



Electric Properties

Dipol moment $\vec{\mu} = \delta \cdot \vec{l}$

l : distance between the centres of gravity of 2 equal and opposite charges of magnitude δ .

The structure and polarity of molecules:

a) Non-polar molecules \rightarrow (H_2, N_2)

Linear AB_2 (CO_2)

trigonal AB_3 (BF_3)

tetrahedral $AB_4, CH_4, SiCl_4$

b) polar molecules

Molecules containing lone electron pair (NH_3)

Molecules AB (HCl, NO)

tetrahedral ABC_3

less-symmetric molecules (HNO_3, H_2SO_4)

Magnetic Properties of particles and substances

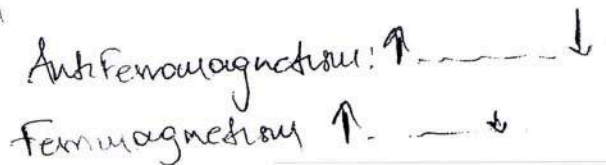
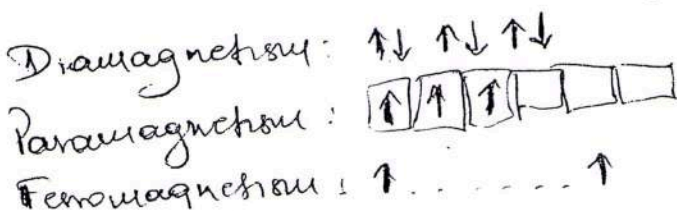
Diamagnetic substances:

Substances repelled by a magnetic field

Diamagnetism is property of all substances, that have electrons paired. (H_2, N_2, He , organic substances). - don't possess magnetic moment

Paramagnetic Substances: Substances, attracted to a magnetic field they have unpaired electrons, which do not mutually interact and they exhibit magnetic moment

Paramagnetism $\left\{ \begin{array}{l} \text{Ferromagnetism} \\ \text{ferrimagnetism} \\ \text{antiferromagnetism} \end{array} \right.$



Optical Properties

Absorption of radiation by particles and substances can be associated with changes in rotation (microwave radiation)

vibration: (infrared radiation).

Electronic Configuration: (ultraviolet, visible, near-infrared radiation) of particles.

Optical Properties are usually associated with the absorption, reflection or emission of visible light.

Colorless, transparent substances (neither absorb, nor reflect visible light, air, glass).

White substances: do not absorb, totally reflect all wave lengths of visible light (BaSO₄, MgO)

Black Substances: Totally absorb all wavelengths of visible light (graphite, platinum sponge).

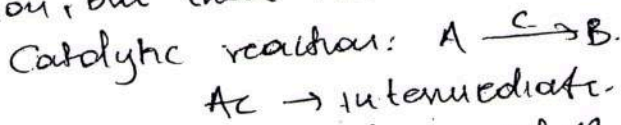
Colour substances

Absorb or reflect only some wavelengths of visible light, human eyes catch those wavelengths in which are not absorbed or which are reflected.

Catalysis

Special type of reactions containing catalyst, substance lowering the activation energy of reactions.

Catalyst: Substance that is not involved in the stoichiometry of the reaction, but that increases the reaction rate.



Catalysis: heterogenous (a catalyst is in another phase than the reactants)

homogenous (a catalyst is in the same phase as reactants)

Enzymatic (a catalyst - enzyme is in the same phase as reactants)

Law of conservation of mass

During chemical reactions there is no detectable loss or gain in total mass.

In a chemical change the total mass of reactants always equals the total mass of the product.

Law of conservation of Energy

Energy, like mass, is indestructible. Energy may be changed from one form to another, but it cannot be created or destroyed.

Law of constant composition states, that the proportion by weights of the element present in any pure compound is always the same.

Once we have determined the composition of pure substance, we know that the composition of all pure specimens of the same substance will be the same.

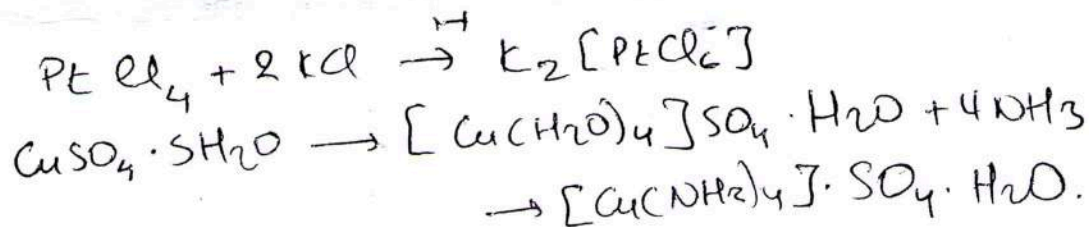
Coordination Chemistry - coordination complex compounds

A coordination compound or metal complex might be defined as a compound in which is called central atom or ion is attached to a group of ions or molecules, ligands.

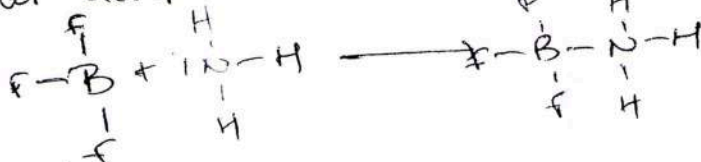
These ligands are considered to be of 2 types:

- Bonded to central atom via carbon atoms: organometallic compounds and ligands they do not: \rightarrow coordination e.

There is, of course, no sharp dividing line, also there is a clear distinction between the chemistry of coordination compounds and the chemistry of ionic solids.



