CHEMISTRY

FOR

Senior Secondary School

2

EDUBASE

AkadaLearn

For detail referencing and credit please see www.akadalearn.com/publication_credits

TABLE OF CONTENTS

FIRST TERM

SECOND TERM

WEEK1	RATE OF REACTIONS
WEEK 2	TYPES OF CHEMICAL REACTIONS
WEEK 3	CHEMICAL EQUILIBRIUM
WEEK4	NON - METALS: HYDROGEN
WEEK5	OXYGEN
WEEK 6	HALOGENS
WEEK 7	NITROGEN FAMILY
WEEK 8	COMPOUNDS OF NITROGEN
WEEK 9	SULPHUR
WEEK 10	COMPOUNDS OF SULPHUR

THIRD TERM

WEEK 1	WATER (CONTINUED)
WEEK 2	SOLUBILITY
WEEK 3	INTRODUCTION TO ORGANIC CHEMISTRY – HYDROCARBONS
WEEK 4	MASS AND VOLUME RELATIONSHIPS
WEEK 5	ACID- BASE REACTION
WEEK 6	SATURATED HYDROCARBONS- ALKANES
WEEK 7	UNSATURATED HYDROCARBON- ALKENES
WEEK 8	HYDROCARBONS - ALKYNES
WEEK 9	ALKANOLS

SS2 FIRST TERM NOTES ON CHEMISTRY

Week: 1

Topic: Periodic Table

Introduction

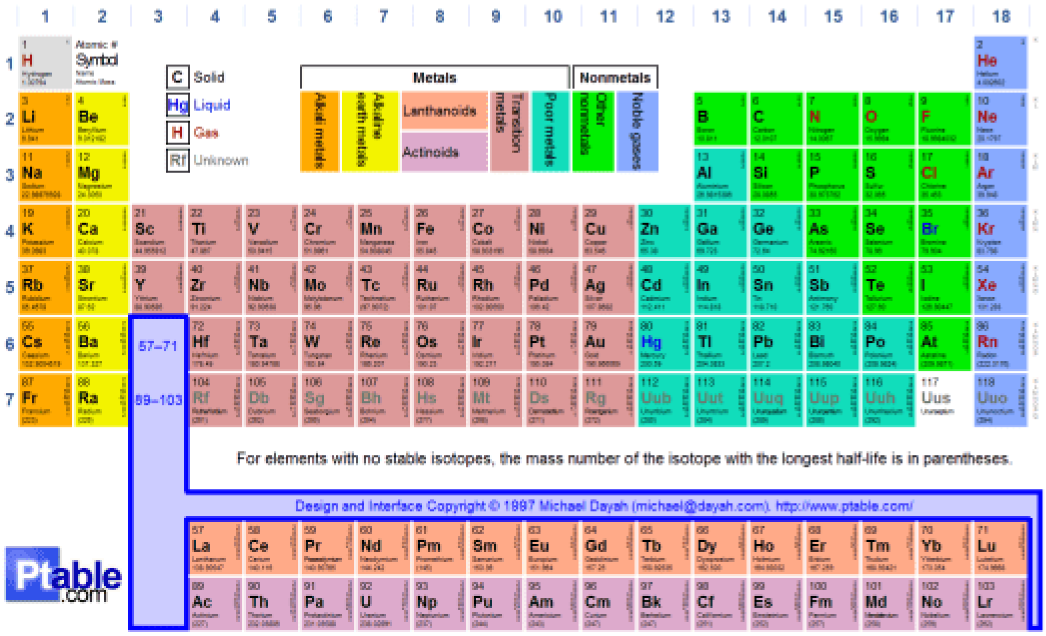
The most important classification in chemistry is the arrangement of the elements in the periodic table.

In 1869, Mendeleev, a Russian scientist, was the first to construct a periodic table. He arranged the elements in order of increasing relative atomic mass. He pointed out that elements with similar properties kept recurring at regular intervals or periods.

Mendeleev's periodic table had many gaps. He predicted that there were undiscovered elements which could fill these gaps. He even predicted the possible properties of these elements. Later, elements such as scandium, gallium, germanium etc. were discovered, which not only fitted exactly into Mendeleev's table, but also had the properties he predicted.

Periodic table helps us to correlate the properties of the elements and thus remember their chemistry. With the discovery of the electronic structure of the atoms, it became clear that elements do vary. regularly, not with their relative atomic mass, but with their atomic number. The modern periodic law states that the properties of the elements are a periodic function of their atomic numbers.

Periodic Table of Elements



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H	Atomic # Symbol																2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57–71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89–103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals, Alkaline earth metals, Lanthanoids, Actinoids, Transition metals, Poor metals
Nonmetals: Other nonmetals, Noble gases

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

Design and Interface Copyright © 1997 Michael Dayah (michael@dayah.com). http://www.ptable.com/

Ptable.com

Electronic Configuration of Atoms as the Basis of the Periodic Table

The atomic number is the number of protons in an atom. As an atom is neutral, the number of protons is equal to the number of electrons. The electrons and their arrangement in the atom of an element are responsible for many of the properties of the element.

An atom consists of a central positively charged nucleus with electrons revolving around it at great speed. The electrons are negatively charged and revolved around the nucleus in a spherical region called shells or orbits or energy levels situated at various distances from the nucleus. Electrons in shell nearer to the nucleus possess less energy than those further away. Starting from the shell nearest the nucleus, the shells are named as K, L, M, N, O,... These corresponding to the energy levels numbered, 1, 2, 3, 4, 5,... An atom may have several electron shells but all the electrons in a given shell possess approximately equal energy. The maximum possible number of electrons in a shell is given by the formula $2n^2$, where n is the energy level number of the shell.

Groups and Periods

The modern form of periodic table is divided into eight vertical columns known as groups and seven horizontal rows known as periods.

GROUPS: The vertical columns of elements or groups, are numbered from 0 to 7. Elements in the same group have the same number of electron in the outermost shell of their atom i.e. they have the same number of valence electrons. Hydrogen does not fit into any group. But for convenience, it is placed in Group 1 because of the single electron. In Group 0, helium has two electrons, while the other elements have eight valence electrons. Besides the eight main groups, there are also the transition groups of elements. These lie between Group 2 and 3 in the periodic table.

PERIODS: The horizontal rows of elements, or periods, are numbered from 1to 7. Elements in the same periods have the same number of electron shells i.e. elements of periods 2 have two electron shells (K,L), those of periods 3 have three (K,L,M), and so on. The number of valence electrons of the elements in the same periods increases progressively by one across the period from left to right. Among the elements in the periods 6 and 7 are the elements of the lanthanides and actinide series respectively. They are also known as the inner transition elements.

Metals, Metalloids and Non –Metals

The periodic table shows a diagonal division of the elements into metals and non-metals. The metals are found on the left side of this line and the non-metals on the right. The metalloids occur along the boundary line.

Electronic Configuration and Periodic Table

Group 1 and Group 2 make up the S-block. The elements in this block are the reactive alkali metals and alkaline earth metals. Group 3 to 7 and 0 form the P-block. Electrons are added progressively to the P-orbital s as we move across the table from Group 3 to 7 and0. The elements in the P-block change from moderately active metals in Group 3 to the very active non-metals in Group 7, and finally the unreactive noble gases in Group 0. The transition elements occur between Group 2 and 3 and form the D-block because they contain D electrons in addition to the S and P electrons. The lanthanides and the actinides also occur between Group 2 and 3 in periods 6 and 7 respectively. They form the F-block because they contain F electrons in addition to the S, P, and D electrons.

Assessment

1. Mendelev's periodic table was arranged in order of their
   a. atomic numbers
   b. molecular shapes and orbitals
   c. increasing relative atomic mass
   d. orbital configuration
2. Elements in the same group of periodic table have
   a. similar electronic configuration
   b. similar orbital configuration
   c. the same number of valence electrons
   d. the same number of electrons
3. S-block elements of the periodic table are made up of
   a. groups 1, 2 , 3
   b. groups 1 and 2
   c. groups 3
   d. groups 3 to 7
4. In the periodic table, elements are arranged according to their
   a. atomic masses
   b. mass numbers
   c. atomic numbers
   d. valence electrons

Answers

1. C
2. C
3. B
4. C

Week: 2

Topic: Periodic Table and Atomic Properties

Electronic Configuration and Periodic Table

Group 1 one's electrons

Group 2 two s electrons

Group 3 two s electrons + one p electron

Group 4 two s electrons + two p electrons

Group 5 two s electrons + three p electrons

Group 6 two s electrons + four p electrons

Group 7 two s electrons + five p electrons

Group O two s electrons + six p electrons

Atomic and Ionic Sizes

Atomic size: They are given by atomic radius. The **atomic** radius of a **chemical** element is a measure of the **size** of its **atoms**, usually the mean or typical distance from the center of the nucleus to the boundary of the surrounding cloud of electrons.

Atomic size across a period: The size of atom of elements in the same periods decreases steadily as the atomic number increases because across the periods, electrons are being added to the shell and these tend to pull them towards the nuclei. As a result, atomic radius decreases with increasing atomic number. This simply means that atomic size decreases across a period. The atomic radius decreases with increasing atomic number, while the attractive force exerted by the nucleus on the outermost electrons of the atom increases across a period. Thus the elements become progressively more electronegative from left to right.

·**Atomic size down a group:** There is an increase in atomic radius as the atomic number increases down a given group. Therefore, atomic size increases down a group. Thus the elements of any one group become decreasingly electronegative with increasing atomic number i.e as we go down the group.

Ionic size: Ions of elements are formed by electron loss or gain. Ionic sizes are given by ionic radii. In a group of ions having the same number of electrons, the ionic radius decreases as the atomic number increases. The *ionic radius* is the measure of an atom's *ion* in a crystal lattice. It is half the distance between two *ions* that are barely touching each other. Since the boundary of the electron shell of an atom is somewhat fuzzy, the *ions* are often treated as though they were solid spheres fixed in a lattice.

- the ionic radii of positive ions are smaller than the corresponding atomic radii
- the ionic radii of negative ions are greater than the corresponding atomic radii
- in a group of ions having the same number of electrons, the ionic radius decreases as the atomic number increases

Periodicity of Some Properties

Periodicity is the recurrence of similar phenomena at regular intervals. The important properties of elements which show periodicity are:

·Melting and Boiling Point

·Electrical and Thermal Conductivities

·Ionization Energies and Electron Affinities

·Electronegativity's

Variations in Physical Properties

1. **Melting and Boiling Point**: within a period, the melting and boiling points of metallic elements increases from left to right, those of non-metallic elements decreases. Within a group, the melting and boiling points of metallic elements decrease down the group, and those of non-metallic elements increase down the group.

2. **Electrical and Thermal Conductivities**: These properties of elements decrease across the period and increase down the group. Thus, metals are good electrical and thermal conductors, and non-metals are poor electrical and thermal conductors.

3. **Ionization Energy:** This is the energy required to remove a valence electron from an atom of the element to form an ion. Generally, there is a tendency for ionization of energies to increase across a period and decrease down to a group. The first ionization energy of an element is the amount of energy required to remove one electron from each atom in a mole of gaseous atoms producing one mole of gaseous ions with a positive charge. The ionization energy of an atom is affected by
– the distance of the outermost electron from the nucleus: Across the period, as the atomic size increases, the atomic radius decreases. As the distance decreases, the attraction of positive nucleus for the electron will increase. More energy is needed to remove the outer most electron
– the size of the positive nuclear charge : As the nuclear charge increases, its attraction to the outermost electron increases and so more energy is needed to remove the outer most electron. Hence ionization energy increases
– the screening effects of the inner electrons: The outermost electrons are repelled by other electrons in the atom, besides being attracted by the positively charged nucleus. The outermost electrons are screened or shielded from the nucleus by the repelling effect of the innermost electrons.

4. **Electron Affinity:** This is the amount of energy released when an electron is added to a neutral atom in the gaseous state to form a gaseous negative ion. “Electron Affinity is the energy released when a gaseous atom gains an electron in form of a gaseous negative ion. E.g

$E_{(g)} + e^- \rightarrow E_{(g)}$ The **electron affinity** is a very specific measure of the tendency for atoms to gain electrons. Specifically, it is the amount of energy released by an electron when the electron joins or attaches to an isolated atom. This measurement is very sensitive to the difference between the types of orbitals and to the number of electrons in those orbitals. Consequently, the zigs and zags in a graph of electron affinity are even more pronounced than in the graph of ionization energy. Electron affinity has a large negative value. Electron affinity increases with decrease of atomic radii across the period from left to right and decreases with increase of atomic radii down the group. This is because atoms with smaller atomic radii tend to have stronger attraction for electrons and so form a negative ion more readily. Electron affinity increase across the period from left to right (except the noble gases) and decrease down the group.

5. **Electronegativity:** The electronegativity of an atom is the power of that atom in a molecule to attract electrons. In other word, it is the ability of an atom in a molecule to attract electrons to itself. Electronegativities of elements increase across a period but decrease down a group.The most electronegative elements are the reactive non-metals in the top right hand corner of the periodic table.

Variations in Chemical Properties

Elements in same group tend to resemble one another in their chemical behaviors because they have the same number of valence electrons.

Group 1 – Alkali metals

Group 2 – Alkaline Earth metals

Group 7 – Halogens

Group 0 – noble gases.

The above groups show similarities in their chemical properties.

Group 1 elements

- one valence electron each
- they include – lithium, sodium, potassium
- they have great reactivity
- they form stable compounds (they lose one electron to form a positively charged univalent ion)

Group 2 elements

- two valence electrons each
- they include metallic elements like beryllium, magnesium, calcium
- they are less reactive than group 1 elements
- each of their atoms form a positively charged bivalent ion by losing 2 electrons

Group 7 elements

- seven valence electrons
- they include fluorine, chlorine, bromine, iodine
- each atom has to gain an electron to attain an octet structure
- they are very reactive
- they form negatively charged univalent ions
- the halides are stable and unreactive

Group O

- they are colourless and monoatomic molecules
- they include helium, neon, argon

- they are unreactive in nature
- they have stable duplet or octet structure

Families of Elements

Group 1 – Alkali Metals (Sodium and Potassium)

- they are divalent elements with two valence electrons
- The members of the alkaline earth metals include: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra).
- on heating, their trioxonitrate (v) salts decompose with difficulty to give oxygen and dioxnitrate(v) salts
  $2K_{(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_{2(g)}2KNO_{3(s)} \rightarrow 2KNO_{2(s)} + O_{2(g)}$
  heat
    - Hydrogen is not considered an alkali metal because the gas does not exhibit the typical properties of the group.Where alkali metals lose their valence electron, hydrogen normally shares its valence electron. The fact that hydrogen can actually gain an electron when forming hydrides further illustrates that it is not truly a member of the alkali metal family.
    - Ionize to lose their electron, so the ion has a +1 charge. They are electropositive.

$Na \text{ ——-> } Na^+ + e^-$

- Vigorous exothermic reaction with water to produce hydrogen gas and an alkalis, so they are known as alkali

$2K_{(s)} + 2H_2O_{(l)} \text{ ———-> } 2KOH_{(aq)} + H_{2(g)}$

- The oxides of alkali metals also dissolve in water to form very strong alkalis.

$Na_2O_{(s)} + H_2O_{(l)} \text{ ———-> } 2NaOH_{(aq)}$

  - On heating, their trioxonitrate (V) salts decompose with difficulty to give oxygen and dioxonitrate (III) salts.

$2KNO_{3(s)}$ ————> $2KNO_{2(s)} + O_{2(g)}$

Group 2 – The Alkali Earth Metals (Calcium and Magnesium)

- they react with cold water vigorously to liberate hydrogen gas and form alkalis
- they are electropositive
- they are good conductors of electricity'
- their reducing property increases down the group
- they are good reducing agents (they donate their outermost electrons easily)
- they form electrovalent compounds
- they ionize readily to form positive ions by donating electrons
- they are univalent (one valence electron)
- The members of this family include: lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs) and francium (Fr). They are soft metallic solids, with metal properties such as:
  - Shiny and lustrous
  - High thermal and electrical conductivities
  - Low densities, increasing with atomic mass
  - Relatively low melting points, decreasing with atomic mass
- they are electron donors and form electrovalent compounds
- they are reducing in nature
- They have characteristic metal properties but are harder, more dense, and melt at higher temperatures than the alkali metals.
- Shiny, lustrous, oxidize easily

- High thermal and electrical conductivities
- Ionize to lose their valence electrons, so the ion has a +2 charge
- Ca ———> Ca^{2+} + 2^{e-}
    - Their reaction with water increases down the group.
    - Beryllium does not react with water, even when heated red-hot. Magnesium does not react with liquid water but does react with steam. Calcium and the elements below it react with water at room temperature, although more slowly than the alkali metal adjacent to them on the periodic table.

$Ca_{(s)} + 2H_2O_{(l)}$ —————> $Ca(OH)_{2(aq)} + H_{2(g)}$

$Mg_{(s)} + H_2O_{(g)}$ —————> $MgO_{(s)} + H_{2(g)}$

- Magnesium and calcium are essential for living organisms. 99% of the calcium in the human body is found in the skeletal system.
- Their trioxonitrate (V) salts decompose readily on heating to give the oxides, oxygen and the brown gas, nitrogen (IV) oxide.

$2Ca(NO_3)_{2(s)}$ ————> $2CaO_{(s)} + O_{2(g)} + 4NO_{2(g)}$

- Their trioxocarbonates (IV) are insoluble in water. They decompose on heating to give the oxides and carbon (IV) oxide.

$MgCO_{3(s)}$ —————> $MgO_{(s)} + CO_{2(g)}$

Calcium reacts slowly with cold water while Magnesium reacts with steam only. Both liberate hydrogen from water while Calcium forms a hydroxide, Magnesium forms an oxide.

$Ca_{(s)} + 2H_2O_{(l)} \rightarrow CaOH_{(aq)} + H_{2(g)}$

$Mg_{(s)} + H_2O_{(l)} \rightarrow MgO_{(aq)} + H_{2(g)}$

Group 3 – Aluminium

- trivalent element
- potential donor of 3 electrons
- forms electrovalent compounds
- Aluminium oxide is insoluble in water

Aluminium reacts with steam above 600°C to liberate Hydrogen. It forms both oxides and hydroxides i.e its amphoteric in nature

$Al^2O_{3(s)} + 2NaOH_{\ (aq)} + 3H_2O \rightarrow\ 2NaAl(OH)_{4\ (aq)}$ – complex salt

Group 4 – carbon, silicon, tin, lead

- tetravalent elements
- they form covalent compounds
- they change from non-metallic to metallic down the group
- there is a corresponding decrease in electronegativity down the group
- they exhibit 2 oxidation states, +2 and +4

- The carbon group is made up of elements called tetrels, which refers to their ability to carry a charge of 4. Members of this group have 4 valence electrons which include carbon, silicon, germanium, tin and lead. The best known member of this group is carbon, which commonly forms 4 bonds.

Carbon is unique among the elements because of its ability to combine with itself and other elements to form an almost limitless number of compounds. The hydrides of carbon are very numerous and are known as hydrocarbons. Examples are methane, CH_4, ethane, C_2H_4, benzene, C_6H_6 etc.

Carbon is found in nature in the form of coal and diamonds. The difference between them is their crystalline structure, which gives them very different physical properties. Diamond is the hardest of all known substances.

Group 5 – Nitrogen, Phosphorus

- non-metals
- two common valencies 3 and 5
- they are electron acceptors

Nitrogen makes up about 80% of the air. At normal temperatures and atmospheric pressures, molecular nitrogen is almost inert. They form several oxides such as:

- Nitrogen (III) oxide, N_2O_3,
- Phosphorus (III) oxide, P_4O_6,
- Nitrogen (V) oxide, N_2O_5

All these oxides are acidic and will combine with water to form acids. Nitrogen and phosphorus also form similar hydrides, NH_3 and PH_3.

