plating. Evaporation of a solution containing [Ag(NH$_3$)$_2$]$^+$ ions leaves dangerous residues which explode violently and are supposed to contain silver amide, AgNH$_2$, and silver azide, AgN$_3$. This indicates that bonds between Ag—N are of different type. This is represented as,

$$[H_3N \rightarrow Ag \leftarrow NH_3]^+$$
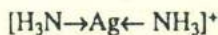
Ammonical AgNO$_3$ solution produces beautiful mirror of silver with reducing agent, such as glucose, when warmed. This reaction is used for producing mirrors on industrial scale.

With KCN silver salts form [Ag(CN)$_2$]$^-$; the thiosulphate complex, [Ag(S$_2$O$_3$)$_2$]$^{-3}$, is formed during the fixing process of photography by dissolution of AgBr in Na$_2$S$_2$O$_3$.

Divalent compounds of silver : There are some Ag^{+2} compounds formed by special reactions. AgF$_2$ is formed when fluorine gas is passed over silver powder or by the action of ClF$_3$ on AgCl. Argentic oxide, AgO, is formed by precipitation from AgNO$_3$ solution with potassium persulphate, K$_2$S$_2$O$_8$,

or by oxidising Ag_2O with hot alkaline $KMnO_4$, solution. Stable complexes of divalent Ag contain Ag atom bonded to four or more N atoms in the complexing groups, e.g., 2—2—dipyridyl complex of Ag^{+2}. Dipyridyl N atoms are bonded to Ag^{+2} as shown below :

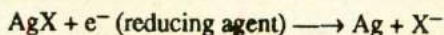$$\left[\begin{array}{c} PyN \\ PyN \end{array} \diagdown Ag \diagup \begin{array}{c} NPy \\ NPy \end{array} \right]^{+2}$$
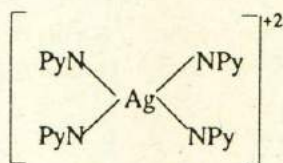
Divalent complexes, like those of copper, have an odd electron and is highly coloured having magnetic properties. Ag^{+2} has great oxidizing power and does not exist in aqueous solutions.
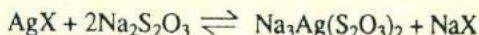
The Processing of Photographic Films

1. The photographic films : Photographic films are thin sheets of cellulose acetate or other polymer films coated with a colloidal suspension of small silver halide crystals in gelatin. Pure solutions of silver nitrate, potassium bromide and potassium iodide are mixed in the presence of gelatin for the preparation of the photographic emulsion. The particle size and the amounts of silver halides are used to determine the "sensitivity" or "speed" of the film.

2. Exposure : The film is exposed when the image is focussed upon the light-sensitive photographic emulsion on the film. The silver crystals become "activated" when exposed to light and they become reduced. The chemical change is not well understood, but the silver halide crystals receive the most light (from the lighted areas of the object) and are more readily reduced than those-receiving little light (from the dark areas of the object), during the development of the film.

3. Developing : After exposure, the film is developed by placing it in an alkaline solution of an organic reducing agent, such as hydroquinone or pyrogallol. The reducing agent acts upon the grains of silver halide with a speed proportional to the intensity of the illumination during exposure and reduces them to metallic silver :

$$AgX + e^- \text{ (reducing agent)} \longrightarrow Ag + X^-$$

4. Fixing : After developing, the film is fixed by treating it with a solution of sodium thiosulphate (hypo) to dissolve the unreduced silver halide :

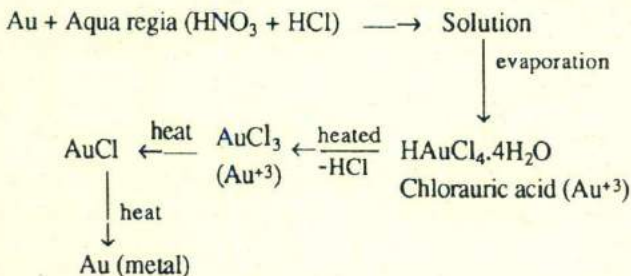$$AgX + 2Na_2S_2O_3 \rightleftharpoons Na_3Ag(S_2O_3)_2 + NaX$$

The metallic silver remaining on the film forms the visible image and is called a negative, since the bright portions of the original image are now dark and the dark portions of the original are now bright.

5. Printing : The printing process is essentially the same as that of making a negative. Since the sensitive printing paper is illuminated through the negative, the image is once again reversed, and now corresponds to the original image as regards bright and dark areas on the print.
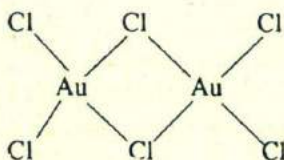
6. Toning : The printing may be toned by replacing part of the silver of the image by gold or platinum. To do this, the print is treated with solutions of $NaAuCl_4$ or K_2PtCl_6. The more active silver displaces these noble metals from their salts to give a thin deposit of gold (red tone) or platinum (dark gray).