Coordination bond
donor-acceptor bond \rightarrow covalent bond



Structure of Coordination compounds

Coordination number: is number of groups that immediately surround the metal

Coordination Geometry: arrangement of the ligands

Types of central atoms: neutral metals, or metal cations, with empty orbitals (transition metal elements).

Types of ligands

The majority of ligands are ions or neutral molecules, that can be thought of as electron pair donors.

Common ones are: F^- , Cl^- , OH^- , NH_3 ,

Ligands, they donate one electron pair to one metal atom are called monodentate ligand.
donor-atom O.N.S.

Ligands that contain 2 or more atoms each of which can form a two electron donor bond to the same metal ion are called polydentate ligands \rightarrow called chelate ligands, since they appear to grasp the carb between the two or more donor atoms.

When the ligands are bonded to 2 or more various central atoms, they are called bridging ligands.

Coordination number: Number of groups, ligands, that immediately surround the central atom.

! Coordination number must be higher than oxidation state of central atom.



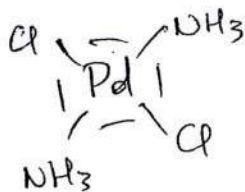


Isomerism in coordination compounds

1. Geometrical



cis



trans

2. Optical

- Optical isomers are molecules that are mirror images of each other that cannot be superimposed. They are not identical, even though all their internal distances and angles are identical.
- Optical isomers \rightarrow enantiomorphs

3. Linkage

different modes of binding e.g. SCN^- as the donor atom either sulphur (S) or nitrogen (N) may be used ambidentate ligand.

4. Ionization

Compounds of the same empirical formula differing in anion coordination to the central metal within the crystal lattice



5. Coordination

In compounds where both cation and anion are complex \rightarrow the distribution of ligands can vary.

IF

The complex is anion the suffix -ate is attached to the name of the central atom and this suffix is followed by the oxidation number.

IA naming the complex whether it is cationic or neutral, the ligands are listed beginning with the negative ones, then the central metal is mentioned followed by a roman numeral in parentheses giving its oxidation number.

The formula for the complex unit (molecules) is enclosed in square brackets.

Designation for ligands (some ligands have special names)

NH_3 amine $-\overset{+}{\text{N}}-$ H_2O aqua

NO nitrosyl CO carbonyl

anionic ligands end in -o

O^{2-} oxo H^- hydrido OH^- hydroxo CH_3COO^- acetato

F^- fluoro Cl^- chloro SO_3^{2-} sulphito CH_3 methyl

O_2^{2-} peroxo S^{2-} thio SO_4^{2-} sulphato C_6H_5 phenyl

Organic substances (compounds) with lone electron pairs pyridine, benzene, aliphatic alcohols.

Complex Cations

$[\text{Cu}(\text{H}_2\text{O})_4]\text{NO}_3$ tetraaquacopper (II) nitrate

$[\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ tetraamine copper (II) sulfate monohydrate

$[\text{Co}(\text{NH}_3)_6]^{3+}$ hexaamine cobalt (III) ion

$[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$ dichloro tetraaminecobalt (III) chloride

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ hexaamine platinum (IV) chloride.

The ligands are listed beginning with the negative ones, then the central metal is mentioned followed by a roman numeral in parenthesis giving its oxidation state

Complex anions

When the complex unit is an anion, the metal is designated by a word ending -ate and sometimes by using latin form: -urate, Ferrate with the formal oxidation number in parenthesis

$[\text{Fe}(\text{CN})_6]^{4-}$ hexacyanoferrate (II) anion (ion)

$\text{K}_3[\text{Fe}(\text{CN})_6]$ potassium hexacyanoferrate (III)

$\text{K}_2[\text{PtCl}_6]$ potassium hexachloroplatinate (IV)

$\text{K}^+[\text{Pt}(\text{NH}_3)\text{Cl}_3]^{-1}$ potassium trichloroamine platinate (II)

$\text{K}_2[\text{Cr}(\text{NH}_3)(\text{CN})_5]$ potassium pentacyanoamine chromate (III)

Acids, Bases, Neutralization, hydrolysis

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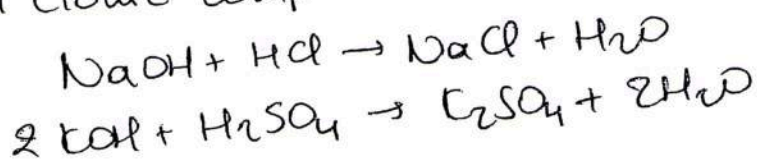
- Acids: Characteristic sour taste, the ability to react with certain metals under liberation of H_2 gas, the ability to react with the hydroxides and oxides of metal to form salt and water.

- Bases: the soapy feeling of their aqueous solutions the ability to react with acids to form salt and water.

• Acid is a substance that liberates hydrogen cations H^+ (in water medium)

• Base is a substance that liberates the OH^- anions (in water medium)

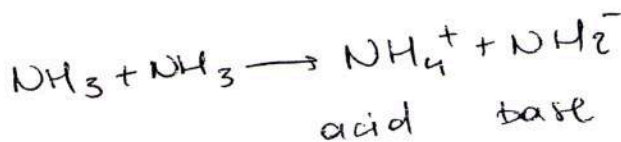
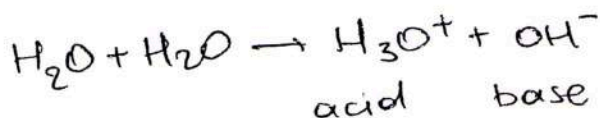
Acids and bases react with one another to form water and all ionic compound)



This type of reaction is called a neutralization reaction is exothermic.