Group 6 – Oxygen and Sulphur

- non – metals
- electron acceptors
- oxidizing agents
- Oxygen is soluble in water while sulphur is insoluble

Group 7 (halogens or salt formers)

- most reactive elements
- they are non-metals
- they exist as diatomic molecules

- they are colored
- they ionize to form univalent negative ions which react with metallic ions to form electrovalent compounds
- their hydrides are covalent gases at room temperature and dissolve readilty in water to form acids
- They can be hammered or bent into shape easily

- They are less reactive than alkali metals such as sodium
- They have high melting points – but mercury is a liquid at room temperature
- They are usually hard and tough
- They have high densities
- These large atoms exhibit a range of oxidation states.

Halogens are highly active with high electron affinities. In fact, the letter X is sometimes used in chemical equations to indicate any one of the halogen elements. Fluorine gas is so reactive that it is difficult and dangerous to use, requiring specialized lab equipment. Unlike fluorine, chlorine reacts slowly with water to form relatively stable aqueous solutions. Chlorine is often added to drinking water and swimming pools, where the $HOCl_{(aq)}$ that is produced serves as a disinfectant. Halides are all very soluble in water and dissolve to form the hydrohalic acids

Trends exhibited by Halogens

1. A change in state (at 25C) – fluorine and chlorine are gases, bromine is liquid and iodine is solid
2. Their colours become darker – fluorine is yellow, chlorine is greenish yellow, bromine is reddish brown and iodine is black
3. Their melting and boiling points increase progressively

4. The ease with which they ionise to form negative ions decrease

Group O (rare or noble gases) – helium, neon, argon, krypton, xenon and radon

- No bonding electrons
- they are unreactive
- they exist freely as monoatomic molecules
- their melting and boiling points increase while their ionization energy decres down the group from helium to radon

Transition Elements (between group 2 and 3) – Iron, Copper, Silver, Gold

- metals with high tensile strengths and high boiling points
- their ions are coloured
- they have variable valencies
- they can form complex ions

Assessment

1. .... is the energy required to remove a valence electron from an atom of the element to form an ion
   a. Electron affinity
   b. Electronegativity
   c. Ionization Energy
   d. Atomization Energy
2. The .... of an atom is the power of that atom in a molecule to attract electrons
   a. Electron affinity
   b. Electronegativity

c. Ionization Energy
d. Atomization Energy

3. Ionization energy of an atom is affected by
   a. distance of the outer most electron from the nucleus
   b. the size of positive nuclear charge
   c. the screening effect of the inner electron
   d. solvent medium

4. Which of the following decreases across the period
   a. Atomic size
   b. Electron Affinity
   c. Electronegativity
   d. Inert tendencies

5. The following groups show great similarity in their chemical properties except
   a. Group 1
   b. Group 7
   c. Group 0
   d. Group 5

6. Special properties of transition elements as result of
   a. ability to produce coloured ions
   b. ability to have variable valencies
   c. ability to possess partially filled d-orbitals
   d. inert octet electrons

7. Elements in the same group in the periodic table have the same
   a. number of valence electrons
   b. number of shells
   c. atomic number
   d. electronic configuration

Answers

1. C
2. B
3. D
4. A
5. D
6. C
7. A

Week: 2

Topic: Oxidation – Reduction Reaction

Oxidation-reduction reactions involve the transfer of electrons between substances. They take place simultaneously, which makes sense because if one substance loses electrons, another must gain them. Oxidation-reduction reactions involve two opposing yet complementary processes : oxidation and reduction. For example, all single-replacement reactions are redox reactions.

Electrochemistry: The study of the interchange of chemical and electrical energy.

Oxidation:

- The loss of electrons. Since electrons are negative, this will appear as an increase in the charge (e.g., Zn loses two electrons; its charge goes from 0 to +2). Metals are oxidized.
- Addition of oxygen i.e oxygen is combined with a substance
- Removal of hydrogen
- Addition of electronegative elements and removal of electropositive elements

Oxidizing agent (OA):

- These are species that reduces and thus, causes oxidation.
- Electron acceptor
- Oxidation number decreases in the positive direction

Reduction:

- The gain of electrons. When an element gains electrons, the charge on the element appears to decrease, so we say it has a reduction of charge (e.g., Cl gains one electron and goes from an oxidation number of 0 to -1). Non-metals are reduced.
- Removel of oxygen from a substance
- Addition of hydrogen
- Addition of electropositive elements and removal of electronegative elements

Reducing agent (RA):

- The species that is oxidized and thus causes reduction.
- Electron donor
- Oxidation number increases in positive direction

Oxidation number: The assigned charge on an atom. You've been using these numbers to balance formulas.

Half-reaction: An equation that shows either oxidation or reduction alone.

Rules for Assigning Oxidation States

A reaction is considered a redox reaction if the oxidation numbers of the elements in the reaction change in the course of the reaction. We can determine which elements undergo a change in oxidation state by keeping track of the oxidation numbers as the reaction progresses. You can use the following rules to assign oxidation states to the components of oxidation-reduction reactions:

1. The oxidation state of an element is *zero*, including all elemental forms of the elements (e.g., N_2, P_4, S_8, O_3).

2. The oxidation state of a monoatomic ion is the same as its charge.

3. In compounds, fluorine is always assigned an oxidation state of -1.

4. Oxygen is usually assigned an oxidation state of -2 in its covalent compounds. Exceptions to this rule include peroxides (compounds containing the O_2^{2-} group), where each oxygen is assigned an oxidation state of -1, as in hydrogen peroxide (H_2O_2).

5. Hydrogen is assigned an oxidation state of +1. Metal hydrides are an exception: in metal hydrides, H has an oxidation state of -1.

6. The sum of the oxidation states must be zero for an electrically neutral compound.

7. For a polyatomic ion, the sum of the oxidation states must equal the charge of the ion.

Example

Assign oxidation numbers to each element in the following:

1. H_2S
2. MgF_2
3. PO_4^{3-}

Explanation

1. The sum of the oxidation numbers in this compound must be zero since the compound has no net charge. H has an oxidation state of +1, and since there are two H atoms, +1 times 2 atoms = +2 total charge on H. The sulfur S must have a charge of -2 since there is only one atom of sulfur, and +2 - 2 = O, which equals no charge.

2. F is assigned an oxidation state of -1 (according to rule 3), and there are two atoms of F, so this gives F a total charge of -2. Mg must have a +2 oxidation state since +2 − 2 = 0 and the compound is electrically neutral.

3. This time the net charge is equal to -3 (the charge of the polyatomic ion—according to rule 7). Oxygen is assigned a -2 oxidation state (rule 4). Multiply the oxidation number by its subscript: -2 X 4 = -8. Since there is only 1 phosphorus, just use those algebra skills: P + -8 = -3. Phosphorus must have a +5 charge.

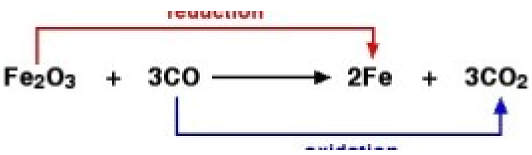
Oxidation and reduction in terms of oxygen transfer

Definitions;

·Oxidation is gain of oxygen.

·Reduction is loss of oxygen.

For example, in the extraction of iron from its ore:



Because both *red*uction and *ox*idation are going on side-by-side, this is known as a *redox* reaction.

Oxidation and Reduction in Terms of Hydrogen Transfer

These are old definitions which aren't used very much nowadays. The most likely place you will come across them is in organic chemistry.

Definitions

·Oxidation is loss of hydrogen.

·Reduction is gain of hydrogen.

Notice that these are exactly the opposite of the oxygen definitions.

For example, ethanol can be oxidized to ethanal:

You would need to use an oxidizing agent to remove the hydrogen from the ethanol. A commonly used oxidizing agent is potassium dichromate (VI) solution acidified with dilute sulphuric acid.

Ethanal can also be reduced back to ethanol again by adding hydrogen to it. A possible reducing agent is sodium tetrahydridoborate, $NaBH_4$. Again the equation is too complicated to be worth bothering about at this point.

An update on oxidizing and reducing agents

·Oxidizing agents give oxygen to another substance or remove hydrogen from it.

·Reducing agents remove oxygen from another substance or give hydrogen to it.

Oxidation and Reduction in Terms of Electron Transfer

This is easily the most important use of the terms oxidation and reduction.

Definitions;

- *Oxidation is loss of electrons.*
- *Reduction is gain of electrons.*

It is essential that you remember these definitions. There is a very easy way to do this. As long as you remember that you are talking about electron transfer:

A simple example;

The equation shows a simple redox reaction which can obviously be described in terms of oxygen transfer.

$CuO + Mg \longrightarrow Cu + MgO$

Copper (II) oxide and magnesium oxide are both ionic. The metals obviously aren't. If you rewrite this as an ionic equation, it turns out that the oxide ions are spectator ions and you are left with:

If you look at the equation above, the magnesium is reducing the copper(II) ions by giving them electrons to neutralize the charge. Magnesium is a reducing agent.

Looking at it the other way round, the copper (II) ions are removing electrons from the magnesium to create the magnesium ions. The copper(II) ions are acting as an oxidizing agent. For example, what an oxidizing agent did in terms of electrons:

·An oxidizing agent oxidizes something else.

·Oxidation is loss of electrons (OIL RIG).

·That means that an oxidizing agent takes electrons from that other substance.

·So an oxidizing agent must gain electrons.

Example 1: Determine which element is oxidized and which element is reduced in the following reactions (be sure to include the oxidation state of each):

1. $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$
2. $2Al + 3Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$
3. $CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$

Solutions:

1. Zn is oxidized (Oxidation number: 0 → +2) and acts as the reducing agent; H^+ is reduced (Oxidation number: +1 → 0) and acts as the oxidizing agent.

2. Al is oxidized (Oxidation number: 0 → +3) and acts as the reducing agent; Cu^{2+} is reduced (+2 → 0) and acts as the oxidizing agent.

3. This is not a redox type because each element has the same oxidation number in both reactants and products: O= −2, H= +1, C= +4.

<u>Example 2</u>: The thermite reaction in which iron atoms of ferric oxide lose (or give up) O atoms to Al atoms, producing Al_2O_3.

$Fe_2O_{3(s)} + 2Al_{(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(l)}$

<u>Example 3</u>: When powdered zinc metal is mixed with iodine crystals and a drop of water is added, the resulting reaction produces a great deal of energy. The mixture bursts into flames, and a purple smoke made up of I_2 vapor is produced from the excess iodine. The equation for the reaction is

$Zn_{(s)} + I_{2(s)} \rightarrow ZnI_{2(s)} + \text{energy}$

Identify the elements that are oxidized and reduced, and determine the oxidizing and reducing agents.

Explanation

1. Assign oxidation numbers to each species. Zn and I_2 are both assigned values of 0 (rule 1). For zinc iodide, I has an oxidation number of −1 (group 7A—most common charge), which means that for zinc, the oxidation number is +2.

2. Evaluate the changes that are taking place. Zn goes from 0 to +2 (electrons are lost and Zn is oxidized). The half-reaction would look like this:

$Zn^0 \rightarrow Zn^{2+} + 2e^-$

And I_2 goes from 0 to −1 (it gains electrons and so is reduced). This half-reaction would look like this:

$I_2^0 + 2e^- \rightarrow 2I^-$

3. Here, zinc metal is the reducing agent—it causes the reduction to take place by donating electrons—while iodine solid is the oxidizing agent; iodine solid accepts electrons.

Balancing in Basic and Acidic Solution

·Balancing in acidic solution is similar to balancing in neutral solutions however, instead of three steps to follow, there are six. These rules are:

·Write and balance the half reactions.

·Balance oxygen, O, by adding with H_2O

·Balance hydrogen, H, by adding H^+ (acidic)

·Balance charge by adding electrons (you should be adding the same number of electrons as H^+ ions)

·Multiply both half reactions by some integer to cancel out electrons

·Add the half reactions together and cancel out what appears on both sides

<u>Example 1</u>: Balance the redox reaction in acidic solution:

$MnO_4^- + I^- \rightarrow Mn^{2+} + I_{2(s)}$

<u>Solution</u>

·Write and balance the half reactions:
$MnO_4^- + I^- \text{–>} Mn^{2+} + I_{2(s)}$
O.S: +7 -2 −1 +2 0 (Mn is reduced and I^- is oxidized)
Oxidation Rx: $2I^-_{(aq)} \text{–>} I_{2(s)} + 2e^-$
Reduction Rx: $MnO_4^- + 5e^- \text{–>} Mn^{2+}$

·Balance oxygen, O, by adding H_2O
Oxidation Rx: $2I^-_{(aq)} \text{–>} I_{2(s)} + 2e^-$
Reduction Rx: $MnO_4^- + 5e^- \text{–>} Mn^{2+} + 4H_2O$

·Balance hydrogen, H, by adding $H^{+<}$

Oxidizing and Reducing Agents

An oxidizing agent is substance which oxidizes something else. In the above example, the iron (III) oxide is the oxidizing agent. A reducing agent reduces something else. In the equation, the carbon monoxide is the reducing agent.

- Oxidizing agents give oxygen to another substance.
- Reducing agents remove oxygen from another substance.

Example 1: Identify reducing and oxidizing agents

Identify the reducing and oxidizing agents in the balanced redox reaction:

Cl2(aq) + 2Br−(aq)→2Cl−(aq) + Br2(aq)Cl2(aq) + 2Br−(aq)→2Cl−(aq) + Br2(aq)

Oxidation half reaction

2Br−(aq)→ Br2(aq) 2Br − (aq) →Br2(aq)

Oxidation States: -1 0

Reduction Half Reaction

Cl2(aq) → 2Cl −(aq) Cl2(aq) → 2Cl −(aq)

Oxidation States: 0 −1

Overview

- B^- *loses* an electron; it is *oxidized* from Br^- to Br_2; thus, Br^- is the *reducing agent*.
- Cl_2 *gains* one electron; it is *reduced* from Cl_2 to 2 Cl^-; thus, Cl_2 is the *oxidizing agent.*

For example, consider the overall reaction for aerobic cellular respiration:

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

The oxygen (O_2) is being reduced, so it is the oxidizing agent. The glucose ($C_6H_{12}O_6$) is being oxidized, so it is the reducing agent.

Example of Redox Reaction

The formation of iron(III) oxide;

$4Fe + 3O_2 \rightarrow 2Fe_2^{3+}O_3^{2-}$

In the above equation, the Iron (Fe) has an oxidation number of 0 before and 3+ after the reaction. For oxygen (O) the oxidation number began as 0 and decreased to 2−. These changes can be viewed as two "half-reactions" that occur concurrently:

1. Oxidation half reaction: $Fe^0 \rightarrow Fe^{3+} + 3e^-$
2. Reduction half reaction: $O_2 + 4e^- \rightarrow 2\,O^{2-}$

Iron (Fe) has been oxidized because the oxidation number increased. Iron is the reducing agent because it gave electrons to the oxygen (O_2). Oxygen (O_2) has been reduced because the oxidation number has decreased and is the oxidizing agent because it took electrons from iron (Fe). ferric

Common Oxidizing Agents

- Oxygen (O_2)
- Ozone (O_3)
- Hydrogen peroxide (H_2O_2) and other inorganic peroxides, Fenton's reagent
- Fluorine (F_2), chlorine (Cl_2), and other halogens
- Nitric acid (HNO_3) and nitrate compounds
- Sulfuric acid (H_2SO_4)
- Peroxydisulfuric acid ($H_2S_2O_8$)

- Peroxymonosulfuric acid (H_2SO_5)
- Chlorite, chlorate, perchlorate, and other analogous halogen compounds
- Hypochlorite and other hypohalite compounds, including household bleach (NaClO)

Common Reducing Agents

- Hydrogen without or with a suitable catalyst e.g. a Lindlar catalyst
- Sodium amalgam (Na(Hg))
- Sodium-lead alloy (Na + Pb)
- Amalgam (chemistry) Zinc amalgam (Zn(Hg)) (reagent for Clemmensen reduction)
- Diborane
- Sodium borohydride ($NaBH_4$)
- Compounds containing the Fe^{2+} ion, such as iron(II) sulfate
- Compounds containing the Sn^{2+} ion, such as tin(II) chloride
- Sulfur dioxide (sometimes also used as an oxidizing agent), Sulfite compounds
- Dithionates, e.g. $Na_2S_2O_6$
- Thiosulfates, e.g. $Na_2S_2O_3$ (mainly in analytical chemistry)
- Iodides, e.g. KI (mainly in analytical chemistry)
- Hydrogen peroxide (H
  2O
  2) – mostly an oxidizer but occasionally acting as a reducing agent! (Typically in analytical chemistry.)
- Hydrazine (Wolff-Kushner reduction)

Balancing a Redox Reaction

Balancing an oxidation-reduction reaction can be a bit tricky. You can use the steps you used previously to balance other equations to start, but then you have to take into account the key ions and oxidation numbers. Here’s a list of steps to help you balance a redox equation.

1. **Identify the reactants and the products**.
    1. Write the unbalanced equation in ionic form and exclude any spectator ions.
    2. Give each atom an oxidation number and identify each atom that changes its oxidation number. Ignore any atom that doesn’t change.
2. **Write and balance the half-reactions.**
    1. Separate the equation into its half-reactions.
    2. Balance the atoms other than hydrogen and oxygen.
    3. Balance the oxygen atoms by adding water molecules.
    4. Balance the hydrogen atoms by adding a hydronium ion for each hydrogen atom and adding an equal number of water molecules to the other side of the equation.
    5. Balance the charge by adding electrons if needed.
3. **Make the electrons equal and combine the half-reactions.**

Example

Balance the equation of hydrogen sulfide in air reacting to form sulfur dioxide and water.

H2S + O2 = SO2 + H2O

1. Identify the reactants and the products and assign oxidation numbers.

+1 -2 0 +4 -2 +1 -2

H2S + O2 = SO2 + H2O

2. Write and balance the half-reactions.

Note that sulfur is changing from a -2 oxidation number to a +4 oxidation number, so it had to lose six electrons. -2 + (-4) = -6.

Oxygen is changing from a zero oxidation number to a -2, gaining two electrons. 0 + (-2) = -2. Since free oxygen atoms travel in pairs, the actual number of electrons gained is -4.

-2 +4

S = S + 6e^-

0 -2

O2 + 4 e^- = 2O

3. The two half-reactions need to be balanced so that the electrons lost by sulfur are the same number gained by oxygen.

-2 +4

2S =2S + 12e^-

0 -2

3O2 + 12e^- = 6O

So from these half-reactions, you know that a 2 has to go in front of the H2S and a 3 has to go in front of the O2 on the reaction side. On the product side, the six oxygen atoms needed for balance are divided between the SO2 and the H2O.

The final equation is:

2H2S + 3O2 = 2SO2 + 2H2O

Assessment

1. Oxidation reaction may be defined as the following except
   a. Reaction in which electron is lost
   b. reaction in which there is an increase in oxidation number

c. reaction in which oxygen is gained
d. reaction in which hydrogen is gained

2. From the reaction: $2I^{-}_{(aq)} + 2Fe^{3+}_{(aq)} \rightarrow I_{2(s)} + 2Fe^{2+}_{(aq)}$.
   Which is the reducing agent
   a. I–
   b. $2Fe^{3+}$
   c. I_2
   d. $2Fe^{2+}$

3. From C(s) + ZnO(s) → CO_2(g) + 2Zn(s)
   The oxidation number of free carbon is
   a. -4
   b. +4
   c. 0
   d. +2

4. What is the oxidation number of chromium sodium heptaoxochromate (vi)
   a. +3
   b. +12
   c. +6
   d. +2

5. Which of the following does not define Oxidation
   a. Removal of electrons
   b. Addition of Oxygen
   c. Increase of oxidation number in the positive direction
   d. Removal of hydrogen

6. $Cl_2 + 2KBr \rightarrow 2KCl + Br_2$
   In the above reaction, Chlorine is
   a. an oxidizing agent
   b. a reducing agent
   c. an electron
   d. an acid

Answers

1. B
2. C
3. C
4. A
5. B
6. A

Week 3

Topic: Electrolysis

What is Electrolysis?