Compounds of Gold

Gold forms two series of compounds having Au^+ and Au^{+3} oxidation states. A good example is the compounds obtained by dissolving gold in aqua regia :

Au + Aqua regia (HNO_3 + HCl) $\longrightarrow$ Solution

$\downarrow$ evaporation

$AuCl \xleftarrow{heat} AuCl_3 \xleftarrow[-HCl]{heated} HAuCl_4.4H_2O$
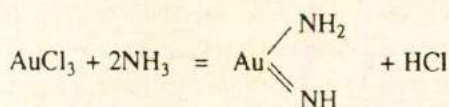   (Au^{+3})   Chlorauric acid (Au^{+3})

$\downarrow$ heat

Au (metal)

All compounds of gold are decomposed by heat because of their thermal instability. AuCl undergoes disproportionation reactions forming $AuCl_3$ and Au. $AuCl_3$ has 4 bonds per gold atom having the structure :

Au(OH)$_3$ formed by precipitation is a weak base and dissolves in hot KOH to form potassium aurate, KAuO$_2$.

A large number of complexes of gold is known. Univalent gold gives KAu(CN)$_2$ and Au^{+3} gives KAu(CN)$_4$. These are used in the extraction of gold and in gold-plating.
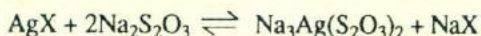
Gold fulminate, Au(N$_2$H$_3$) is obtained by ammonolysis when AuCl$_3$ is treated with ammonia. This explodes violently on heating :

$$AuCl_3 + 2NH_3 = Au\!\!\begin{array}{c} \diagup NH_2 \\ \diagdown NH \end{array} + HCl$$

QUESTIONS AND PROBLEMS

1. How does gold show a variable oxidation states? Explain the disproportionation of Au$^+$ compounds.
2. Discuss the principle involved in the extraction of gold by the cyanide process.
3. Describe the electrolytic refining of copper.
4. How do you explain the stability of Cu^{+1} and Cu^{+2} compounds ?
5. What happens when Cu salts are dissolved in (i) aqueous ammonia; (ii) KCN solution; (iii) tartaric acid solution and (iv) strong solution of NaOH?
6. (a) Discuss briefly the principles underlying the extraction of copper from its sulphide ore.

   (b) How is copper obtained in the pure conditions ?

   (c) Mention the composition and use of three important alloys of copper.
7. Compare the chemistry of copper and silver.
8. What are the advantages of the process of electroplating ? Explain in detail the method for silver plating.
9. How is copper extracted from sulphide ores ? Describe the method adopted for very poor ores. Describe copper ion complexes and its important alloys.

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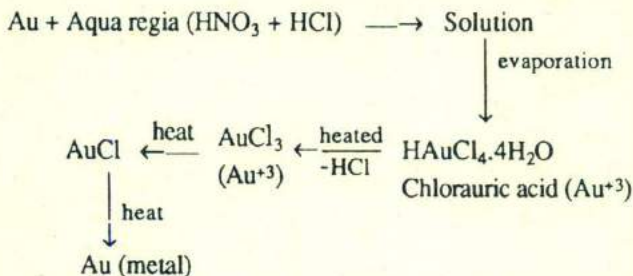$$AgX + 2Na_2S_2O_3 \rightleftharpoons Na_3Ag(S_2O_3)_2 + NaX$$

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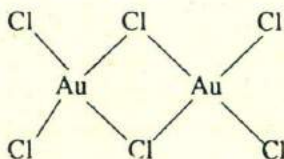
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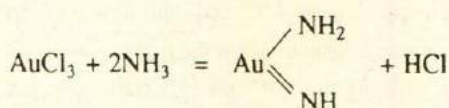$\qquad\qquad\quad (Au^{+3}) \qquad\qquad$ Chlorauric acid (Au^{+3})
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10. Explain electroplating with reference to gold plating.

11. Describe the occurrence and extraction of copper from its ores. Name the most important alloys of copper and give their compositions and uses.

12. Write a note on the occurrence and extraction of either silver or gold.

13. Write notes on; (a) electroplating and (b) silvering of mirrors.

14. Give a comparative study of the chemistry of copper, silver and gold and their principal compounds.

    Justify their inclusion in the same group of the Periodic Table with the alkali metals.

15. (a) Explain the process of hydrometallurgy of copper.

    (b) What are Fehling solution and Tollen's Reagent? Compare their actions on reducing substances.

16. What are coinage metals ? From a study of the properties of coinage metals and their compounds, justify their inclusion in the same group of the Mendellef's Periodic Table. Mention some important applications of the coinage metals.

17. Write short notes on :

    (a) The cyanide process for extraction of gold.

    (b) Reactions involved in copper metallurgy.

18. What are the sources of gold ? Describe in detail the cyanide process for the extraction of gold.

19. Write brief accounts on electro-refining of gold.

20. Discuss : (i) Properties of coinage metals are different from those of the alkali metals.

    (ii) Copper can be determined iodometrically.

21. A certain hydrate analyzes as follows : Cu—29.7%, H—2.8%, S—15.0% and O—52.5%. Determine the empirical formula of the hydrated compound.

22. A chemist wants to calculate Avogadro Number by the inspection of a solid cube of AgCl. The density of the cube is 5.56 g/cm^3. The spacing between the Ag^+ and Cl^- ions in the cube is 2.773 $\overset{\circ}{A}$ from their centres. Calculate the Avogadro's Number.

23. How is it possible to float the copper bearing particles in an ore of copper to the surface of a tank of water ?

24. List the major steps in the refining of copper. For what purposes copper is used ?

25. List the unique properties of Cu,.Ag and Au that allow their extensive use as coinage metals.

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