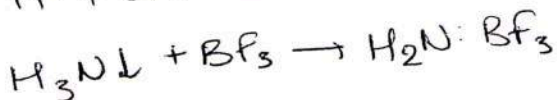
• B.L. Acids are defined as proton donors

Bases * as proton acceptors



• Lewis \rightarrow the most general definition

acids: electron pair accep
bases: electron pair donor



• Elements that can give up electrons with relatively ~~easy~~ difficulty are called electropositive elements (known as metals). Elements that do not easily give up electrons are known as non-metals. If an element generally tends to take on electrons in compound formation it is called electronegative.

• The transition elements of the d and f blocks

The transition elements are defined as elements that have partly filled d or f shells in compound. There are 61 transition elements with certain common properties:

- They are all metals
- They are hard, strong, high melting, high boiling, they conduct heat and electricity
- They form alloys
- Many of them are sufficiently electropositive to dissolve in mineral acids
- They exhibit variable valence, their ions and compounds are coloured in one or not in all oxidation states
- Because of partially filled shells they form at least some paramagnetic compounds

They are subdivided into 3 main groups:

- d-block elements
- the lanthanide
- the actinide

D-block elements (have partially filled d-shells only)

- Sc (scandium) First transition series $Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu$
partially filled 3d shell
- Second transition series (partially filled 4d shell)
 $Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag$
- Third transition series (partially filled d shell) Hf, Ta, Re, Os, Ir, Pt
Au

• The lanthanides 15 elements La ($Z=57$) \rightarrow Lu ($Z=71$) electrons enter 4f shell. Lu $4f^{14} 5d 6s^2$. The all of these elements have very similar chemical and physical properties

• The actinides: 15 elements immediately following Ac (Actinium) (electrons enter the 5f shell) and they show moderately homologous chemical behaviour.

18 The periodic table and the chemistry of elements: Inorganic chemistry deals with many compounds formed by many elements (more than 100) they compounds of gases, liquids, solids.

Types of the elements: 1. Monoatomic elements: He, Ne, Ar, Kr (noble gases)

2. Diatomic molecules Halogens: The formation of a single electron pair. $\text{F}-\text{F}$ $\text{Cl}-\text{Cl}$ Nitrogen, Oxygen: multiple bonding

3. Discrete polyatomic molecules P_4 , Se_8 $\text{N}=\text{N}$ $\text{O}=\text{O}$
Sulphur has many allotropes (multitau sulfur rings) the largest ring known is S_{20}

Elements with extended structures

In some elements, atoms form 2, 3, or 4 single covalent bonds to each other to give chains, planar or three-dimensional network extended structures. The most important elements that do this are C, P, S, Si, As, Se, Ge, Sb, Te, Sn, Bi

C: diamond (has cubic cell, but it can be viewed as starting of infinite layers. All atoms in the diamond structure are equivalent, each being surrounded by a perfect tetrahedron of four other atoms)

Si, Ge and Sn: have also diamond structure $\alpha\text{-Sn} \rightarrow \beta\text{-Sn}$
C: graphite has the layer structure, which weak forces between the layers. The layers can easily slip over one another

P: red form: black form obtained by heating white P under pressure.





The periodic system

* Electron configuration of atoms.

- The chemical elements exhibit regular and periodic trends in their chemical and physical properties when arranged in order increasing atomic numbers.

In general: the periodic properties of the elements depend on the arrangement of the electrons, on the energies required to completely remove one or more electrons from their atoms.

π

The Chemistry of the Elements in Relation to their position in the Periodic Table.

Hydrogen $1s^1$.

1. Loss of the $1s$ valence electron to form the proton H^+ (never exists as such except in gaseous state ion beams). It is associated with other atoms (in water $\rightarrow H_3O^+$).

2. Acquisition of an electron to form hydride ion H^- ($1s^2$ -helium structure); this ion exists only in crystalline hydrides of the most electropositive metals (NaH, CaH₂).

3. Formation of an electron pair bond (e.g. nonmetals form covalent bonds to hydrogen).

The chemistry of hydrogen-containing substances depends greatly on the nature of the other elements and groups in the compounds.

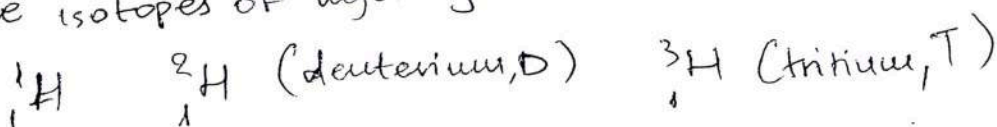
Helium $1s^2$ (noble gases $ns^2 np^6$).

The properties vary systematically with size. To enter into chemical combination with other atoms was found at Kr. Much greater reactivity has Xe and many compounds of Xe with O and F are known.

π

Hydrogen H

forms more compounds than any other element.
Three isotopes of hydrogen are known:



The normal form of the elements is the diatomic molecule.

H_2 D_2 T_2 H_2 HT DT .

D_2O (heavy water), uses as a moderator in nuclear reaction.

Molecular hydrogen is a colorless and odorless gas, insoluble in water.

Industrially H is obtained by steam reforming of methane



Hydrogen burns in air to form water and reacts explosively with oxygen and the halogens.