Ionic substances contain charged particles called ions. For example, lead bromide contains positively charged lead ions and negatively charged bromide ions.

Electrolysis is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them. In other word, electrolysis is the decomposition of certain compounds in aqueous or molten state, when electric current is passed through them.

Electrolyte: These are solutions or molten compounds of inorganic acids, bases and salts that conduct electricity. They dissociate into their ions on the passage of electric voltage. There are two types of ions, these are:

1. **Anion**: It is a negatively charged ion that moves to the anode during electrolysis.
2. **Cation:** It is a positively charged ion that moves to the cathode during electrolysis.

Strong electrolytes: are electrolytes that give strongly conducting solution and dissociate readily into ions. Examples are HNO_3, NaCl

Weak electrolytes: They are electrolytes that produce weakly conducting solutions and only partially dissociate into their ions on the passage of electric current and voltage. Examples include HgCl, CH_3COOH acid.

Non-Electrolytes: These are solutions of organic substances, which produce molecules instead of ions and are therefore poor conductors of electricity. Examples include sugar, ethanol and glycerine.

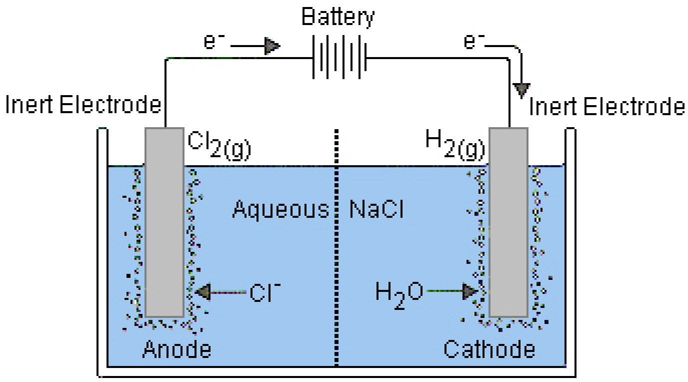
Conductors: are solid substances except mercury that allow electric current to pass through them. For example metals like copper and aluminium, and non-metal like graphite (carbon)

Non-conductors: are solid or liquid substances that do not allow an electric current to pass through them. For example diamond (carbon), rubber/plastics, benzene, dry wood etc.

Electrodes: These are rods or plates that connect the wiring of the circuit to the electrolyte. The positive electrode is the anode and is the electrode through which the electric current enters the electrolyte. The negative electrode is the cathode and is the electrode through which the current leaves the electrolyte.

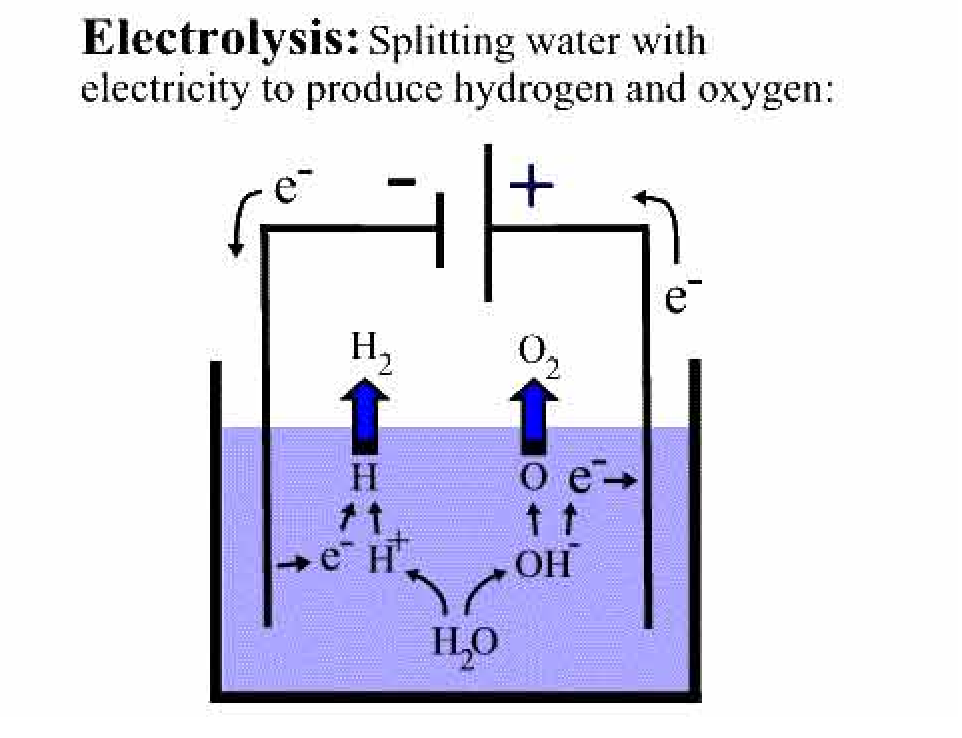
Electrolytic Cell: This is an assembly of two electrodes in an electrolyte, and is used for the electrolysis of a substance. In earlier days, the set up was known as voltammeter.

Simple Electrolytic Cell



Mechanism of Electrolysis

For electrolysis to work, the ions must be free to move. Ions are free to move when an ionic substance is dissolved in water or when melted. For example, if electricity is passed through molten lead bromide, the lead bromide is broken down to form lead and bromine. The electrodes connect to a battery. When they are electrically charged, one electrode becomes the negative terminal or cathode, and the other becomes the positive terminal or anode. The positive terminal attracts negatively charged ions and the negative terminal attracts positively charged ions.



Here is what happens during electrolysis:

·Positively charged ions move to the negative electrode during electrolysis. They receive electrons and are reduced.

·Negatively charged ions move to the positive electrode during electrolysis. They lose electrons and are oxidised.

The substance that is broken down is called the electrolyte.

Arrhenius Theory of Electrolytic Dissociation

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of electrolytic dissociation or ionic theory. The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.

$AB \rightarrow A^+ + B^-$

$NaCl \rightarrow Na^+ + CL^-$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

$A^+B^-_{(aq)} \rightarrow A^+_{(aq)} + B^-_{(aq)}$

(ii) The process of splitting of the molecules into ions of an electrolyte is called ionization. The fraction of the total number of molecules present in solution as ions is known as degree of ionization or degree of dissociation. It has been observed that all electrolytes do not ionize to the same extent. Some are almost completely ionized while others are feebly ionized. The degree of ionization depends on a number of factors.

(iii) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e.,

$AB \leftrightarrow A^+ + B^-$

Applying the law of mass action to above equilibrium

$[A^+]$ /[AB] =K

K is known as ionization constant. The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes.

(iv) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs. The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

(v) The electrolytic solutions is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

NaCl <–> Na^+ + Cl^- (Both ions are equal)

$BaCl_2$ <–> Ba^{2+} + $2Cl^-$ (Anions are double that of cations)

Na_2SO_4 <–> $2Na^+$ + (Anions are double that of cations)

(vi) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

(vii) The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

Factors affecting Preferential Discharge of Electrolysis

There are certain factors that affect the discharge of electrons at electrodes.

Factors Affecting the Preferential Discharge of Ions in Electrolysis

1. The position of ion in electrochemical series.
2. The concentration of ion.
3. The nature of electrode.

A. **Relationship between position of ions in the electrochemical series and the order of discharge of ions.**

1. a) For cations
   Electrochemical series of cations:

K^+ ——-> Least easy to discharge
Na^+
Ca^{2+}

Mg^{2+}
Al^{3+}
Zn^{2+}
Fe^{2+}

Sn^{2+}
Pb^{2+}
H^+
Cu^{2+}
Hg^{2+}

Ag^+ ———-> Most easy to discharge

The cation has a lower position in the electrochemical series are preferentially discharged.

1. b) For anions

Electrochemical series of anions

OH^- ——> Most easy to discharge
I^-
Br^-
Cl^-

NO_3^-
SO_4^{2-} ———> Least easy to discharge

The anion has a higher position in the electrochemical series are preferentially discharged.

B. Concentration of the ions in the electrolyte – Irrespective of the position of the ions in the electrochemical series, there is a tendency to promote the discharge of the most concentrated ion present. Increasing the concentration of a given ion tends to promote its discharge. For example, in concentrated sodium chloride solution (i.e. brine), the two cations present are the chlorine ion and the hydroxyl ion. Although the hydroxyl ion is more easily oxidized than the chlorine ion, it is the chlorine ion which will be discharged because its concentration is much greater than that of the hydroxyl ion. However, if the concentration of a particular ion is high, then this can alter the preferential discharge. The effect of concentration is evident when the two competing ions are closely positioned in the electrochemical series.
Also, if dilute hydrochloric acid is electrolyzed, hydrogen gas is produced at the cathode and oxygen gas at the anode. However, when concentrated hydrochloric acid is electrolyzed, hydrogen gas is still liberated at the cathode, but chlorine gas (and NOT oxygen gas) is now produced at the anode instead. The higher concentration of the chloride ions favors their discharge over the hydroxide ions.

C. **Nature of the Electrode**: Electrodes which take no part in the electrolytic reaction are described as inert electrodes. Some electrodes which have strong affinity for certain ions may influence ionic discharge. This is not as important as either of the other two factors, except in certain cases. For example, in the electrolysis of molten sodium chloride using a mercury cathode, sodium ions are discharged in preference to hydrogen ions which are lower in the series.

Assessment

Use the following options to answer the questions below.

Cation, Electrode, Strong electrolytes, Ionization, Electrolysis, Non-conductors, Anion, Electrolyte, Electrolytic Cell, Electromagnetic Cell, Weak Electrolytes, Conductors

1. .... is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them?
2. .... are solid substances except mercury that allow electric current to pass through them
3. .... are solutions of organic substances, which produce molecules instead of ions and are therefore poor conductors of electricity
4. .... is a positively charged ion that moves to the cathode during electrolysis.
5. .... is an assembly of two electrodes in an electrolyte, and is used for the electrolysis of a substance.
6. .... is a solution or molten compound of inorganic acids, bases and salts that conduct electricity
7. HNO_3 is a ....
8. The process of splitting of the molecules into ions of an electrolyte is called ....

Answers

1. Electrolysis
2. Conductors
3. Non-Electrolytes
4. Cation

5. Electrolytic Cell
6. Electrolyte
7. Strong electrolyte
8. Ionization

Week 4

Topic: Electrolysis of Specified Electrolytes

Electrolysis of Specified Electrolytes

Electrolysis of Molten Sodium Chloride

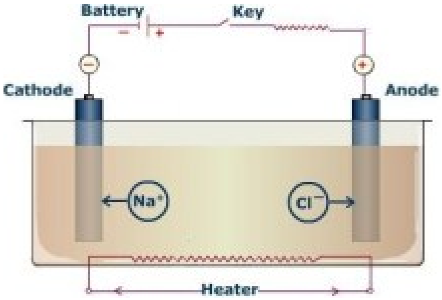
When molten sodium chloride is electrolyzed the products obtained are, sodium metal at cathode and chlorine gas at anode. The electrolysis of molten sodium chloride is as follows.

These ions carry the current, Na^+ ions move towards cathode, and Cl^- ions move towards anode. On reaching the respective electrodes, these ions get involved in electrode reactions as follows;

At cathode: $Na^+ + \underset{\text{from anode}}{e^-} \longrightarrow \underset{\text{liberated at cathode}}{Na}$

At anode: $Cl^- \longrightarrow 1/2Cl_2 + \underset{\text{to the cathode}}{e^-}$

Overall reaction: $Na^+ + Cl^- \xrightarrow{\text{electrolysis}} Na + 1/2Cl_2$



Electrolysis of molten sodium chloride

Electrolysis of Copper (II) Tetraoxosulphate (VI) Solution

When a solution of copper(II) tetraoxosulphate (VI) is electrolyzed using platinum electrodes, the products of electrolysis are copper at cathode and oxygen gas at anode. After electrolysis the solution around the anode is found to contain sulphuric acid. This can be explained as follows:

The electrolyte $CuSO_4$ when dissolved in water dissociates to give Cu^{2+} and SO_4^{2-}ions.

$$CuSO4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Electrolysis of brine

Brine is a solution of sodium chloride (NaCl) and water (H_2O). The electrolysis of brine yields hydrogen and chlorine at the electrodes and a concentrated solution of sodium hydroxide. The process of electrolysis involves using an electric current to bring about a chemical change and make new chemicals. The electrolysis of brine is a large-scale process used to manufacture chlorine from salt. Two other useful chemicals are obtained during the process, sodium hydroxide (NaOH) and hydrogen (H_2).

It is important that the chlorine and sodium hydroxide produced in the process are separated they react when they come into contact with each other.

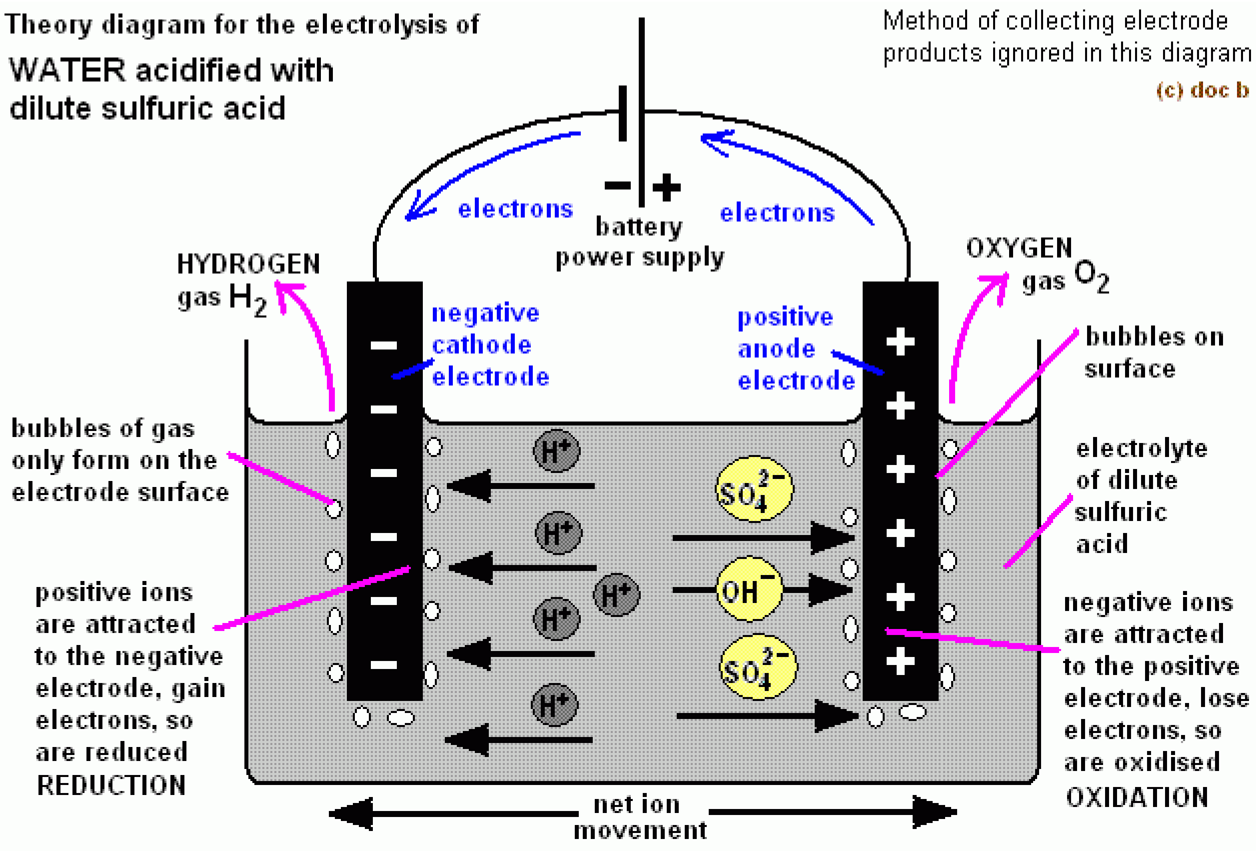
At the anode: Chlorine is discharged as follows

$Cl^{-}_{(aq)} \rightarrow Cl + e$

$Cl + Cl \rightarrow Cl_{2(g)}$

At the cathode: The sodium ions which are attracted to the cathode form a loose association eith the mercury to produce sodium amalgam. The amalgam is drained from the cell at one end and led to a second tank while fresh mercury is supplied. In the second tank, the amalgam is treated with water, it decomposes to produce sodium hydroxide, hydrogen and mercury.

Electrolysis of Acidified Water



At the cathode: Hydrogen ions which are the only cations present migrate to the cathode where they acquire an electron each to form neutral hydrogen atoms. These atoms combine in pairs to produce the diatomic molecules of gaseous hydrogen

$H_{+ (aq)} + e^{-} \rightarrow H$

$H + H \rightarrow H_{2(g)}$

At the anode: Both So42- and OH- migrate to the anode where OH is preferentially discharged. Each OH- loses its electron to the anode to become neutral. Two OH groups react to form one molecule of water and gaseous oxygen is produced. When the oxygen atoms combine, they form a diatomic oxygen.

$OH^{-}{}_{(aq)} \rightarrow OH + e^{-}$

$OH + OH \rightarrow H_2O_{(l)} + O$

$O + O \rightarrow O_{2(g)}$

Electrolytic Cell

This is an assembly of two electrodes in an electrolyte and is used for the electrolysis of a substance. An **electrolytic cell** is an electrochemical **cell** that undergoes a redox reaction when electrical energy is applied. ... An **electrolytic cell** has three component parts: an **electrolyte** and two electrodes (a cathode and an anode).
The **electrolyte** is usually a solution of water or other solvents in which ions are dissolved.

Uses of Electrolysis

Electrolysis has wide applications in industries. Some of the important applications are, as follows,

1. Production of hydrogen by electrolysis of water.
2. Manufacture of heavy water.

iii. The metals like K, Mg, Al, etc., are obtained by electrolysis of fused electrolytes.

1. Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.
2. In this method pure metal is deposited at cathode from a solution containing the metal ions etc.
3. Compounds like NaOH, KOH, etc. are synthesized by electrosynthesis method.

Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating. In other word, it is the process of coating a cheaper metal with a more expensive one, such as copper or silver.

How it works

- The negative electrode should be the object that is to be electroplated
- The positive electrode should be the metal that you want to coat the object with
- The electrolyte should be a solution of the coating metal, such as its metal nitrate or sulphate

Here are two examples.

Electroplating with silver

The object to be plated, such as a metal spoon, is connected to the negative terminal of the power supply. A piece of silver is connected to the positive terminal. The electrolyte is silver nitrate solution.

Electroplating with copper

The object to be plated, such as a metal pan, is connected to the negative terminal of the power supply. A piece of copper is connected to the positive terminal. The electrolyte is copper (II) tetraoxosulphate (VI) solution.

This arrangement can also be used to purify copper during copper manufacture. In this case, both electrodes are made from copper. The negative electrode gradually gets coated with pure copper as the positive electrode gradually disappears.