The bonding of hydrogen:

H^- with highly electropositive metals NaH , CaH_2 (also as a ligand "hydrides")

H^+ with nonmetals HCl , AsH_3

Hydrogen Bond: $X-H \cdots Y$.

When hydrogen is bonded to another atom X (F, O, N or Cl), the bond is quite polar with H bearing partial positive charge, it can interact with another negative or electron-rich atom Y to form so called hydrogen bond.

Classic examples: NH_3 , H_2O , HF (with abnormally highly boiling point)

↑
The group of noble gases
(Valence Electron Shell)
 $ns^2 np^6$.

He, Ne, Ar, Kr, Xe, Rn , are minor constituents of the atmosphere.

Helium (He) occurs in radioactive minerals, neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) are obtained from fractionation of liquid air.

The gases were originally termed inert, with no chemical reactivity at all. The noble gases provided the key to the problem of valency, the interpretation of the periodic table and the concept of the closed electron shell configuration.

A main use of helium is as the liquid cryoscopy.

Argon may be used to provide an inert atmosphere in laboratory apparatus, in welding and in gas-filled electric light bulbs.

Neon is used for discharge lighting tubes.

The chemistry of Xenon (Xe)

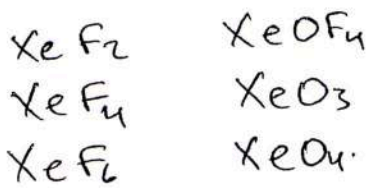
In 1962 the first compound containing a noble gas was reported. The red crystalline solid of composition



Now there are known compounds of xenon with bonds to fluorine and oxygen, and one with bond to nitrogen. (Compounds with bonds to other elements are highly unstable).

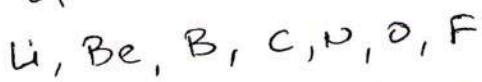
Xenon reacts directly only with fluorine, but oxygen compounds can be obtained from its fluorides.

Some xenon compounds (colorless crystals):



The other noble gas atoms have higher ionization energies and their compounds are less stable than those of xenon.

Elements of the first short period



Li^+ - high reactivity to oxygen, nitrogen, water and many other elements.

Be^{2+} - occur with the most electronegative elements.

BeF_2 , Be-F bonds have covalent character

Anion formation first appears for carbon, which forms C_2^{2-} and other polyatomic ions.

C^{4-} is uncertain

N^{3-} ions are stable in nitrides of highly electropositive elements. Oxide (O^{2-}), Fluoride (F^-) are common in solids

In aqueous solutions $\text{O}^{2-} + \text{H}_2\text{O} \rightarrow 2\text{OH}^-$



Carbon is non metal, forms single, double and triple bond to itself, or to nitrogen, oxygen and a few other elements. It is also able to form chains of carbon-carbon bond (catenation) in compounds

Nitrogen N_2

is relatively unreactive because of the great strength of the $N \equiv N$ bond.

Nitrogen compounds are covalent, only with electropositive elements, ionic nitrides (N^{3-}) may be formed.

Oxygen O_2

The diatomic molecule of oxygen has two unpaired electrons (is paramagnetic) and is very reactive.

The oxide ions O^{2-} , O_2^{2-} , O_2^{2-} exist in crystalline solids.

Hydroxide ions OH^- exist both in solids and solutions.

Fluorine: is extremely reactive due to the low bond energy in F diatomic molecule)

Ionic compounds contain F^- ions

Covalent compounds contain $X-F$ bonds. Due to the high electronegativity of Fluorine such covalent bonds are generally quite polar in the sense $X^+ \rightarrow F^-$.

↑

The group 1.A

Elements: Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb) and Cesium (Cs)

ns^1

$M^+ \rightarrow$ compounds are ionic in nature
Sodium and its salts are of great importance $NaCl$ (table salts)
 Na_2SO_4 , Na_2CO_3 .

Potassium salts are used in fertilizers.

Na^+ , K^+ are of physiological importance in animals and plants.
 Li^+ salts are used in the treatment of certain mental disorders.

Preparation and Properties

Li and Na are obtained by electrolysis of fused salts and of an melting eutectics such as $CaCl_2 + NaCl$

The metals are highly electropositive and react directly with most other elements and many compounds on heating.

Li is usually the least and the Cs (cesium) most reactive.

Reactivity with water

Na reacts vigorously
& inflames

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Rb } react explosively
Cs }

The most important compounds

oxides M_2O peroxides M_2O_2
superoxides MO_2 hydroxides $M(OH)$

$M(OH) \rightarrow$ water soluble and are used whenever strong alkali bases are required

NaOH KOH

Ionic salts

Salts of all acids are known, they are colorless, crystalline, ionic. They are water soluble, characterized by high melting point and electrical conductivity.

$Na_2SO_4, K_2CO_3, NaNO_3, KNO_3$





CHEMISTRY

LECTURE 9

The Group II A:

Elements: beryllium (Be), Magnesium (Mg), Calcium (Ca), strontium (Sr), barium (Ba), Radium (Ra), ns^2 .

- Beryllium occurs in the mineral beryl $Be_3Al_2(SiO_3)_6$. Be compounds are exceedingly toxic, causing degeneration of lung tissue.

- Mg, Ca, Sr and Ba are distributed in minerals and in the sea water

$CaCO_3$ limestone, marble

$CaCO_3, MgCO_3$ dolomite

$KCl \cdot MgCl_2 \cdot 6H_2O$ carnallite

The number of bonding electrons is 2. M^{2+} .

$SrSO_4$ strontianite

$BaSO_4$ baryte.