Assessment

Explain what happens when an electric current is passed through each of the following solutions

- Copper (II) chloride solution
- Aqueous sodium chloride

- Aqueous tetraoxosulphate (vi) acid

Calculate the amount of gold deposited when a current of 5A is passed through a solution of gold salt for 2hrs 15mins. If the same current is used find the time taken for 6.0g of gold to be deposited. (Au = 197, 1 faraday = 96500 C)

1. Which of these is not an application of **electrolysis?**
   a. Rust removal
   b. Electroplating
   c. Making leather
   d. Manufacture of bleach
2. Particles which move towards **cathode** are called
   a. anions
   b. cations
   c. photons
   d. positrons
3. In an **electrolytic** cell the electrode at which the electrons enter the solution is called the _____ ; the chemical change that occurs at this electrode is called ______.
   (a) anode, oxidation
   (b) anode, reduction
   (c) cathode, oxidation
   (d) cathode, reduction
4. What mass (in grams) of nickel could be electroplated from a solution of nickel(II) chloride by a current of 0.25 amperes flowing for 10 hours?
   (a) 12 g
   (b) 5.5 g
   (c) 0.046 g
   (d) 2.7 g
5. In the standard notation for a **voltaic cell**, the double vertical line “||” represents:
   (a) a salt bridge
   (b) gas electrode

(c) a wire (metal) connection
(d) a standard hydrogen electrode

Answers

1. C
2. B
3. D
4. D
5. A

Week 5

Topic: Application of Electrochemical Cell

Types of Electrochemical Cell

Daniel Cell

Anode (negative terminal): Oxidation / Zinc strip immerses in zinc sulphate solution.
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$ / Zinc strip becomes thinner.

- Cathode (positive terminal): Reduction / Copper strip immerses in copper(II) sulphate solution.
  $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ / A brown layer formed around copper strip. / Concentration Cu^{2+} ions decreases cause the intensity blue colour of solution decreases.
- Zinc is more electropositive than copper. Electrons are flowed from zinc strip to copper strip through the external circuit. (Note: Conventionally, electrons flow in the opposite direction of electrical current).
- Overall equation: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

As a result, the solution containing Zn(s) becomes more positively charged while the solution containing Cu(s) becomes more negatively charged. In order for the voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^-, an anion into the anode solution and K^+, a cation into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to neutralize charge in the cell compartments.

The diagram of this electrical cell : $Zn_{(s)} \mid Zn^{2+}{}_{(aq)} \parallel Cu^{2+}{}_{(aq)} \mid Cu_{(s)}$

Use ‖ to separate anode(-) and cathode(+) and so represents the salt bridge in between.

Leclanche Cell – In a Leclanche cell, the anode and the cathode are a zinc rode and a carbon rod respectively. The electrolyte is an ammonium chloride solution (wet cell) and paste (dry cell). he **Leclanché cell** is a battery invented and patented by the French scientist Georges **Leclanché** in 1866. The battery contained a conducting solution (electrolyte) of ammonium chloride, a cathode (positive terminal) of carbon, a depolarizer of manganese dioxide, and an anode (negative terminal) of zinc.

At the anode: Zinc ions lose two electrons each to dissolve in the electrolyte as positively charge zinc ions.

At the cathode: the ammonium ions accept electrons to become reduced to ammonia and hydrogen gas. The latter is removed by manganese(iv) oxide to prevent it from adhering to the cathode.

The Leclanche cell is a primary cell as it produces electric current by using up the chemicals of which it is composed.

$$Zn_{(s)} / Zn^{2+}_{(aq)} \mid NH^{+}_{4(aq)} / NH_4OH_{(aq)}, C;$$

$$E^0_{cell} = 1.5 \text{ volt}$$

The chemical changes that takes place in the Lecanche cell is complicated, but the main reactions may be regarded as –

At anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$

At cathode: $2NH^{+}_{4} + 2e \rightarrow 2NH_{3(g)} + H_{2(g)}$

Hydrogen gas is oxidized by MnO_2 and water is formed which intern reacts with ammonia and ammonium hydroxide is produced.

Therefore, the cathodes reduction may be represented as,

$$2NH_4^+ + 2MnO_2 + 4H_2O + 2e \rightarrow 2NH_4OH + 2Mn(OH)_2$$

Therefore, the total cell reaction is,

$$Zn + 2NH_4^+ + 2MnO_2 + 4H_2O \rightleftharpoons 2NH_4OH + 2Mn(OH)_2$$

The surface area of carbon rod is increased by using the mixture of carbon and MnO_2 powder. The polarization effect of hydrogen gas produced in the reduction reaction at the cathode is removed by the absorption of H_2 gas by MnO_2. Similarly, the polarization effect of ammonia gas is also removed by the dissolution of ammonia in water. In dry cell the zinc container takes part into oxidation reaction. As a result, on prolong use it is being perforated, paste leaks out from the cell.

Leclanche cell is irreversible cell. That means, it converts chemical energy into electrical energy by an irreversible process. Therefore, the original change cannot be restored by applying electrical energy from the external sources.

Lead Accumulator

The lead accumulator is the commonly used car battery. This is a secondary or storage cell as it must be charged by passing a direct current through it. The charged cell can then produce an electric current when required. The cathode of a fully charged lead accumulator is lead(iv) oxide and its anode is metallic lead. The electrolyte is dilute tetraoxosulphate(vi) acid solution.

At the anode (discharging cell)

The lead atoms release two electrons each to become oxidized to lead(II) ions which then combine with tetraoxosulphate(vi) ions in the electrolyte to become deposited on the anode as lead(ii) tetraoxosulphate (vi).

At the cathode

The electrons from the anode are accepted at the cathode where the lead(iv) oxide and the hydrogen ions from the electrolyte undergo reduction to produce lead(ii) iron and water

Here stored chemical energy is converted to electrical energy or current is drawn from the cell.

$$H_2SO_4 \longrightarrow 2H^+ + SO4^{2-}$$

The hydrogen ions go to the +ve electrode and SO_4^{2-} to the -ve electrode. After giving their charges they react with the electrodes and reduce the active material to lead sulphate.

Therefore, at the -ve electrode

$$Pb + SO_4^{2-} - 2e^- \longrightarrow PbSO_4$$

At the +ve electrode,

$$PbO_2 + 2H^+ + 2e^- \longrightarrow PbO + H_2O$$

$$PbO + H_2SO_4 \longrightarrow PbSO_4 + H_2O$$

$$PbO_2 + 2H^+ + 2e^- + H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$$

Both plates (but only half of the active materials) are converted into $PbSO_4$ (whitish). Water is formed thus lowering the specific gravity of H_2SO_4(electrolyte).

The emf of the cell falls and sulphuric acid is consumed.

PRIMARY CELL – A primary cell is a battery that is designed to be used once and discarded, and not recharged with electricity and reused like a **secondary cell**(rechargeable battery). In general, the electrochemical reaction occurring in the **cell** is not reversible, rendering the **cell** unrechargeable.

This type of cells become dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are dry cell, mercury cell, etc.

(a) Dry Cell. It is a compact form of Leclanche cell known after its inventor, a French chemist, G Leclanche. In this cell, anode consists of zinc container while cathode is a graphite rod surrounded by powdered: MnO_2 and carbon.

(**b) Mercury Cell**. It is miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices

SECONDARY CELLS-This type of cells can be recharged by passing direct current through them and can be used again and again. Some examples are lead-storage battery, nickel-cadmium storage cell, etc. Examples

(a) Lead-storage Battery. It is the most frequently used battery in automobiles.

(b) Nickel-cadmium Storage Cell. It is another rechargeable cell. It consists of cadmium anode and the cathode is made of a metal grid containing nickel (IV) oxide.

Applications of Electrochemical Cells

- torches
- electrical appliances such as cellphones (long-life alkaline batteries)
- digital cameras (lithium batteries)
- hearing aids (silver-oxide batteries)
- digital watches (mercury/silver-oxide batteries)
- military applications (thermal batteries)

- Electroplating – Electroplating occurs when an electrically conductive object is coated with a layer of metal using electrical current. Sometimes, electroplating is used to give a metal particular properties or for aesthetic reasons:
    - corrosion protection
    - abrasion and wear resistance
    - the production of jewelery

Assessment

Mention 2 examples of secondary cells

What are the uses of electrochemical cells

Explain the Daniel Cell and its uses

WEEK 6

Topic: Ionic Theory

Content:

Differences between:

1. **Ionic Theory**
2. **Electrovalent and Covalent Bond**
3. **Electrolytes and Non-electrolytes**
4. **Weak and Strong Electrolytes**
5. **Conductors and Non-conductors**

Ionic theory

The theory was first presented by Arrhenius in 1887 to explain electrolysis. The theory proposed that when an electrolyte is melted or dissolved in water, some of it not all of the molecules of the substance dissociate into freely moving charged particles called ions. The process of dissociation is known as association. The metallic ions, ammonium ions and hydrogen ions are positively charged while the hydroxide ions are negatively charged. When we pass an electric current through an electrolyte, the free ions lose their random movement. The positive ions become attracted to the cathode (negative electrode) and are known as cations. The negative ions are attracted to the anode (positive electrode) and they are called anions. Therefore the current through the electrolyte is carried by the movement of ions to the electrodes and not by the flow of electrons in the electrolyte.

The modern theory opposes that the ions in such solids are pulled away from one another either as a result of the heat energy applied when the solid melts or with the help of the solvent molecules when the solid dissolves.

We can prove the existence of ions during electrolysis

- using a compound with a coloured cation and/or a coloured anion and showing the migration of the coloured ions
- showing the formation of a coloured compound when the migrating ions meet.

A. Covalent and Electrovalent Bonds

Covalent Bonds

Covalent chemical bonds involve the sharing of a pair of valence electrons by two atoms, in contrast to the transfer of electrons in ionic bonds. Such bonds lead to stable molecules if they share electrons in such a way as to create a noble gas configuration for each atom.

Ionic Bonds (Electrovalent Bonds)

In an ionic bond, an electron is actually transferred from the less electronegative atom (metals) to the more electronegative element (non-metals). Ionic bonds are the result of an electrostatic attraction between ions that have opposite charges; in other words, cations and anions. Ionic bonds usually form between metals and nonmetals. Ionic bonds are very strong, so compounds that contain these types of bonds have high melting points and exist in a solid state under standard conditions.

Differences Between Covalent and Electrovalent Bond

Covalent Bonds	**Ionic Bonds**	
Polarity	**Low**	**High**
Formation	A covalent bond is formed between two non-metals that have similar electronegativity's. Neither atom is "strong" enough to attract electrons from the other. For stabilization, they share their electrons from outer molecular orbit with others.	An ionic bond is formed between a metal and a non-metal. Non-metals(-ve ion) are "stronger" than the metal(+ve ion) and can get electrons very easily from the metal. These two opposite ions attract each other and form the ionic bond.
Shape	Definite shape	No definite shape
What is it?	Covalent bonding is a form of chemical bonding between two nonmetallic atoms which is characterized by the sharing of pairs of electrons between atoms and other covalent bonds.	Ionic bond, also known as electrovalent bond is a type of bond formed from the electrostatic attraction between oppositely charged ions in a chemical compound. These kinds of bonds occur mainly between a metallic and a nonmetallic atom.
Melting point	low	High
Examples	Methane (CH4), Hydro Chloric acid (HCl)	Sodium chloride (NaCl), Sulphuric Acid (H2SO4)
Occurs between	Two non-metals	One metal and one non-metal

Covalent Bonds	**Ionic Bonds**	
Boiling point	Low	High
State at room temperature	Liquid or gaseous	Solid

Electrovalent compounds

- Electrovalent compounds are formed by complete transfer of electrons in KCl ($K^{\cdot} + {}^{\cdot}Cl^{:} — K^{+} Cl^{-}$)
- Electrovalent compounds are made up of ions.
- Electrovalent compounds are heard, crystalline solids e.g. Na Cl, Mg CL_2
- Electrovalent compounds are usually soluble in water but insoluble in non-polar solvents like CI_4
- Electrovalent compounds generally have high melting and boiling points.
- Electrovalent compounds are good conductors of electricity in the molten state and in aqueous solutions but insulators in the solid state.

Covalent Compounds

- Covalent compounds are formed by mutual sharing of electrons as in NH_3
- Covalent compounds are made up of molecules.
- Covalent compounds are usually liquids or gases. E.g. CH_4, $C_2 H_6$, NH_3

- Covalent compounds are soluble in non-polar solvents like benzene or carbon tetrachloride and in soluble in polar solvents like water.
- Covalent compounds generally have low melting and boiling points.
- Covalent compounds are bad conductors of electricity.

B. Electrolytes and Non-electrolytes

Electrolytes: These are solutions or molten compounds of inorganic acids, bases and salts that conduct electricity. They dissociate into their ions on the passage of electric voltage. Electrolytes are substances that produce ions. These compounds can produce ions when they are in molten stage, or when they are dissolved in a solvent (water). Because of the ions, electrolytes can conduct electricity. Sometimes there may be solid state electrolytes. Moreover, some gases like carbon dioxide produce ions (hydrogen and bicarbonate ions) when it is dissolved in water. There are two types of electrolytes, strong electrolytes and weak electrolytes. Strong electrolytes readily produce ions when they are soluble. For example, ionic compounds are strong electrolytes. Molten sodium chloride or aqueous NaCl solutions have completely dissociated into Na^+ and Cl^- ions, thus they are good electricity conductors. Strong acids and bases are also good electrolytes. Weak electrolytes produce few ions when they are soluble in water. For instance, weak acids like acetic acid and weak bases are weak electrolytes.

Non-Electrolytes: These are solutions of organic substances, which produce molecules instead of ions and are therefore poor conductors of electricity. The compounds which are not split into positive and negative ions in a solution are called non electrolytes. The molten stage of these compounds doesn’t generate ions either. Absence of ions in the medium, makes them nonconductive. Mostly compounds with non-polar covalent bonds/ organic compounds belong into this group. Examples include sugar, ethanol and glycerin.

What is the difference between Electrolytes and Non electrolytes?

– Electrolytes can produce ions when they are dissolved in water, but non electrolytes can't produce ions.

– Ionic compounds and some compounds with polar bonds can be electrolytes. Compounds with non-polar bonds are mostly non electrolytes.

– Electrolytes in solutions can conduct electricity contrary to non-electrolytes.

C. Weak and Strong Electrolytes

Strong Electrolytes: They are electrolytes that give strongly conducting solution and dissociate readily into ions. Examples are HNO_3, NaCl. Strong electrolytes readily produce ions when they are soluble. They completely dissociate to produce ions in a solution. For example, ionic compounds are strong electrolytes. Molten sodium chloride or aqueous NaCl solutions have completely dissociated into Na^+ and Cl^- ions; thus, they are good electricity conductors. Strong acids and bases are also good electrolytes.

Weak Electrolytes: They are electrolytes that produce weakly conducting solutions and only partially dissociate into their ions on the passage of electric current and voltage. Examples include HgCl, CH_3COOH acid. They acids and bases on partially ionize in solution. Because of the limited number of ions, solutions of **weak electrolytes** do not conduct electricity as well as strong electrolytes. Weak electrolytes produce few ions when they are soluble in water. They dissociate partially and produce few ions. In a solution of weak electrolytes, there will be dissociated ions as well as the neutral molecules of the substance. Therefore, the current conducted by such a solution is very low compared to a strong electrolytic solution. For instance, weak acids like acetic acid and weak bases are weak electrolytes.

D. Conductors and Non-conductors

Conductors: are solid substances except mercury that allow electric current to pass through them. For example, metals like copper and aluminum, and non-metal like graphite (carbon). A **conductor** easily transfers energy in the form of electricity and/or heat.

Non-conductors: are solid or liquid substances that do not allow an electric current to pass through them. For example, diamond (carbon), rubber/plastics, benzene, dry wood etc.

Assessment

1. Aluminum (Al) is preferred in overhead power cables because
   a. it is a good conductor
   b. it acts as an insulator, in case of lightening
   c. it prevents accidents
   d. it is lighter in weight
2. Examples of non-conductors include
   a. Sulphur
   b. phosphorus
   c. wood
   d. all of the above
3. Electrolyte liquid may include
   a. solutions
   b. molten solids
   c. ethanol
   d. gases
4. Since ions are held in fixed positions by strong forces, electricity is not conducted by
   a. electrodes
   b. electrolytes
   c. insulators
   d. metals

5. Easy to shape materials like ceramics are used as
    a. conductors
    b. insulators
    c. electrodes
    d. catalysts
6. One of the following is a non-electrolyte
    a. acetic acid
    b. sugar
    c. ethanol
    d. glycerin

Answers

1. D
2. D
3. C
4. C
5. B
6. A

Week: 7

Topic: Electrolysis

What is Electrolysis?

Ionic substances contain charged particles called ions. For example, lead bromide contains positively charged lead ions and negatively charged bromide ions.

Electrolysis is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them. In other word, electrolysis is the decomposition of certain compounds in aqueous or molten state, when electric current is passed through them.

Electrolyte: These are solutions or molten compounds of inorganic acids, bases and salts that conduct electricity. They dissociate into their ions on the passage of electric voltage. There are two types of ions, these are:

1. **Anion**: It is a negatively charged ion that moves to the anode during electrolysis.
2. **Cation**: It is a positively charged ion that moves to the cathode during electrolysis.

Strong electrolytes: are electrolytes that give strongly conducting solution and dissociate readily into ions. Examples are HNO_3, NaCl

Weak electrolytes: They are electrolytes that produce weakly conducting solutions and only partially dissociate into their ions on the passage of electric current and voltage. Examples include HgCl, CH_3COOH acid.

Non-Electrolytes: These are solutions of organic substances, which produce molecules instead of ions and are therefore poor conductors of electricity. Examples include sugar, ethanol and glycerine.

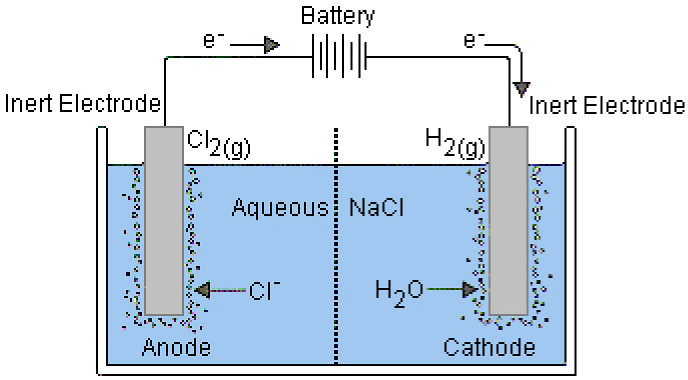
Conductors: are solid substances except mercury that allow electric current to pass through them. For example metals like copper and aluminium, and non-metal like graphite (carbon)

Non-conductors: are solid or liquid substances that do not allow an electric current to pass through them. For example diamond (carbon), rubber/plastics, benzene, dry wood etc.

Electrodes: These are rods or plates that connect the wiring of the circuit to the electrolyte. The positive electrode is the anode and is the electrode through which the electric current enters the electrolyte. The negative electrode is the cathode and is the electrode through which the current leaves the electrolyte.

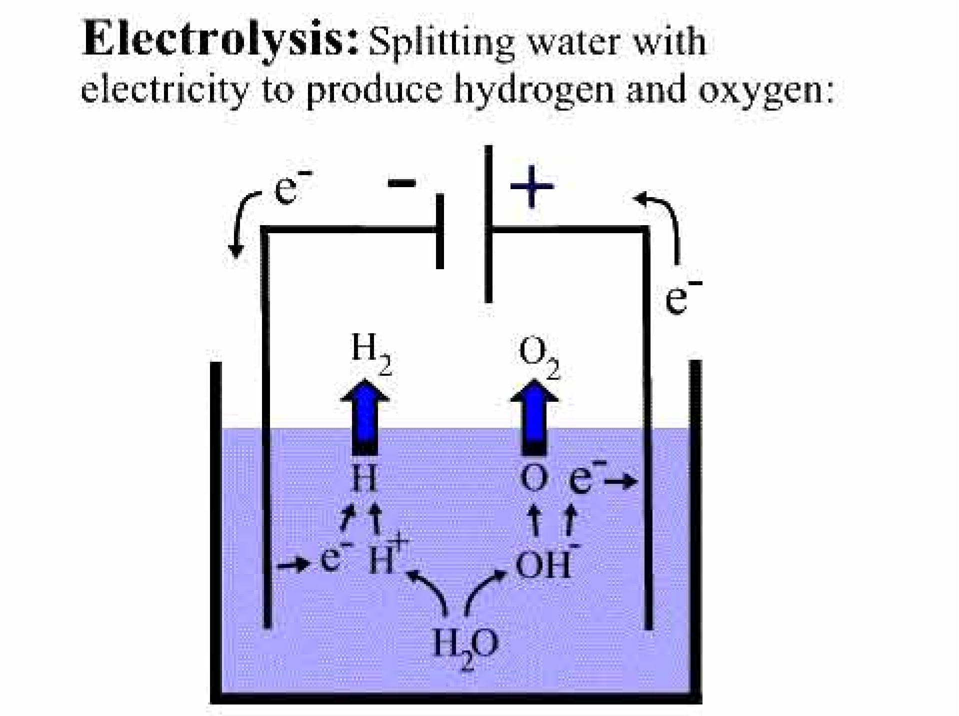
Electrolytic Cell: This is an assembly of two electrodes in an electrolyte, and is used for the electrolysis of a substance. In earlier days, the set up was known as voltameter.