Beryllium and its compounds

Compounds of beryllium are mostly covalent in nature, even BeF_2 and BeO show evidence of covalent character. BeX_2 molecules should be linear. $BeCl_2$ - forms chains

The metal or the hydroxide dissolve in strong base to give the beryllate ion $[Be(OH)_4]^{2-}$ (behavior comparable to that of Al and $Al(OH)_3$

$[Al(OH)_4]^-$.

Mg, Ca, Sr, Ba, Ra.

Oxides: MO Hydroxides $M(OH)_2$

Halides MX_2 (X: I, F, Cl, Br) (iodide, fluoride, chloride, bromide)

All the known halides appear to be essentially ionic. CaF_2 is used for prisms in spectrometers.

• Hydrides: MH_2 are ionic, with exception of MgH_2 , which is more covalent in nature

• Oxo salts: Carbonates CO_3^{2-} (insoluble in water)

$MgCO_3$: is used in stomach powder to absorb acid

$CaCO_3$: (marble - mineral)

Sulfates SO_4^{2-}

$MgSO_4 \cdot 7H_2O$ used as a mild laxative

$CaSO_4 \cdot 2H_2O$ gypsum

$BaSO_4$ used as a "barium meal" as it is opaque to x-rays and provides:

→ suitable shadow in the stomach

- Boron B: No ionic compounds involving simple B^{3+} boron cations are known. Boron does form three covalent bonds using sp^3 hybrid orbitals in a trigonal plane.

BX_3 compounds are coordinatively unsaturated and act as a strong Lewis acids (electron pair acceptor). The chemistry of boron has only a few features in that with aluminum.

The oxide B_2O_3 and $B(OH)_3$ are acidic. $Al(OH)_3$ is a boric hydroxide, with weak amphoteric properties, dissolving in strong base (NaOH).

- Isolation of the element: Boron forms a number of allotropes that are difficult to purify because of the high melting points. Boron is made as an amorphous powder by reduction of the oxide B_2O_3 with Mg.



by reduction of boron trihalides with Zn. $2BCl_3 + 2Zn \rightarrow 2ZnCl_2 + 2B$

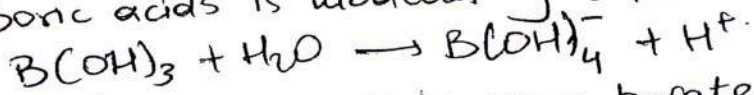
Compounds with Oxygen

Boric Acid HBO_2

HBO_3 (three hydrogen boric acid, white needles)

$B(OH)_3$ units are linked together by hydrogen bonds to form infinite layers.

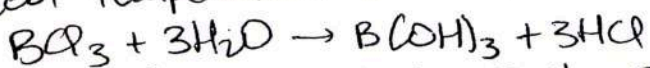
Boric acids is moderately soluble in water.



$B(OH)_4^-$ ion occurs in many borate-type minerals

Trihalides of boron

BF_3 BCl_3 BBr_3 are obtained by direct interaction at elevated temperature and react very easily with water:



Borane - molecular hydrides B_2H_6 , B_4H_{10} , B_9H_{15}

The Group III B.

Elements: Aluminum (Al), gallium (Ga), indium (In), thallium (Tl)

These elements are more metallic than boron and the chemistry in compounds is more ionic. All four elements give trivalent compounds. univalent state is known for Ga, In and Tl.

Aluminium is the commonest metallic element in the earth's crust and occurs in rocks bauxite. $(Al_2O_3 \times n H_2O)$ } used for
cryolite (Na_3AlF_6) } preparation
of Al.

Oxides: Al_2O_3 the only oxide of aluminium.

Alumina: has many polymorphs or hydrated materials. eg $\alpha-Al_2O_3$
 $\delta-Al_2O_3$.

Halides: of all four elements are known.





Carbon C

The electronic structure in its ground state is
 $1s^2 2s^2 2p^2$

The ion C^{4+} does not arise in any normal chemical process, but C^{4+} may possibly exist in some carbides.

A unique feature of carbon is its property for bonding to itself with single C-C, double C=C and triple bonds C≡C (such types of carbon compounds are objects for study in the field of organic chemistry)

Allotropy of carbon: diamond, graphite, amorphous carbon

Diamond and graphite differ in their physical and chemical properties because of differences in arrangement and bonding of the atoms

- Diamond - cubic, tetrahedral arrangement
- Graphite - loosed layered structure
- Diamond is denser (3.51 g cm^{-3}), than graphite (2.22 g cm^{-3}).
- Diamond can be produced from graphite only by the action of high pressure and high temperature, naturally occurring diamonds must have been formed when these conditions were provided by geological processes.
- Diamond will burn in air at 600°C to 800°C but its chemical reactivity is much lower than of graphite or amorphous carbon.

CARBIDES

Formally C^{4-}



are formed by the direct interaction of carbon with metals or metal oxides at high temperatures.

CARBON MONOXIDES CO.

colorless toxic gas is formed when carbon is burned in a deficiency of oxygen. At all temperatures there is the equilibrium $2CO \rightleftharpoons C + O_2$

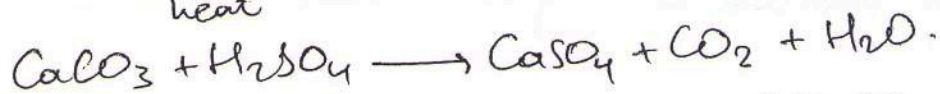
CO is formally the anhydride of formic acid $HCOOH$.

The toxicity of CO arises from its ability to bind to the Fe atom in hemoglobin in the blood.