Simple Electrolytic Cell



Mechanism of Electrolysis

For electrolysis to work, the ions must be free to move. Ions are free to move when an ionic substance is dissolved in water or when melted. For example, if electricity is passed through molten lead bromide, the lead bromide is broken down to form lead and bromine. The electrodes connect to a battery. When they are electrically charged, one electrode becomes the negative terminal or cathode, and the other becomes the positive terminal or anode. The positive terminal attracts negatively charged ions and the negative terminal attracts positively charged ions.



Here is what happens during electrolysis:

·Positively charged ions move to the negative electrode during electrolysis. They receive electrons and are reduced.

·Negatively charged ions move to the positive electrode during electrolysis. They lose electrons and are oxidised.

The substance that is broken down is called the electrolyte.

Arrhenius Theory of Electrolytic Dissociation

In order to explain the properties of electrolytic solutions, Arrhenius put forth, in 1884, a comprehensive theory which is known as theory of electrolytic dissociation or ionic theory. The main points of the theory are:

(i) An electrolyte, when dissolved in water, breaks up into two types of charged particles, one carrying a positive charge and the other a negative charge. These charged particles are called ions. Positively charged ions are termed cations and negatively charged as anions.

$AB \rightarrow A^+ + B^-$

$NaCl \rightarrow Na^+ + CL^-$

$K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$

In its modern form, the theory assumes that solid electrolytes are composed of ions which are held together by electrostatic forces of attraction. When an electrolyte is dissolved in a solvent, these forces are weakened and the electrolyte undergoes dissociation into ions. The ions are solvated.

$A^+B^-_{(aq)} \rightarrow A^+_{(aq)} + B^-_{(aq)}$

(ii) The process of splitting of the molecules into ions of an electrolyte is called ionization. The fraction of the total number of molecules present in solution as ions is known as degree of ionization or degree of dissociation. It has been observed that all electrolytes do not ionize to the same extent. Some are almost completely ionized while others are feebly ionized. The degree of ionization depends on a number of factors.

(iii) Ions present in solution constantly re-unite to form neutral molecules and, thus, there is a state of dynamic equilibrium between the ionized and non-ionized molecules, i.e.,

$AB \leftrightarrow A^+ + B^-$

Applying the law of mass action to above equilibrium

$[A^+] / [AB] = K$

K is known as ionization constant. The electrolytes having high value of K are termed strong electrolytes and those having low value of K as weak electrolytes.

(iv) When an electric current is passed through the electrolytic solution, the positive ions (cations) move towards cathode and the negative ions (anions) move towards anode and get discharged, i.e., electrolysis occurs. The ions are discharged always in equivalent amounts, no matter what their relative speeds are.

(v) The electrolytic solutions is always neutral in nature as the total charge on one set of ions is always equal to the total charge on the other set of ions. However, it is not necessary that the number of two sets of ions must be equal always.

$NaCl$ <–> $Na^+ + Cl^-$ (Both ions are equal)

$BaCl_2$ <–> $Ba^{2+} + 2Cl^-$ (Anions are double that of cations)

Na_2SO_4 <–> $2Na^+ +$ (Anions are double that of cations)

(vi) The properties of electrolytes in solution are the properties of ions present in solution. For example, acidic solution always contains H^+ ions while basic solution contains OH^- ions and characteristic properties of solutions are those of H^+ ions and OH^- ions respectively.

(vii) The conductivity of the electrolytic solution depends on the nature and number of ions as the current is carried through solution by the movement of ions.

Factors affecting Preferential Discharge of Electrolysis

There are certain factors that affect the discharge of electrons at electrodes.

Factors Affecting the Preferential Discharge of Ions in Electrolysis

1. The position of ion in electrochemical series.
2. The concentration of ion.
3. The nature of electrode.

A. **Relationship between position of ions in the electrochemical series and the order of discharge of ions.**

1. a) For cations
   Electrochemical series of cations:

K^+ ——-> Least easy to discharge
Na^+
Ca^{2+}

Mg^{2+}
Al^{3+}
Zn^{2+}
Fe^{2+}

Sn^{2+}
Pb^{2+}
H^+
Cu^{2+}
Hg^{2+}

Ag^+ ———-> Most easy to discharge

The cation has a lower position in the electrochemical series are preferentially discharged.

1. b) For anions

Electrochemical series of anions

OH^- ——> Most easy to discharge
I^-
Br^-
Cl^-
NO_3^-
SO_4^{2-} ———> Least easy to discharge

The anion has a higher position in the electrochemical series are preferentially discharged.

B. **Concentration of the ions in the electrolyte** – Irrespective of the position of the ions in the electrochemical series, there is a tendency to promote the discharge of the most concentrated ion present. Increasing the concentration of a given ion tends to promote its discharge. For example, in concentrated sodium chloride solution (i.e. brine), the two

cations present are the chlorine ion and the hydroxyl ion. Although the hydroxyl ion is more easily oxidized than the chlorine ion, it is the chlorine ion which will be discharged because its concentration is much greater than that of the hydroxyl ion. However, if the concentration of a particular ion is high, then this can alter the preferential discharge. The effect of concentration is evident when the two competing ions are closely positioned in the electrochemical series.
Also, if dilute hydrochloric acid is electrolyzed, hydrogen gas is produced at the cathode and oxygen gas at the anode. However, when concentrated hydrochloric acid is electrolyzed, hydrogen gas is still liberated at the cathode, but chlorine gas (and NOT oxygen gas) is now produced at the anode instead. The higher concentration of the chloride ions favour their discharge over the hydroxide ions.

C. **Nature of the Electrode**: Electrodes which take no part in the electrolytic reaction are described as inert electrodes. Some electrodes which have strong affinity for certain ions may influence ionic discharge. This is not as important as either of the other two factors, except in certain cases. For example in the electrolysis of molten sodium chloride using a mercury cathode, sodium ions are discharged in preference to hydrogen ions which are lower in the series.

Assessment

Use the following options to answer the questions below.

Cation, Electrode, Strong electrolytes, Ionization, Electrolysis, Non-conductors, Anion, Electrolyte, Electrolytic Cell, Electromagnetic Cell, Weak Electrolytes, Conductors

1. ………… is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current is passed through them.
2. ………… are solid substances except mercury that allow electric current to pass through them

3. ………… are solutions of organic substances, which produce molecules instead of ions and are therefore poor conductors of electricity
4. ………… is a positively charged ion that moves to the cathode during electrolysis.
5. ………. is an assembly of two electrodes in an electrolyte, and is used for the electrolysis of a substance.
6. ………. is a solution or molten compound of inorganic acids, bases and salts that conduct electricity
7. HNO_3 is a ………
8. The process of splitting of the molecules into ions of an electrolyte is called ……..

Answers

1. Electrolysis
2. Conductors
3. Non-Electrolytes
4. Cation
5. Electrolytic Cell
6. Electrolyte
7. Strong electrolyte
8. Ionization

Week 9

Topic: Electrolysis of Specified Electrolytes

Electrolysis of Specified Electrolytes

Electrolysis of Molten Sodium Chloride

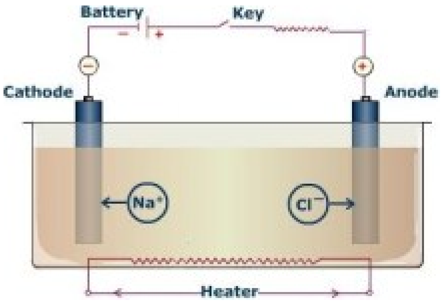
When molten sodium chloride is electrolyzed the products obtained are, sodium metal at cathode and chlorine gas at anode. The electrolysis of molten sodium chloride is as follows:

These ions carry the current, Na^+ ions move towards cathode, and Cl^- ions move towards anode. On reaching the respective electrodes, these ions get involved in electrode reactions as follows;

At cathode: $Na^+ + \underset{\text{from anode}}{e^-} \longrightarrow \underset{\text{liberated at cathode}}{Na}$

At anode: $Cl^- \longrightarrow 1/2Cl_2 + \underset{\text{to the cathode}}{e^-}$

Overall reaction: $Na^+ + Cl^- \xrightarrow{\text{electrolysis}} Na + 1/2Cl_2$



Electrolysis of molten sodium chloride

Electrolysis of Copper (II) Tetraoxosulphate (VI) Solution

When a solution of copper(II) tetraoxosulphate (VI) is electrolyzed using platinum electrodes, the products of electrolysis are copper at cathode and oxygen gas at anode. After electrolysis the solution around the anode is found to contain sulphuric acid. This can be explained as follows:

The electrolyte $CuSO_4$ when dissolved in water dissociates to give Cu^{2+} and SO_4^{2-} ions.

$$CuSO_{4(aq)} \longrightarrow Cu^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Electrolysis of brine

Brine is a solution of sodium chloride (NaCl) and water (H_2O). The electrolysis of brine yields hydrogen and chlorine at the electrodes and a concentrated solution of sodium hydroxide. The process of electrolysis involves using an electric current to bring about a chemical change and make new chemicals. The electrolysis of brine is a large-scale process used to manufacture chlorine from salt. Two other useful chemicals are obtained during the process, sodium hydroxide (NaOH) and hydrogen (H_2).

It is important that the chlorine and sodium hydroxide produced in the process are separated they react when they come into contact with each other.

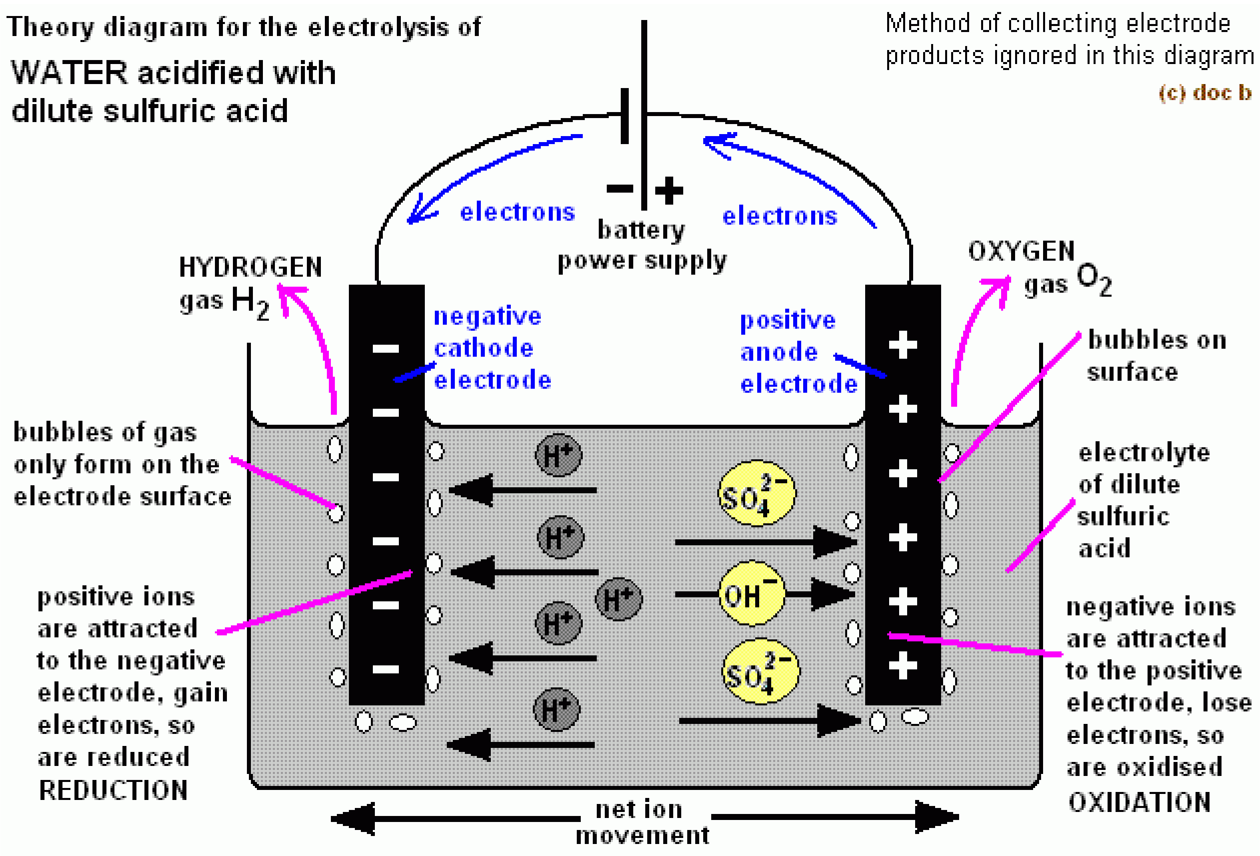
At the anode: Chlorine is discharged as follows

$Cl^-_{(aq)} \rightarrow Cl + e$

$Cl + Cl \rightarrow Cl_{2(g)}$

At the cathode: The sodium ions which are attracted to the cathode form a loose association eith the mercury to produce sodium amalgam. The amalgam is drained from the cell at one end and led to a second tank while fresh mercury is supplied. In the second tank, the amalgam is treated with water, it decomposes to produce sodium hydroxide, hydrogen and mercury.

Electrolysis of Acidified Water



At the cathode: Hydrogen ions which are the only cations present migrate to the cathode where they acquire an electron each to form neutral hydrogen atoms. These atoms combine in pairs to produce the diatomic molecules of gaseous hydrogen

$H_{+\,(aq)} + e^- \rightarrow H$

$H + H \rightarrow H_{2(g)}$

At the anode: Both So42- and OH- migrate to the anode where OH is preferentially discharged. Each OH- loses its electron to the anode to become neutral. Two OH groups react to form one molecule of water and gaseous oxygen is produced. When the oxygen atoms combine, they form a diatomic oxygen.

$OH^-_{(aq)} \rightarrow OH + e^-$

$OH + OH \rightarrow H_2O_{(l)} + O$

$O + O \rightarrow O_{2(g)}$

Electrolytic Cell

This is an assembly of two electrodes in an electrolyte and is used for the electrolysis of a substance. An electrolytic cell is an electrochemical cell that undergoes a redox reaction when electrical energy is applied. ... An electrolytic cell has three component parts: an electrolyte and two electrodes (a cathode and an anode).
The electrolyte is usually a solution of water or other solvents in which ions are dissolved.

Uses of Electrolysis

Electrolysis has wide applications in industries. Some of the important applications are, as follows,

1. Production of hydrogen by electrolysis of water.
2. Manufacture of heavy water.

iii. The metals like K, Mg, Al, etc., are obtained by electrolysis of fused electrolytes.

1. Non-metals like hydrogen, fluorine, chlorine are obtained by electrolysis.
2. In this method pure metal is deposited at cathode from a solution containing the metal ions etc.
3. Compounds like NaOH, KOH, etc. are synthesized by electrosynthesis method.

vii. Electroplating: The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating. In other word, it is the process of coating a cheaper metal with a more expensive one, such as copper or silver.

How it works

- The negative electrode should be the object that is to be electroplated
- The positive electrode should be the metal that you want to coat the object with
- The electrolyte should be a solution of the coating metal, such as its metal nitrate or sulphate

Here are two examples.

Electroplating with silver

The object to be plated, such as a metal spoon, is connected to the negative terminal of the power supply. A piece of silver is connected to the positive terminal. The electrolyte is silver nitrate solution.

Electroplating with copper

The object to be plated, such as a metal pan, is connected to the negative terminal of the power supply. A piece of copper is connected to the positive terminal. The electrolyte is copper (II) tetraoxosulphate (VI) solution.

This arrangement can also be used to purify copper during copper manufacture. In this case, both electrodes are made from copper. The negative electrode gradually gets coated with pure copper as the positive electrode gradually disappears.

Assessment

Explain what happens when an electric current is passed through each of the following solutions

- Copper (II) chloride solution
- Aqueous sodium chloride

- Aqueous tetraoxosulphate (vi) acid

Calculate the amount of gold deposited when a current of 5A is passed through a solution of gold salt for 2hrs 15mins. If the same current is used find the time taken for 6.0g of gold to be deposited. (Au = 197, 1 faraday = 96500 C)

1. Which of these is not an application of electrolysis?
   a. Rust removal
   b. Electroplating
   c. Making leather
   d. Manufacture of bleach
2. Particles which move towards cathode are called
   a. anions
   b. cations
   c. photons
   d. positrons
3. In an electrolytic cell the electrode at which the electrons enter the solution is called the _____ ; the chemical change that occurs at this electrode is called ______.
   (a) anode, oxidation
   (b) anode, reduction
   (c) cathode, oxidation
   (d) cathode, reduction
4. What mass (in grams) of nickel could be electroplated from a solution of nickel(II) chloride by a current of 0.25 amperes flowing for 10 hours?
   (a) 12 g
   (b) 5.5 g
   (c) 0.046 g
   (d) 2.7 g
5. In the standard notation for a voltaic cell, the double vertical line “||” represents:
   (a) a salt bridge
   (b) gas electrode

(c) a wire (metal) connection
(d) a standard hydrogen electrode

Answers

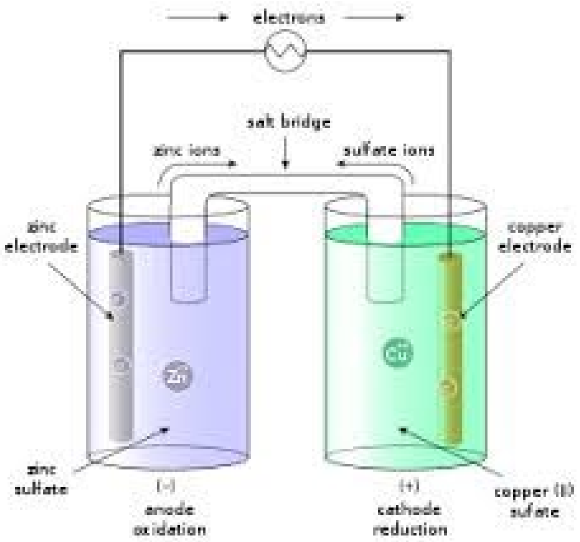
1. C
2. B
3. D
4. D
5. A

Week 10

Topic: Application of Electrochemical Cell

Types of Electrochemical Cell

Daniel Cell



Anode (negative terminal): Oxidation / Zinc strip immerses in zinc sulphate solution.
Zn(s) –> Zn^{2+}(aq) + 2e / Zinc strip becomes thinner.

- Cathode (positive terminal): Reduction / Copper strip immerses in copper(II) sulphate solution.
  Cu^{2+}(aq) + 2e –> Cu(s) / A brown layer formed around copper strip. / Concentration Cu^{2+} ions decreases cause the intensity blue colour of solution decreases.

- Zinc is more electropositive than copper. Electrons are flowed from zinc strip to copper strip through the external circuit. (Note: Conventionally, electrons flow in the opposite direction of electrical current).

- Overall equation: Zn(s) + Cu^{2+}(aq) –> Zn^{2+}(aq) + Cu(s)

As a result, the solution containing Zn(s) becomes more positively charged while the solution containing Cu(s) becomes more negatively charged. In order for the voltaic cell to work, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^-, an anion into the anode solution and K^+, a cation into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to neutralize charge in the cell compartments.