CARBON DIOXIDE CO_2

is present in the atmosphere, in volcanic gases and in certain spring waters

CO_2 can be prepared by the action of strong inorganic (mineral) acids on carbonates (salts of carbonic acid), or by thermal decomposition



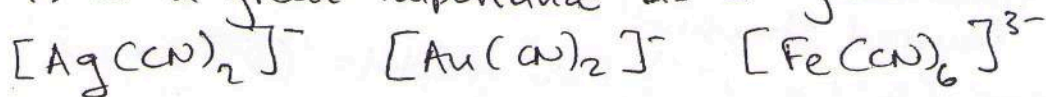
CO_2 is anhydride of carbonic acid H_2CO_3 .

COMPOUNDS WITH C-N BONDS (Cyanides)

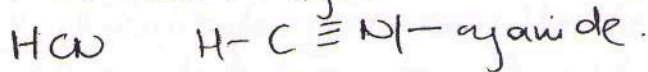
Cyanogen - $(\text{CN})_2$ - the flammable gas

Hydrogen cyanide HCN (covalent, molecular substance), it is extremely poisonous, colorless gas and is evolved when cyanides are treated with acids. In aqueous solution HCN weak acid. Salts: NaCN , KCN

CN^- is of a great importance as a ligand.



Fusion of alkali cyanides with sulphur gives thiocyanate ion SCN^-



HCNO - cyanate

HCNS - thiocyanate

COMPOUNDS WITH C-S BONDS

Carbon disulphide (disulfide) CS_2 (very toxic pale yellow liquid)



in reaction with chlorine CCl_4 is formed



Silicon, Germanium, Tin, Lead
Si, Ge, Sn, Pb

Silicon is second only to oxygen in its natural abundance and occurs as silica minerals as quartz SiO_2 .

Germanium, tin and lead are rare elements

SnO_2 cassiterite. (in granites, sands and clays)

Carbon dioxide

is a gas dioxide $\langle \text{O} = \text{C} = \text{O} \rangle$, whereas SiO_2 is a giant molecule with Si atoms singly bound to four oxygen atoms giving like SiO_4 tetrahedra.

4

- Oxidation states in compounds II, IV.
- Hydrides MH_4 colorless gases, but only monosilane SiH_4 is of any importance.
- Chlorides MCl_4
- Oxides SiO_2 (quartz, enstoballite) -
(silica)

4

Lead Pb

of the mentioned four elements, only Pb has well-defined cationic chemistry. Pb^{2+} lead salts are only sparingly soluble in water. PbSO_4 or PbCrO_4 are insoluble soluble salts, eg $\text{Pb}(\text{NO}_3)_2$ are toxic.

4

NITROGEN N

Electron configuration $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

N can complete its valence shell on the following ways:

Electron gain to form nitride ion N^{3-} (nitrides with most electropositive metals)

Formation of electron-pair bonds with electron gain-electron loss.

Occurrence and properties

Nitrogen occurs in nature mainly as dinitrogen (78% by volume of the earth's atmosphere)

Isotopes $^{14}_7\text{N}$ $^{15}_7\text{N}$

Dinitrogen is totally unreactive due to the great strength of the $\text{N} \equiv \text{N}$ bond.

Nitrogen is obtained by liquefaction and fractionation of air; and could be prepared by thermal decomposition of sodium azide.



Typical reactions at elevated temperature



H

NITRIDES

OF electropositive metals can be regarded as ionic ($\text{Li}_3\text{N}, \text{Ca}_3\text{N}_2$)
 OF transition metals are often nonstoichiometric
 OF nonmetals are covalent ($\text{BN}, \text{P}_3\text{N}_5$)

H

NITROGEN + HYDROGEN

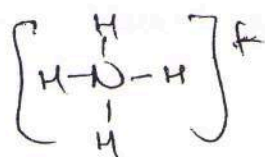
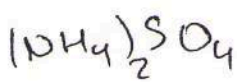
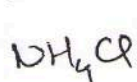
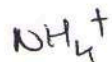
Ammonia NH_3

(prepared by Haber process $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$).

NH_3 : colorless, pungent gas, extremely soluble in water, solution is weak base.

NH_4OH ammonium hydroxide

Ammonium salts



Hydrazine N_2H_4 tetrahedral arrangement

Hydroxylamine NH_2OH

H

NITROGEN OXIDES

N_2O nitrous oxide N^I

NO nitric oxide N^{II}

* NO_2 nitrogen dioxide N^{IV}

N_2O_3 dinitrogen trioxide N^{IV}

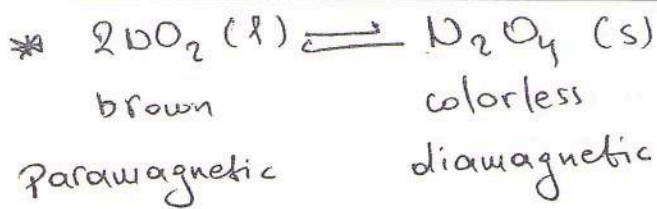
N_2O_5 dinitrogen pentoxide N^V

H

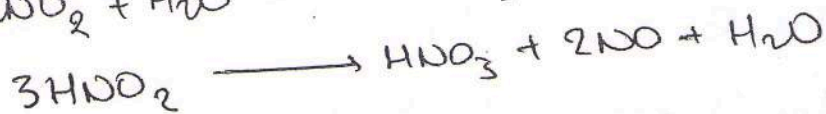
ACIDS

HNO_2 nitrous acid \longrightarrow salts nitrite NO_2^-

HNO_3 nitric acid \longrightarrow nitrate NO_3^-



(23)

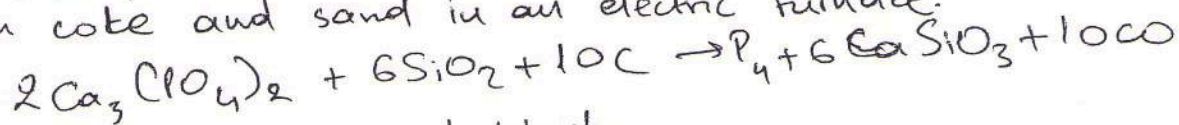


Phosphorus (P), arsenic (As), antimony (Sb), bismuth (Bi)
 $ns^2 np^3$

Valence shell of the atoms are similar to the electron configuration of nitrogen (NH_3, PH_3).

Phosphorus is a true non metal in its chemistry, while As, Sb and Bi show an increasing trend to metallic character and cationic behaviour.

Phosphorous can be obtained by reduction of phosphate rock with coke and sand in an electric furnace.



P: white, red and black

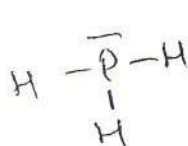
↓
 very poisonous.

As, Sb and Bi are obtained as the metals by reduction of their oxides with carbon or hydrogen.

→
HYDRIDES EH_3

Phosphine PH_3 (sparingly soluble in water, is very weak base)

AsH_3 SbH_3



PH_4^+ (NH_4^+)

→
HALIDES $\text{EX}_3, \text{EX}_5^-$

The trihalides, except PF_3 , are obtained by direct halogenation

PF_3 : colourless, toxic gas

PCl_3 : low-boiling liquid

AsCl_3 : similar to those of phosphorous

SbCl_3

BiCl_3 : white crystalline solid, hydrolyzed by water to BiOCl

P^{III} and As^{III} oxides are acidic

Sb^{III} amphoteric

Bi^{III} strictly basic

P_2O_5 correct molecular formula P_4O_{10}

P_4O_{10} : most effective drying agent, it reacts with water to form a mixture of phosphoric acid, composition depends on the quantity of water.





The d-block elements and their compounds

3d 4d 5d

1) All the d-block elements are metals, are good conductors, most are malleable, ductile and silver-white in colour. (Exception copper → red brown gold → yellow).

2) The d-block elements lose their valence s-electrons when they form compounds.

3) Most of them can also lose a variable number of d electrons, and hence show variable valence. This makes these elements useful as catalyst and in partnership with proteins and enzymes.

4) The d-block elements are excellent Lewis acids (electron pair acceptors) and form coordinate bonds with molecules or ions that can act as Lewis bases (electron pair donors).

Complexes of the d-metals are often brightly colored and magnetic and are used in analysis, color science and catalysis.

Trends in chemical properties

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn
Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd
La, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg.

Except for mercury (Hg), the elements ~~are~~ at the ends of each row of the d-block occur in only one oxidation state.

Scandium is found only in oxidation state +3, zinc only +2; All the other elements of each row are found in at least two oxidation states (eg. CuCl; CuCl₂)

Elements close to the center of each row have the widest range of oxidation states.

Manganese (Mn) at the center of its row, has seven oxidation states.

Although most d-metal oxides are basic, the oxides of a given element show a shift toward acidic character with increasing oxidation number.

CrO	+2	basic
Cr ₂ O ₃	+3	amphoteric
CrO ₃	+6	acidic

scandium: is a reactive metal, more so than calcium does.

Titanium: (Ti) is a light strong metal, unlike scandium, it is resistant to corrosion, because of forming oxide on its surface. The most stable oxidation state of Ti is +4, with both its 4s electrons and its 2 3d electrons lost.

TiO₂: titanium dioxide, white, non toxic solid, used as the white pigment in paints and paper.

Compounds containing Ti in oxidation state +3 are very sensitive to moisture and traces of oxygen.

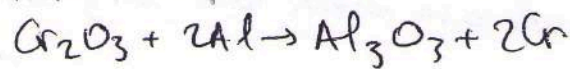
Vanadium (V): → silver grey metal, produced by reduction vanadium oxide with calcium.



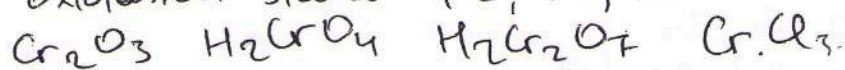
V₂O₅ → Vanadium pentoxide

Used as an oxidizing agent or catalyst in the contact process for the manufacture of H₂SO₄.

Chromium: (Cr) is a bright lustrous, corrosion resistant metal. It gets its name from its colorful compounds. Chromium metal is produced by the reaction with aluminum.



Oxidation states +2, +3, +6



Manganese: (Mn): gray metal, can be prepared by the reaction with Al.



Manganese occurs in wide variety of oxidation states. The most stable state is +2; most common are +3, +4, +7.

MnO₂ → brown-black solid

KMnO₄ (potassium permanganate): It is used for oxidation in organic chemistry and also as mild disinfectant.

Iron (Fe): the most widely used of all d-metals, the most abundant element on earth.

Its principal ores:

hematite	Fe ₂ O ₃
magnetite	Fe ₃ O ₄
pyrite	FeS ₂

Pure iron is relatively flexible and malleable, but the carbon atoms make cast iron very hard and brittle.

A healthy adult human body contains around 3 gr of iron, mostly as hemoglobin (around 2 mg is lost daily).