The diagram of this electrical cell : $Zn_{(s)} \,|\, Zn^{2+}{}_{(aq)} \,\|\, Cu^{2+}{}_{(aq)} \,|\, Cu_{(s)}$

Use ‖ to separate anode(-) and cathode(+) and so represents the salt bridge in between.

Leclanche Cell – In a Leclanche cell, the anode and the cathode are a zinc rode and a carbon rod respectively. The electrolyte is an ammonium chloride solution (wet cell) and paste (dry cell). he Leclanché cell is a battery invented and patented by the French scientist Georges Leclanché in 1866. The battery contained a conducting solution (electrolyte) of ammonium chloride, a cathode (positive terminal) of carbon, a depolarizer of manganese dioxide, and an anode (negative terminal) of zinc.

At the anode: Zinc ions lose two electrons each to dissolve in the electrolyte as positively charge zinc ions.

At the cathode : the ammonium ions accept electrons to become reduced to ammonia and hydrogen gas. The latter is removed by manganese(iv) oxide to prevent it from adhering to the cathode.

The Leclanche cell is a primary cell as it produces electric current by using up the chemicals of which it is composed.

$$Zn_{(s)} / Zn^{2+}_{(aq)} \,|\, NH^{+}_{4(aq)} / NH_4OH_{(aq)}, C;$$

$$E^{0}_{cell} = 1.5 \text{ volt}$$

The chemical changes that takes place in the Lecanche cell is complicated, but the main reactions may be regarded as –

At anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e$

At cathode: $2NH_4^+ + 2e \rightarrow 2NH_{3(g)} + H_{2(g)}$

Hydrogen gas is oxidized by MnO_2 and water is formed which intern reacts with ammonia and ammonium hydroxide is produced.

Therefore, the cathodes reduction may be represented as,

$$2NH_4^+ + 2MnO_2 + 4H_2O + 2e \rightarrow 2NH_4OH + 2Mn(OH)_2$$

Therefore, the total cell reaction is,

$$Zn + 2NH_4^+ + 2MnO_2 + 4H_2O \rightleftharpoons 2NH_4OH + 2Mn(OH)_2$$

The surface area of carbon rod is increased by using the mixture of carbon and MnO_2 powder. The polarization effect of hydrogen gas produced in the reduction reaction at the cathode is removed by the absorption of H_2 gas by MnO_2. Similarly the polarization effect of ammonia gas is also removed by the dissolution of ammonia in water. In dry cell the zinc container takes part into oxidation reaction. As a result on prolong use it is being perforated, paste leaks out from the cell.

Leclanche cell is irreversible cell. That means, it converts chemical energy into electrical energy by an irreversible process. Therefore the original change can not be restored by applying electrical energy from the external sources.

Lead Accumulator

The lead accumulator is the commonly used car battery. This is a secondary or storage cell as it must be charged by passing a direct current through it. The charged cell can then produce an electric current when required. The cathode of a fully charged lead accumulator is lead(iv) oxide and its anode is metallic lead. The electrolyte is dilute tetraoxosulphate(vi) acid solution.

At the anode (discharging cell)

The lead atoms release two electrons each to become oxidized to lead(II) ions which then combine with tetraoxosulphate(vi) ions in the electrolyte to become deposited on the anode as lead(ii) tetraoxosulphate (vi).

At the cathode

The electrons from the anode are accepted at the cathode where the lead(iv) oxide and the hydrogen ions from the electrolyte undergo reduction to produce lead(ii) iron and water

Here stored chemical energy is converted to electrical energy or current is drawn from the cell.

$$H_2SO_4 \longrightarrow 2H^+ + SO4^{2-}$$

The hydrogen ions go to the +ve electrode and SO_4^{2-} to the -ve electrode. After giving their charges they react with the electrodes and reduce the active material to lead sulphate.

Therefore, at the -ve electrode

$$Pb + SO_4^{2-} - 2e^- \longrightarrow PbSO_4$$

At the +ve electrode,

$$\begin{array}{ll} PbO_2 + 2H^+ + 2e^- & \longrightarrow PbO + H_2O \\ PbO + H_2SO_4 & \longrightarrow PbSO_4 + H_2O \\ \hline \end{array}$$

$$PbO_2 + 2H^+ + 2e^- + H_2SO_4 \longrightarrow PbSO_4 + 2H_2O$$

Both plates (but only half of the active materials) are converted into $PbSO_4$ (whitish). Water is formed thus lowering the specific gravity of H_2SO_4(electrolyte).

The emf of the cell falls and sulphuric acid is consumed.

Primary Cell – Primary cell. A primary cell is a battery that is designed to be used once and discarded, and not recharged with electricity and reused like a secondary cell(rechargeable battery). In general, the electrochemical reaction occurring in the cellis not reversible, rendering the cell unrechargeable.

This type of cells become dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are dry cell, mercury cell, etc.

(a) Dry Cell. It is a compact form of Leclanche cell known after its inventor, a French chemist, G Leclanche. In this cell, anode consists of zinc container while cathode is a graphite rod surrounded by powdered :MnO_2 and carbon.

(b) Mercury Cell. It is miniature cell which finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices

SECONDARY CELLS

This type of cells can be recharged by passing direct current through them and can be used again and again. Some examples are lead-storage battery, nickel-cadmium storage cell, etc. Examples

(a) Lead-storage Battery. It is the most frequently used battery in automobiles.

(b) Nickel-cadmium Storage Cell. It is another rechargeable cell. It consists of cadmium anode and the cathode is made of a metal grid containing nickel (IV) oxide.

Applications of Electrochemical Cells

- torches
- electrical appliances such as cellphones (long-life alkaline batteries)
- digital cameras (lithium batteries)
- hearing aids (silver-oxide batteries)

- digital watches (mercury/silver-oxide batteries)
- military applications (thermal batteries)
- Electroplating – Electroplating occurs when an electrically conductive object is coated with a layer of metal using electrical current. Sometimes, electroplating is used to give a metal particular properties or for aesthetic reasons:
    - corrosion protection
    - abrasion and wear resistance
    - the production of jewelery

Assessment

Mention 2 examples of secondary cells

What are the uses of electrochemical cells

Explain the Daniel Cell and its uses

Week: 11

Topic: Faraday’s Law of Electrolysis

In chemistry, quantitative laws used to express magnitudes of electrolytic effects, first described by the English scientist Michael Faraday in 1833.The quantities of substances produced or consumed by the electrolysis process is dependent upon the following:

- Electric current measured in amperes or amps
- Time measured in seconds
- The number of electrons required to produce or consume 1 mole of the substance

Faraday’s put forward his two laws of electrolysis, these are:

Faraday’s First Law of Electrolysis states that the mass of an element which is deposited on an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte.
Explanation:
If W is the amount of substance which liberates or deposited at the electrode on passing the electricity through the electrolyte and the quantity of electricity is Q, then

or $W = ZQ$
Z is the electrochemical constant for a given substance.
As $Q = I \times T$
We can write the statement of the first law of electrolysis mathematically as under:
$W= ZIt$
If 1 ampere electric current passes through the electrolyte for 1 second then W=Z It means that on passing the current of 1 ampere for 1 second the weight of the substance deposited is equal to the electrochemical constant. For doing the calculations of electrochemical problems, we must know the units too.

unit of charge (Q) = Coulomb (C)
unit of mass (m) = Kilogram (kg)
unit of current (A) = ampere (A)
unit of electrochemical equivalent (Z) = kg/C
Note:
Faraday’s first law of electrolysis is written as:
W = ZIt
W= is actually mass and not weight, as mass is commonly called weight.

The Faraday

Electricity is a flow of electrons. For calculation purposes, we need to know how to relate the number of moles of electrons which flow to the measured quantity of electricity.

The charge that each electron carries is 1.60×10^{-19} coulombs.

1 mole of electrons contains the Avogadro constant, L, electrons – that is 6.02×10^{23} electrons.

That means the 1 mole of electrons must carry

$6.02 \times 10^{23} \times 1.60 \times 10^{-19}$ coulombs

= 96320 coulombs

This value is known as the Faraday constant.

The numbers we are using here are rounded off. For exam purposes, the value of the Faraday constant is given as 9.65×10^{4} C mol^{-1}.

That is 9.65×10^{4} (or 96500) coulombs per mole. So 96500 coulombs is called 1 faraday.

Example 1: How much electric charge is required to oxidise (a) 1 mole of H_2O to O_2

and (b)1 mole of FeO to Fe_2O_3?

Solution:

(a) The oxidation reaction is

$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$

1 mole ——-> 2 moles

Q = 2 × F

= 2 × 96500=193000 coulomb

(b) The oxidation reaction is

$FeO + 1/2\ H_2O \rightarrow Fe_2O_3 + H^+ + e^-$

Q = F = 96500 coulomb

Example 2: How much charge is required to reduce (a) 1 mole of Al^{3+} to Al and

(b)1 mole of to Mn^{2+}?

Solution:

(a) The reduction reaction is

$Al^{3+} + 3e^- \longrightarrow Al$

1 mole ——-> 3 mole

Thus, 3 moles of electrons are needed to reduce 1 mole of Al^{3+}.

Q = 3 × F

= 3 × 96500 = 289500 coulomb

(b) The reduction is

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

1 mole —-> 5 mole

Q = 5 × F

= 5 × 96500 = 48500 coulomb

Example 3: Calculate the quantity of electricity, Q, obtained when a current of 25 amps runs for 1 minute.

Solution:

Q = ?, I = 25A, t = 1 minute = 60 seconds,

Q = I x t

Q = 25 x 60 = 1,500 Coulombs

Example 4: Calculate the current needed to provide 30,000 coulombs of electricity in 5 minutes.

Solution:

Q = 30,000C, I = ?, t = 5 minutes = 5 x 60 = 300 seconds

I = Q ÷ t

I = 30,000 ÷ 300 = 100 amps

Example 5: Calculate the time required to produce 12,000 C of electricity using a current of 10 amps.

Solution:

Q = 12,000C, I = 10A, t = ?

t = Q ÷ I

t = 12,000 ÷ 10 = 1,200 seconds = 1,200 ÷ 60 = 20 minutes

Example 6: Calculate the quantity of electricity obtained from 2 moles of electrons

Solution:

Q = n x F

Q = ?, n = 2 mol, F = 96,500 C mol^{-1}

Q = 2 x 96,500 = 193,000C

Example 7: Calculate the moles of electrons obtained from 250 C of electricity

$n(e) = ?$, $Q = 250C$, $F = 96{,}500\ C\ mol^{-1}$,

$n(e) = Q \div F$

$n(e) = 250 \div 96{,}500 = 2.59 \times 10^{-3}$ mol

Faraday's Second Law of Electrolysis states that when the same quantity of electricity is passed through different electrolytes, the masses of the elements liberated or deposited are in proportion to the chemical equivalents of these elements. Faraday's laws are very useful for the determination of electrochemical equivalents of different substances.

Chemical Equivalent

The chemical equivalent of an element is numerically equal to its relative atomic mass in grams divided by the valency of the ion. Faraday's second law of electrolysis can also be stated as under: "The mass of different substances liberated or deposited by the same quantity of electricity is proportional to the atomic masses divided by the valencies of their ions."

Explanation:

Take three solutions of electrolytes: AgNO3, CuSO4 and Al(NO3)3 in a series, pass some quantity of electricity through them for the same time. Now Ag, Cu and Al metals collect at the cathode. Their masses are directly proportional to their equivalent masses.

According to Faraday, if 96,500 Coulombs (or 1 Faraday) is passed through these electrolytes, we get

which are the equivalent masses of Ag, Cu and Al respectively.

Three equations relate these quantities:

·amperes x time = Coulombs

·96,500 coulombs = 1 Faraday

·1 Faraday = 1 mole of electrons

Calculating the Quantity of Substance Produced or Consumed

To determine the quantity of substance either produced or consumed during electrolysis given the time a known current flowed:

·Write the balanced half-reactions involved.

·Calculate the number of moles of electrons that were transferred.

·Calculate the number of moles of substance that was produced/consumed at the electrode.

·Convert the moles of substance to desired units of measure.

Example 1: A 40.0 amp current flowed through molten iron (III) chloride for 10.0 hours (36,000 s). Determine the mass of iron and the volume of chlorine gas (measured at 25°C and 1 atm) that is produced during this time.

Solution:

·Write the half-reactions that take place at the anode and at the cathode.

Anode (oxidation): $2\ Cl^- \longrightarrow Cl_{2(g)} + 2\ e^-$

Cathode (reduction): $Fe^{3+} + 3\ e^- \longrightarrow Fe_{(s)}$

·Calculate the number of moles of electrons.

I = 40A, t = 10hrs (10 x 60 x 60) = 36000s

Q = I x t

40 x 36000 = 1440000C

1 mole of Fe liberate 3F (3 x 96500)

What mole of Fe will liberate 1440000C

= 1 x 1440000 ÷ (3x 96500)

= 4.97 mole of Fe

1 mole of Cl liberate 2F (2 x 96500)

What mole of Cl will liberate 1440000C?

= 1 x 1440000 ÷ (2 x 96500)

= 7.46 mole of Cl

·Calculate the mass of iron using the molar mass and calculate the volume of chlorine gas using the ideal gas law (PV = nRT).

Molarmass of Fe = 56gmol^{-1}, calculated mole of Fe = 4.97

Mass of Fe deposited = mole x molarmass

4.97 x 56 = 278g

Using ideal gas law: PV = nRT

V = nRT/P

V = 7.46 x 0.0821 x 298/ 1

Volume of Cl_2 = 182L

Calculating the Time Required

To determine the quantity of time required to produce a known quantity of a substance given the amount of current that flowed:

·Find the quantity of substance produced/consumed in moles.

·Write the balanced half-reaction involved.

·Calculate the number of moles of electrons required.

·Convert the moles of electrons into coulombs.

·Calculate the time required.

Example 2: How long must a 20.0 amp current flow through a solution of $ZnSO_4$ in order to produce 25.00 g of Zn metal.

Solution:

·Convert the mass of Zn produced into moles using the molar mass of Zn.

Mass of Zn = 25.00g, molarmass of Zn = 65gmol^{-1}

Mole = mass/molarmass

Mole = 25/65 = 0.3846mol

·Write the half-reaction for the production of Zn at the cathode.

$Zn^{2+}_{(aq)} + 2e^{-} \text{—–>} Zn_{(s)}$

·Calculate the moles of e^{-} required to produce the moles of Zn and convert the moles of electrons into coulombs of charge using Faraday's constant.

1 mole of Zn liberate 2F (2 x 96500)C

0.386 mole will liberate: (2 x 96500 x 0.3846/1) = 74231C

·Calculate the time using the current and the coulombs of charge.

Q = I x t

t = Q / I

t = 74231/20

t = 3712secs = 62 minutes = 1.03hr

<u>Calculating the Current Required</u>

To determine the amount of current necessary to produce a known quantity of substance in a given amount of time:

·Find the quantity of substance produced/or consumed in moles.

·Write the equation for the half-reaction taking place.

·Calculate the number of moles of electrons required.

·Convert the moles of electrons into coulombs of charge.

·Calculate the current required.

Example 3: What current is required to produce 400.0 L of hydrogen gas, measured at STP, from the electrolysis of water in 1 hour (3600s)?

Solution:

·Calculate the number of moles of H_2. (Remember, at STP, 1 mole of any gas occupies 22.4 L.)

Moles of H_2 = 400.0/22.4

= 17.9mol

·The equation for this half-reaction is: $4e^- + 4H_2O_{(l)} \longrightarrow 2H_{2(g)} + 4OH^-_{(aq)}$

·Calculate the number of moles of electrons and convert the moles of electrons into coulombs of charge.

I mole of H_2 liberate 2F (2 x 96500)C

17.9 mole will liberate: 2 x 96500 x 17.9 = 3454700C

·Calculate the current required.

I = Q / t

= 3454700/3600

I = 960A

Example 4: Exactly 0.4 faraday electric charge is passed through three electrolytic

cells in series, first containing AgNO3, second CuSO4 and third FeCl3 solution. How

many gram of each metal will be deposited assuming only cathodic reaction in each cell?

Solution: The cathodic reactions in the cells are respectively.

$Ag^+ + e^- \rightarrow Ag$

1 mole ——> 1 mole

108 g ——-> 1 F

$Cu^{2+} + 2e^{-} \rightarrow Cu$

1 mole ——> 2 mole

63.5 g ——-> 2 F

and $Fe^{3+} + 3e^{-} \rightarrow Fe$

1 mole ——-> 3 mole

56 g ——->3 F

Hence, Ag deposited = 108 × 0.4 = 43.2 g

Cu deposited = 63.5/2×0.4 = 12.7 g

and Fe deposited = 56/3×0.4 = 7.47 g

Example 5: How long has a current of 3 ampere to be applied through a solution of silver nitrate to coat a metal surface of 80 cm2 with 0.005 cm thick layer? Density of silver is 10.5 g/cm^3.

Solution: Mass of silver to be deposited

= Volume × density

= Area ×thickness × density

Given: Area = 80 cm^2, thickness = 0.0005 cm and density = 10.5 g/cm^3

Mass of silver to be deposited = 80 × 0.0005 × 10.5

= 0.42 g

Applying to silver E = Z × 96500

Z = 108/96500 g

Let the current be passed for r seconds.

We know that

$W = Z \times I \times t$

So, $0.42 = 108/96500 \times 3 \times t$

$t = (0.42 \times 96500)/(108 \times 3) = 125.09$ secs

Assessment

1. What quantity of electricity is consumed when 10 amperes was consumed in 1hr during electrolysis?
   a. 36 kilo coulombs
   b. 3600 coulombs
   c. 7200 coulombs
   d. 72 kilo coulombs
2. Calculate the mass of aluminium deposited when a current of 3 amperes is passed through aluminium electrolyte for 2 hrs. (Al = 27, 1 faraday = 96500 C)
   a. 1g
   b. 6.04g
   c. 4.04g
   d. 2.02g
3. One faraday is equal to
   a. 9650 C
   b. 96500 C
   c. One mole of electrons
   d. half mole of electron
4. How long (in hours) must a current of 5.0 amperes be maintained to electroplate 60 g of calcium from molten $CaCl_2$?
   (a) 27 hours
   (b) 8.3 hours
   (c) 11 hours
   (d) 16 hours

Answers

1. A
2. B
3. B
4. D

SECOND TERM NOTES ON CHEMISTRY

Week 1

Topic: Rate of Reactions

Introduction

A chemical reaction is a process that transforms one set of chemical substances to another. The substances that take part in chemical reactions are known as reactants and the substances produced by the reaction are known as products.

The reaction rate is a measure of the change in the concentration of reactants or products over time in a chemical reaction. In other words, the rate of chemical change is the number of moles of the reacting substances which disappear or the number of moles of products which appear per unit time for a given quantity of the reacting species. As products are formed reactants are used up.

Measuring Rates

The only way we can find out about the rate of a particular reaction is to carry out an experiment. The balanced equation for the reaction tells us nothing about its rate. So we need to have some way of measuring either:

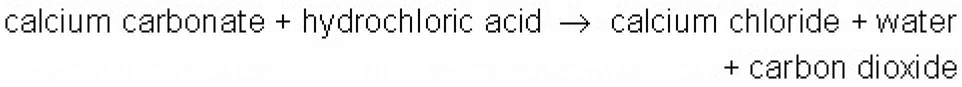
The rate at which reactants are used up in a reaction, or

The rate at which products are formed in a reaction

Reaction Rate = Change in concentration of reactants/products

Time taken for the change

In real experiments, we find some property of the reacting mixture that changes as the reaction takes place and we measure that. That's easy in reactions that produce a gas as one of the products – for example, marble chips (containing calcium carbonate) reacting with hydrochloric acid:


calcium carbonate + hydrochloric acid → calcium chloride + water + carbon dioxide

$CaCO_3(s) + 2\ HCl(aq) \quad CaCl_2(aq) + H_2O(l) + CO_2(g)$

Collision Theory

In a chemical reaction the reacting particles need to collide. However, not all collisions in a reacting mixture result in a reaction. The particles (molecules or ions) in the mixture will have a whole range of different energies. Some have lots of energy and move about quickly; others have a low energy and move more slowly. The collision must also have enough energy so that the chemical bonds can be broken. Collision without enough energy will not lead to a reaction. An effective reaction is a reaction which does have enough energy and does lead to a reaction.