Iron deficiency, or anemia, results in reduced transport of oxygen to the brain and muscles, and an early symptom is chronic tiredness.

Cobalt (Co): silver gray metal, using mainly in alloys with iron.

CoO → blue substance used to color glass and ceramic glazes. We need cobalt in our diet, it is a component of vitamin B₁₂.

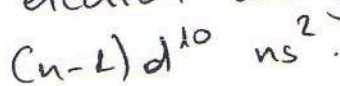
Nickel: (Ni) → Used as alloy with iron hard, silver white metal.

~~Ni(CO)~~ Ni(CO)₄ metal tetracarbonyl.

GROUP 11 (11)

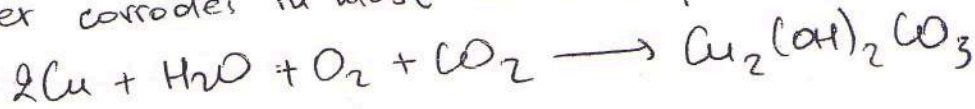
Copper (Cu), Silver (Ag), Gold (Au)

electron configuration



Cu is unreactive, it is excellent electrical conductor is used in alloys with zinc (brass), with tin (bronze), with nickel.

Copper corrodes in moist air in the presence of CO₂.



Cu₂(OH)₂CO₃ pale green.

Basic copper carbonate.

Cu(II) compounds are most stable

Cu(I) salts disproportionate into metallic copper and copper(II) ions.

Silver Ag: oxide state only +1; AgNO₃,

Gold Au: oxidation state +1, +3 is so inert, that is found native as the metal.

GROUP 12 (12)

Zinc (Zn) Cadmium (Cd) Mercury (Hg)

Zinc is found mainly as its sulfide ZnS. (sphalerite)

oxid. state +2

Pure iron is relatively flexible and malleable, but the carbon atoms make cast iron very hard and brittle.

A healthy adult human body contains around 3 gr of iron, mostly as hemoglobin (around 2 mg is lost daily).

Iron deficiency, or anemia, results in reduced transport of oxygen to the brain and muscles, and an early symptom is chronic tiredness.

Cobalt (Co): silver gray metal, using mainly in alloys with iron.

CoO → blue substance used to color glass and ceramic glazes. We need cobalt in our diet, it is a component of vitamin B₁₂.

Nickel: (Ni) → Used as alloy with iron hard, silver white metal.

~~Ni(CO)₄~~ Ni(CO)₄ nickel tetracarbonyl.

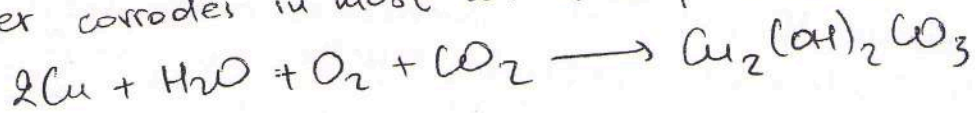
H
GROUP 1b (11)

Copper (Cu), Silver (Ag), Gold (Au)

electron configuration
 $(n-1)d^{10} ns^2$

Cu is unreactive, it is excellent electrical conductor is used in alloys with zinc (brass), with tin (bronze), with nickel.

Copper corrodes in moist air in the presence of CO₂.



Cu₂(OH)₂CO₃ pale green.

Basic copper carbonate.

Cu(II) compounds are most stable

Cu(I) salts disproportionate into metallic copper and copper(II) ions.

Silver Ag: oxide state only +1; AgNO₃,

Gold Au: oxidation state +1, +3 is so inert, that is found native as the metal.

GROUP 2b (12)

Zinc (Zn)

Cadmium (Cd)

Mercury (Hg)

Zinc is found mainly as its sulfide ZnS. (sphalerite)
oxid. state +2

Cadmium: in all compounds +2

Zn and Cd are sibling reactive metals and are familiar to each other but differ sharply from mercury

Zn is amphoteric

- 1) Reacts with acids to form Zn^{2+} cations
- 2) + with alkalis to form the zincate $[Zn(OH)_4]^{2-}$

Mercury (Quicksilver) Hg

Oxid. states +1, +2

Occurs mainly as HgS

Only metallic element that is a liquid at room temperature.

Inorganic elements in biological systems
The chemistry of life involves at least 25 elements

In addition to the "organic" elements C, H, N, O there are 9 other elements that are required they are therefore called macronutrients: are required in small amounts.

V, Cr, Mn, Co, Ni, Cu, Zn, Mo, W, Se, F and Cl.

1) Regulatory action is exercised by Na^+ , K^+ , Mg^{2+} and Ca^{2+} .
The flux of these atoms through cell membranes and other boundary layers send signals that turn metabolic reactions on and off.

2) The structural role (calcium in bones and teeth)

3) Electron transfer chemistry: - in biological systems, Depends on metal containing electron transfer agents.

4) Metaloenzymes or Metallocoenzymes are involved in enzymatic activity depending on the presence of metal ions at the active sites.

Vitamin B₁₂ - contains Cobalt

Alcohol dehydrogenase (Zn)

Superoxide dismutase (Cu, Zn)

Urease (Ni)

5) All aerobic forms of life depend on oxygen carriers (molecules that carry oxygen). e.g. from lungs to tissues where O_2 is used in oxidative processes, that generate energy.

There are 3 major types of oxygen carriers.

Hemoglobin (Fe) found in all mammals

Hemocyanin (Cu) - in some invertebrates

Hemocyanin (Cu) - in arthropods and molluscs.