Chemical reactions occur at different speeds. Some reactions are faster while others are much slower. For example an explosive chemical reaction between two reactants tells us that this is a very fast reaction whereas rusting is a much slower reaction.

Particles need enough kinetic energy to break the bonds and cause a chemical reaction to occur. The minimum amount of kinetic energy that a reaction requires to occur is known as the activation energy. So when the particles collide there must be enough kinetic energy to exceed the activation energy in order for a chemical reaction to occur. Slow reactions such as rusting generally have high activation energies, while explosive chemical reactions generally have low activation energies. The particles with insufficient energy just collide with each other without reacting.

The collision theory states that particles must collide before they can react, and that only collisions with sufficient energy (greater than the activation energy) will result in a reaction.

Factors that influence reaction rate are:

1. Concentration of the reactants
2. Temperature
3. Presence of a catalyst
4. Surface area
5. Nature of reactant
6. Intensity of light

Concentration of the Reactants

Rate of a reaction is directly proportional to the concentration of reactants.

i.e. rate (r) $\propto c^n$ where

$r = kc^n$

Where k = specific rate

c = concentration

n = order of the reaction

Raising the concentrations of reactants makes the reaction happen at a faster rate. For a chemical reaction to occur, there must be a certain number of molecules with energies equal to or greater than the activation energy. With an increase in concentration the number of molecules with the minimum required energy will increase, and therefore the rate of the reaction will increase. The rate of reaction has doubled by doubling the concentration.

The number of collisions and hence the activated collisions between the reactant molecules increase with increase in concentration. Therefore, according to the collision theory, the rate of a reaction should increase with increase in the concentration since the rate is directly proportional to the collision frequency.

The rate of a reaction decreases exponentially with time as the concentration of reactants is decreasing.

Surface Area

In a reaction between a solid and a liquid, the surface area of the solid will affect how fast the reaction occurs. This is because the two types of molecules can bump into each other only at the liquid-solid interface — that is, on the surface of the solid. Therefore, a larger surface area of the solid allows for a faster reaction. Smaller particles have bigger surface areas than larger particles with the same mass. The total exposed surface area will increase when a larger body is divided into smaller pieces (The surface of a solid can be increased by grinding it to a fine powder). Therefore, if a reaction takes place on the surface of a substance, increasing the surface area should increase the quantity of substance available to react and thus increase the rate of the reaction.

For Example, the reaction between zinc and hydrochloric acid occurs within seconds if the zinc metal is finely powdered. But the reaction will be slower when a zinc wire is used.

This is also true with the solid catalysts, which are usually employed in finely powdered form, while carrying out a chemical reaction. E.g. finely powdered nickel is used during the hydrogenation of oils.

Pressure

Increasing the pressure of a gas is the same as increasing its concentration. Increase the pressure of a gas by squeezing it into a smaller volume, and if you have the same mass in a smaller volume, the concentration is higher. Changing the pressure for a reaction that involves only solids or liquids has no effect on the reaction rate.

The partial pressure is another way of expressing the concentration for gases. The number of collisions increases with increase in the partial pressures of gases. Hence the rate of reactions involving gaseous reactants increases with increase in partial pressures. However it has no effect on reactions involving reactants in liquid or solid phases.

It is important to keep in mind that the partial pressures of reactants can be increased by increasing the pressure of overall system. However the partial pressures do not increase when an inert gas or a non reacting gas is added to the reaction mixture at constant volume.

Temperature

It has been observed experimentally that a rise of 10°C in temperature usually doubles or triples the speed of a reaction between molecules. The minimum energy needed for a reaction, the activation energy, stays the same with increasing temperature. Thus, an increase in temperature causes a rise in the energy levels of the molecules involved in the reaction. As a result the rate of the reaction increases. Similarly, the rate of reaction will decrease with a decrease in temperature. The higher the temperature of the reaction, the more quickly it will proceed. At higher temperatures, the molecules are moving around more quickly (they have more kinetic energy); this means they will collide with each other with more energy, and it’s more likely that they will overcome the activation energy needed to start the reaction.

The average kinetic energy increases with increase in absolute temperature. As a result, the number of effective collisions between reactant molecules also increases. Therefore, usually it is observed that the rate of reaction increases with increase in temperature.

Catalyst

Catalyst is a substance which alters the rate of a reaction without being consumed or without undergoing any chemical change during the reaction. Catalysts are substances that increase reaction rate by lowering the activation energy needed for the reaction to occur. Biological catalysts are known as enzymes. A catalyst is not destroyed or changed during a reaction, so it can be used again. For example, at ordinary conditions H_2 and O_2 do not combine. But in the presence of a small quantity of platinum, which acts as a catalyst, they do combine, and the reaction occurs rapidly.

In case of reversible reactions, the catalyst lowers the activation energies of both forward and backward reactions to the same extent and helps in attaining the equilibrium quickly.

Note: When a catalyst increases the rate of forward reaction, it also increases the rate of backward reaction.

Some substances may decrease the rate of a reaction. These are generally referred to as negative catalysts or inhibitors. They interfere with the reaction by forming relatively stable complexes, which require more energy to breakup. Thus the speed of the reaction is reduced.

Nature of Reactants

Rate of a reaction depends on the nature of bonding in the reactants. Usually the ionic compounds react faster than covalent compounds

If you mix two gases or two liquids, this represents a homogeneous reaction, but if reactants are in different phases, for example, if one is a gas and one is a liquid, then the reaction area is limited to the area where they touch each other, and the larger this area, the faster the reaction will proceed. For example, consider a teaspoon of salt dissolving in water. If you were to dump the salt into the beaker of water and let it float to the bottom without stirring it, it would take much longer for it to dissolve than if you stirred the solution.

The reactions between ionic compounds in water occur very fast as they involve only exchange of ions, which were already separated in aqueous solutions during their dissolution.

E.g. AgCl is precipitated out immediately when $AgNO_3$ solution is added to NaCl solution.

This reaction involves only the exchange of ions and hence occurs very fast. Whereas, the reactions between covalent compounds take place slowly because they require energy for the cleavage of existing bonds.

E.g. The esterification of acetic acid occurs slowly since the breaking of bonds requires energy.

Intensity of Light

The rate of some photochemical reactions, which occur in presence of light, increases with increase in the intensity of suitable light used. With increase in the intensity, the number of photons in light also increases. Hence more number of reactant molecules get energy by absorbing more number of photons and undergo chemical change.

E.g. The rate of photosynthesis is more on brighter days.

However, some photochemical reactions involving the free radicals, generated in a chain process, are not greatly affected by the intensity of the light. Just one photon is sufficient to trigger the formation a free radical. This in turn initiate a chain process in which more free radicals are formed repeatedly in each cycle without the need of extra photons.

Controlling the Rate of Reaction

The rate of the reaction can be controlled by changing the frequency of the collisions or changing the energy of the reactant particle.

Factor	Effect on Rate	Explanation
Concentration	Increasing the concentration of a reactant increases the rate	Increasing the concentration means that the particles are more crowded, so there will be more frequent effective collisions increasing the rate of reaction.
Temperature	Increasing the temperature of a reaction increases the rate	Increasing the temperature increases the kinetic energy that the reactants have, which means that they will collide more often and have more energy available to exceed the activation energy. At lower temperatures the particles have less kinetic energy, are moving much slower and so there are less effective collisions.

Surface area	Increasing the surface area of the solid or cutting the solid into smaller pieces increases the rate of reaction	Increasing the surface area increases the number of particles that are exposed to the reactants which increases the number of collisions and so increases the number of effective reactions. So a powder form of a reactant will have a higher rate of reaction than the same reactant in a block form.
Catalyst	Adding a catalyst to the reaction changes the rate of reaction	A catalyst changes the activation energy in a reaction. It basically speeds up a reaction without being used up itself. It can raise the activation energy in some reactions but it usually lowers it. This means that more particles will have enough kinetic energy to overcome the activation energy level.
Pressure	Increasing the pressure of reactions involving gasses increases the rate of reaction	Once the pressure has been increased the gas particles are in a smaller space meaning that more frequent and effective reactions will occur.

Changing the rate of reaction does not change the volume or mass of product formed, instead it only changes how quickly the product is formed.

Assessment

1. Rate of chemical reaction depends on the following factors except
   a. Rate at which gas is evolved
   b. Rate at which products are formed

c. Rate at which colour of reactions change
d. Rate at which the reactants diminish

2. The units of rate of chemical reaction is
   a. Mol dm^{-3} S^{-1}
   b. Mol^{-1} S^{-1}
   c. Mol^{-1}
   d. S Mol^{-1}

3. For most irreversible reactions
   a. the reaction rate increases with time
   b. the reaction rate decreases with time
   c. the rate stabilizes with time
   d. the rate produces a curve with time

4. Minimum or critical amount of energy required before a chemical reaction could occur is called
   a. reaction energy
   b. effective collision
   c. activation energy
   d. activated complex

5. These are factors affecting chemical reaction except
   a. surface area
   b. catalyst
   c. nature of reactants
   d. activating energy

6. What do we do to increase the surface area of the reactants
   a. breaking them into chips
   b. subjecting the reactants to high pressure
   c. altering the direction of the reaction
   d. using reactants to different densities

7. Temperature affects rate of reaction except
   a. it increases the frequency of collision
   b. it burns the reactants with reckless heating
   c. it increases the kinetic energies of the reactant
   d. the number of effective collisions of the reactants

Answers

1. A
2. C
3. B
4. A
5. C
6. B
7. D

Week 2

Topic: Chemical Equilibrium

Introduction

Chemical equilibrium has been reached in a reaction when the rate of the forward reaction is equal to the rate of the reverse reaction. When a chemical reaction has reached equilibrium, collisions are still occurring: the reaction is now happening in each direction at the same rate. This means that reactants are being formed at the same rate as products are being formed, and this is indicated by double arrows. At equilibrium, the reaction can lie far to the right, meaning that there are more products in existence at equilibrium, or far to the left, meaning that at equilibrium there are more reactants. The concentration of the reactants and products in a reaction at equilibrium can be expressed by equilibrium constant, symbolized K or K_{eq}

For the general reaction

$$aA + bB \Leftrightarrow cC + dD$$

$$\text{Equilibrium constant} = K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

In the above expression, the brackets, as always, symbolize the concentration of the reactants and products in molarity. However, while in the above expression we used the plain symbol K to symbolize the equilibrium constant, there are several types of equilibrium constants. For example, K_c symbolizes the equilibrium constant in an aqueous solution, K_p symbolizes the partial pressures of gases in equilibrium, and K_{sp} symbolizes the solubility product of solids classified as insoluble. K values have no units, and a $K > 1$ means that the reaction favours the products at equilibrium, while a $K < 1$ means that the reaction favours the reactants at equilibrium.

Here are a couple of rules to follow when using equilibrium constant expressions:

1. Pure solids do not appear in the equilibrium expression.
2. Pure liquids do not appear in the equilibrium expression.
3. Water, either as a liquid or solid, does not appear in the equilibrium expression.
4. When a reactant or product is preceded by a coefficient, its concentration is raised to the power of that coefficient in the K_{eq} expression.
5. When the K_{eq} of a reaction has been multiplied by a number, the K is raised to the power of the multiplication factor (K^n), so if it has been multiplied by 2, K is squared, if it has been multiplied by 3, K is cubed, and so on.

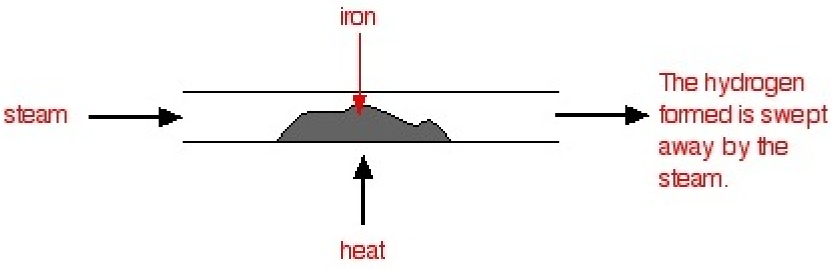
Reversible reactions

A reversible reaction is one which can be made to go in either direction depending on the conditions.

If you pass steam over hot iron the steam reacts with the iron to produce a black, magnetic oxide of iron called triiron tetroxide, Fe_3O_4.

$$3Fe_{(s)} + 4H_2O_{(g)} \longrightarrow Fe_3O_{4(s)} + 4H_{2(g)}$$

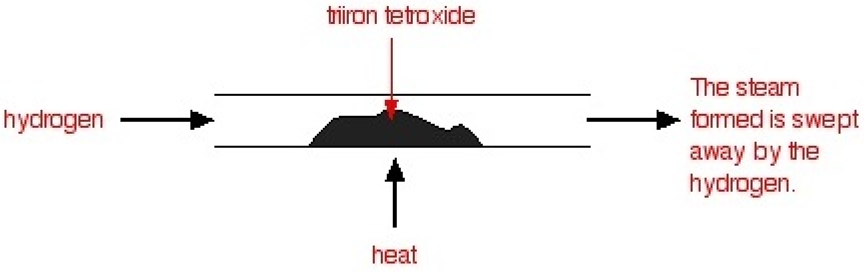
The hydrogen produced in the reaction is swept away by the stream of steam.



Under different conditions, the products of this reaction will also react together. Hydrogen passed over hot triiron tetroxide reduces it to iron. Steam is also produced.

$$Fe_3O_{4(s)} + 4H_{2(g)} \longrightarrow 3Fe_{(s)} + 4H_2O_{(g)}$$

This time the steam produced in the reaction is swept away by the stream of hydrogen.



These reactions are reversible, but under the conditions normally used, they become one-way reactions. The products aren't left in contact with each other, so the reverse reaction can't happen.

Reversible reactions happening in a closed system

A closed system is one in which no substances are either added to the system or lost from it. Energy can, however, be transferred in or out at will.

In the example, iron being heated in steam in a closed container. Heat is being added to the system, but none of the substances in the reaction can escape. The system is closed.

As the triiron tetroxide and hydrogen start to be formed, they will also react again to give the original iron and steam. This has established what is known as a dynamic equilibrium.

During a dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction. This means that both reactants and products will be present at any given point in time.

Le-Chatelier's Principle

Each reversible reaction reaches its own specific equilibrium under a given set of conditions. This equilibrium state depends on

- temperature of the reacting system
- pressure of the reacting system (for gases)
- concentrating of the reacting

Once an equilibrium is established, no further change is apparent as long as the external conditions remain unchanged.

Le Chatelier's Principle states that if an external constraint such as a change in temperature, pressure or concentration, is imposed on a chemical system in equilibrium, the equilibrium will shift so as to annul or neutralize the constraint.

On changing the external conditions, whether the equilibrium will shift towards the reactants or the products can be predicted by the application of Le-Chatelier's principle which states that when a stress (change in concentration, temperature or total pressure) is applied to a system at equilibrium, the system readjusts so as to relieve or offset the stress. In other words, it basically states that if stress is applied to a system at equilibrium, the position of the equilibrium will shift in the direction that reduces the stress to reinstate equilibrium.

Application of Le-Chatelier's principle

In the synthesis of Ammonia (Haber's process)

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) + 96.2\,KJ$$

1 vol 3 vol 2 vol

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

In the example above, if more reactants are added to the system, the reaction will shift in the forward direction, and if more products are added, the reaction will shift in the reverse direction. If the reaction is endothermic and heat is added, the reaction will shift to the right. If heat is added to the system and the reaction is exothermic, heat should be thought of as a product and the reaction will shift to the left The addition of pressure will cause a shift in the direction that results in the fewer number of moles of a gas, while if pressure is relieved, the reaction will shift in the direction that produces more moles of a gas.

This principle is of great importance in chemical industry because it can help to

- define the optimum conditions for the chemical processes employed in industry
- reduce undesirable reversibility
- predict the effect of an altered factor on the equilibrium positionof an untried reaction

There are numerous types of equilibrium problems one may encounter, both qualitative and quantitative.

Qualitative Problems

$2\ N_2\ (g) + 3\ H_2\ (g)\ 2\ NH_3\ (g)$

Suppose additional nitrogen (N_2) was added to the system. First, identify the stress. The stress is too much nitrogen. The equilibrium will shift to the right, towards products, in order to remove the excess nitrogen.

Suppose some ammonia (NH_3) was removed from the system. The stress is not enough ammonia, so the equilibrium will shift to the right to replenish the ammonia removed.

Suppose some hydrogen (H_2) was removed from the system. The stress is not enough hydrogen, so the equilibrium will shift to the left to replenish the hydrogen removed.

Suppose a catalyst is added to the system. Since the catalyst is not a part of the equilibrium, the equilibrium will not shift. The only affect that a catalyst has on an equilibrium is to allow the system to reach equilibrium faster.

Suppose an inert gas, such as helium, as added to the system. Since helium is not a part of this equilibrium, it will not affect the equilibrium.

Quantitative Problem

By examining the amounts of reactants and products at equilibrium, one may numerically see how an equilibrium favours either reactants or products.

For example: Suppose we are given the following equilibrium at 500 K:

$CO(g) + 2\ H_2\ (g)\ CH_3OH(g)$

The equilibrium concentrations are: $[CO] = 0.0911$ M, $[H_2] = 0.0822$ M, $[CH_3OH] = 0.00892$ M, what is the value of the equilibrium constant? Does the equilibrium favour reactants or products?

Solution:

First, we need to write the mass action expression:

$$K_{eq} = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Next, substitute the equilibrium concentrations into the mass action expression, and calculate for the equilibrium constant:

$$K_{eq} = \frac{(0.00982\ M)}{(0.0911\ M)(0.0822\ M)^2} = 14.5\ M^{-2}$$

Since the value of the equilibrium constant is greater than one, (K_{eq} >1), the equilibrium favours the products.

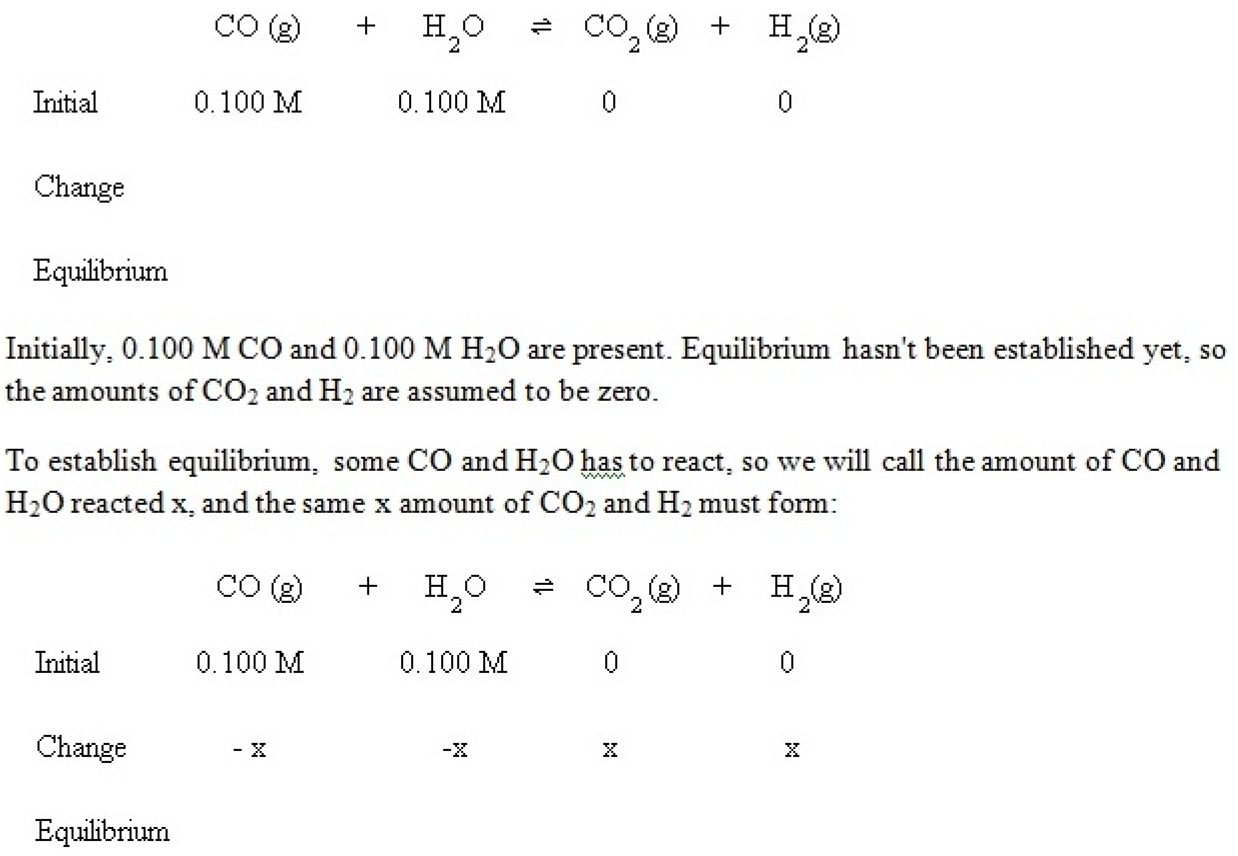
Another type of equilibrium problem deals with finding the equilibrium concentrations given the initial concentrations and the value of the equilibrium constant. Suppose you are given the following equilibrium:

Example 2: $CO(g) + H_2O(g)\ CO_2\ (g) + H_2\ (g)$ $K_{eq} = 23.2$ at 600 K

If the initial amounts of CO and H_2O were both 0.100 M, what will be the amounts of each reactant and product at equilibrium?

Solution:

For this type of problem, it is convenient to set a table showing the initial conditions, the change that has to take place to establish equilibrium and the final equilibrium conditions.



	$CO(g)$	+	H_2O	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial	0.100 M		0.100 M		0		0
Change							
Equilibrium							

Initially, 0.100 M CO and 0.100 M H_2O are present. Equilibrium hasn't been established yet, so the amounts of CO_2 and H_2 are assumed to be zero.

To establish equilibrium, some CO and H_2O has to react, so we will call the amount of CO and H_2O reacted x, and the same x amount of CO_2 and H_2 must form:

	$CO(g)$	+	H_2O	$\rightleftharpoons$	$CO_2(g)$	+	$H_2(g)$
Initial	0.100 M		0.100 M		0		0
Change	- x		-x		x		x
Equilibrium							

The amounts of reactants and products present at equilibrium will be the combination of the initial amounts and the change. Just add the quantities together:

	$CO\ (g)$	+	H_2O	⇌	$CO_2\ (g)$	+	$H_2(g)$
Initial	0.100 M		0.100 M		0		0
Change	- x		-x		x		x
Equilibrium	0.100 -x		0.100 -x		x		x

Substitute the above algebraic quantities into the mass action expression:

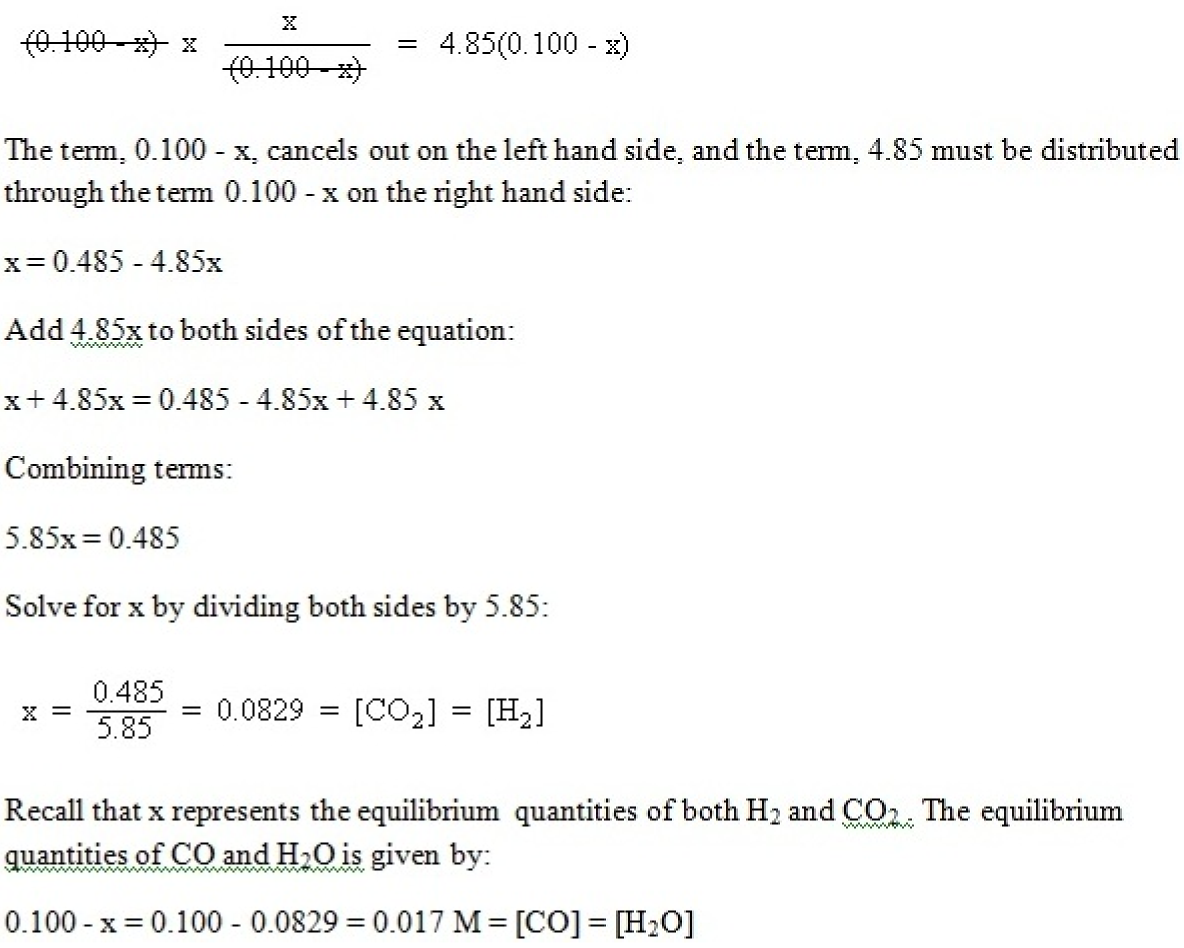
$$K_{eq} = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(x)(x)}{(0.100 - x)(0.100 - x)} = \frac{x^2}{(0.100 - x)^2} = 23.2$$

Since the algebraic expression is a perfect square, begin solving for x by taking the square root of both sides of the equation:

$$\sqrt{\frac{x^2}{(0.100 - x)^2}} = \sqrt{23.2}$$

$$\frac{x}{0.100 - x} = 4.85$$

Multiply both sides by the denominator, 0.100 – x:



$$\cancel{(0.100 - x)} \times \frac{x}{\cancel{(0.100 - x)}} = 4.85(0.100 - x)$$

The term, 0.100 - x, cancels out on the left hand side, and the term, 4.85 must be distributed through the term 0.100 - x on the right hand side:

$x = 0.485 - 4.85x$

Add 4.85x to both sides of the equation:

$x + 4.85x = 0.485 - 4.85x + 4.85\,x$

Combining terms:

$5.85x = 0.485$

Solve for x by dividing both sides by 5.85:

$$x = \frac{0.485}{5.85} = 0.0829 = [CO_2] = [H_2]$$

Recall that x represents the equilibrium quantities of both H_2 and CO_2 . The equilibrium quantities of CO and H_2O is given by:

$0.100 - x = 0.100 - 0.0829 = 0.017\ M = [CO] = [H_2O]$

Factors Affecting Chemical Equilibrium

1. Effect of change of concentration

By increasing or decreasing the concentration of one of the reactants or products, the reaction can be manipulated in the desired direction.

$A + B \leftrightarrow C \quad \Delta H = +ve$

$X + Y \leftrightarrow Z \quad \Delta H = -ve$

- If ΔH is positive, the forward reaction is endothermic and the backward reaction is exothermic
- if ΔH is negative, the forward reaction is exothermic, and backward reaction is endothermic

If a chemical system is in equilibrium and the temperature is lowered, then according to Le Chatelier's principle, the equilibrium position will shift so as to annul the cooling effect by releasing more heat. If the temperature is raised, then the equilibrium position will shift so as to annul the heating effect by absorbing more heat.

To increase the yield of NH3 the concentration of N_2 or preferably H_2 should be increased in the synthesis of ammonia.

2. **Effect of change of pressure**

For a change in pressure to affect a chemical system in equilibrium,

- one of the reactants or products in the reversible reaction must be gaseous
- the total number of moles of gaseous molecules on the left side of the equation must be different from the total number of moles of gaseous molecules on the right side

If high pressure is applied to an equilibrium system, the reaction which involves a reduction in pressure will be favoured. Conversely if low pressure is imposed on an equilibrium system, then the reaction which results in an increase in pressure will be favoured.

Reactions which proceed with decrease in volume are favoured by high pressures.

$2\,SO_2 + O_2 \rightleftharpoons 2\,SO_3$

2 vol 1 vol 2 vol

On the other hand, reactions which proceed with increase in volume are favoured by low pressures.

$N_2O_42 \rightleftharpoons NO_2$

1 vol 2 vol

If the volume remains the same then change in pressure has no effect.

$H_2 + I_2 \rightleftharpoons 2\,HI$

1 vol 1 vol 2 vol

3. Effect of change in temperature

Exothermic reactions will be favoured by decrease in temperature

$3O_2\ (g) \rightleftharpoons 2O_3\ (g)\ -\ 288.7\ KJ.$

Endothermic reactions will be favoured by increase in temperature.

$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g) + 96.2\ KJ$

3. Effect of catalyst

The presence of a catalyst in a reversible reaction does not affect the state of equilibrium but only causes the reaction system to attain equilibrium in a shorter period of time. Catalysts affect the time taken for a reaction to reach equilibrium. A positive catalyst increases rate of both forward and backward reaction by lowering the activation energy of the reaction. Equilibrium is reached at a shorter time. A negative catalyst slows down the rate of reaction so that a longer time is needed to reach equilibrium.

4. Effect of Concentration: In an equilibrium mixture, there is a balance between the concentrations of the reactants and products. If more reactants are introduced into the equilibrium system, the balance will upset. In order to relieve this constraint (increase in the concentration of reactants), the equilibrium position will shift to the right favouring the forward reaction. This results in proportional increase in the

concentration of the products and so equilibrium constant remains unchanged.

Assessment

1. Two boys balanced steady in a sea-saw game is an example of
   a. static equilibrium
   b. dynamic equilibrium
   c. homogeneous equilibrium
   d. mutual equilibrium

2. In the reaction: $SO_{2(g)} + O_{2(g)} \overset{V_2O_5}{\leftrightarrow} SO_{3(g)}$
   The use of double arrows shows
   a. the reaction is in physical equilibrium
   b. contact process
   c. the reaction involves bot forward and backward reactions
   d. the reaction is the rate determining step

3. In most equilibrium reactions, catalyst is not required because
   a. catalyst reduces the energy barrier
   b. most catalysts are easily poisoned when wrongly chosen
   c. catalysts favours both forward and backward reactions
   d. catalyst could be positive or negative

4. When the system $A + B \rightleftharpoons C + D$ is at equilibrium,
   (a) the sum of the concentrations of A and B must equal the sum of the concentrations of C and D.
   (b) the forward reaction has stopped.
   (c) both the forward and the reverse reactions have stopped.
   (d) the reverse reaction has stopped.
   (e) neither the forward nor the reverse reaction has stopped.

5. Consider the equilibrium system:

$2ICl(s) \rightleftharpoons I_2(s) + Cl_2(g)$

Which of the following changes will increase the total amount of of Cl_2 that can be produced?

(a) removing some of the $I_2(s)$
(b) adding more ICl(s)
(c) removing the Cl_2 as it is formed
(d) decreasing the volume of the container
(e) all of the above

Answers

1. B
2. D
3. D
4. E
5. C

Week 3

Topic: Hydrogen

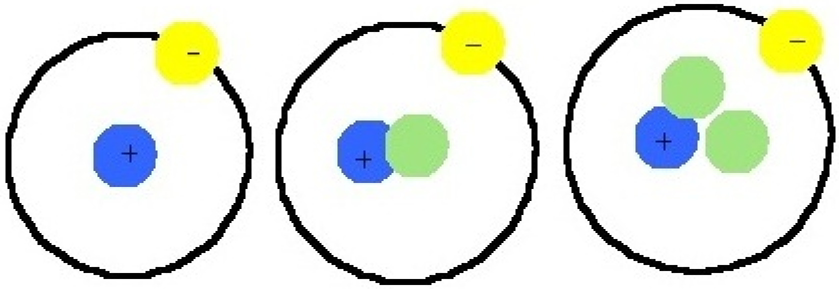
Introduction

Hydrogen was first isolated and shown to be a discrete element by Henry Cavendish in 1766. Before that, Robert Boyle and Paracelsus both used reactions of iron and acids to produce hydrogen gas. Antoine Lavoisier gave hydrogen its name because it produced water when ignited in air. Hydrogen comes from Greek meaning "water producer" ("hydro" =water and "gennao"=to make).

Hydrogen is one of the most important elements in the world. It is all around us. It is a component of water (H_2O), fats, petroleum, table sugar ($C_6H_{12}O_6$), ammonia (NH_3), and hydrogen peroxide (H_2O_2)—things essential to life, as we know it.

Atomic hydrogen, having atomic number 1 and an atomic weight 1.008 amu, is the simplest element. At ordinary temperatures and pressures it is a gas, composed of diatomic molecules, H_2 and is only very slightly soluble in water. In this form, hydrogen is a colourless, odourless, and tasteless gas. The sun and other stars are composed largely of hydrogen. Naturally occurring hydrogen is mostly composed of ^1H atoms and a very small percentage of deuterium. Hydrogen containing compounds can both be ionic and covalent in nature. Examples include acids, bases, and all organic compounds. In organic compounds, hydrogen is covalently bonded.

Isotopes



Protium Deuterium Tritium

Three Hydrogen Isotopes

- **Protium** (^1H) is the most common isotope, consisting of 99.98% of naturally occurring hydrogen. It is a nucleus containing a single proton.
- **Deuterium** (^2H) is another an isotope containing a proton and neutron, consisting of only .0156% of the naturally occurring hydrogen. Commonly indicated with symbol D, D2O is called heavy water, which has a higher density, melting point, and boiling point than regular water. Replacing protium with deuterium (called deuteration) has important implications for the rate of reaction called kinetic-isotope effect.
- **Tritium** (^3H) is a radioactive isotope with a 12.3-year half-life, which is continuously formed in the upper atmosphere due to cosmic rays. It is can also be made in a lab from Lithium-6 in a nuclear reactor. Tritium is also used in hydrogen bombs.

Laboratory Preparation of Hydrogen

- **Preparation of hydrogen gas from water**

Water is the most common and probably most important compound of hydrogen. Hydrogen is liberated when a direct current of electricity is passed through water containing a small amount of an electrically conducting substance such as sulfuric acid, H_2SO_4. The chemical change that occurs is summarized in a chemical equation below:

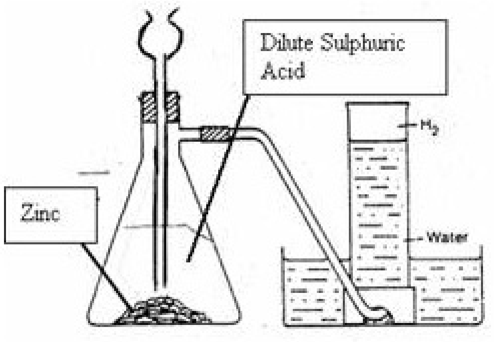
$2\ H_2O(l)$ + electrical energy ——> $2\ H_2(g)$ + $O_2(g)$

- **Preparation of hydrogen gas from active metals**

Several of the most active metals-such as lithium, sodium, potassium, rubidium, cesium, magnesium, and calcium-will react with water to produce hydrogen gas. The net chemical change is summarized in reaction below using the reaction of sodium metal with water as an example. This reaction produces hydrogen gas and sodium hydroxide.

$2Na(s)\ +2\ H_2O(l)$ ——> $2\ NaOH(aq)\ +\ H_2(g)$

- **Preparation of hydrogen gas from metals with acids**



This is the most convenient laboratory method of producing hydrogen. Several of the metals most commonly used are shown in the reactions below. In each of these reactions, the metal reacts with an acid to produce a salt and hydrogen gas. The salts produced in the salts produced in the reactions listed below are magnesium chloride, magnesium sulfate, and zinc phosphate, respectively.

$Mg(s)\ +\ 2\ HCl(aq)$ ——> $MgCl_2(aq)\ +\ H_2(g)$

$Mg(s)\ +\ H_2SO_4(aq)$ ——> $MgSO_4(aq)\ +\ H_2(aq)$

$3Zn(s)\ +\ 2\ H_3PO_4(aq)$ ——> $Zn_3(PO_4)_2(aq)\ +\ 3H_2(g)$

Action of Zinc on and acid

Dilute hydrochloric acid or tetraoxosulphate (vi) acid attacks metallic zinc with the liberationof hydrogen gas. No heating necessary

$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Action of Sodium on Water

Sodium liberates hydrogen from cold water. This reaction is very vigorous and should be carried out with extreme care using only a small piece of sodium

$\mathbf{2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}}$

Physical properties of Hydrogen

Hydrogen is the lightest element known. It is 14.4 less dense than air

It is neutral to moist litmus paper i.e. it has no action on either red or blue litmus paper

Hydrogen is a colourless and odourless gas when pure

It is slightly soluble in water, two part dissolving in 100 parts of water by volume

Chemical Properties of Hydrogen

- Hydrogen wanting to give up its single electron causes it to act like an alkali metal:

$H(g) \rightarrow H^+(g) + e^-$

- A half-filled valence shell with one e- also causes hydrogen to act like a halogen because it wants to gain Noble gas configuration by adding an e^-:

$H(g) + e^- \rightarrow H^-(g)$

- Reactions with Active Metals: Hydrogen accepts e- from an active metal to form ionic hydrides like LiH. By forming an ion with -1 charge, the hydrogen behaves like a halogen.

$2M(s)+H_2(g) \rightarrow 2MH(s)$ M= group 1 metals

Example: $2K(s)+H_2(g) \rightarrow 2KH(s)$ $2K(s)+Cl_2(g) \rightarrow 2KCl(s)$

$M(s)+H_2(g) \rightarrow MH_2(s)$ M= group 2 metals

Example: $Ca(s)+H_2(g) \rightarrow CaH_2(s)$ $Ca(s)+Cl_2(g) \rightarrow CaCl_2(s)$

- Reactions with Non-metals: Unlike metals forming ionic bonds with nonmetals, hydrogen forms polar covalent bonds. Despite being electropositive like the active metals that form ionic bonds with nonmetals, hydrogen is much less electropositive than the active metals, and forms covalent bonds.

Hydrogen + Halogen → Hydrogen Haliden($H_2(g)+ Cl_2(g) \rightarrow HCl(g)$)

Hydrogen + Oxygen → Water ($H_2(g)+O_2(g) \rightarrow H_2O(g)$)

- Hydrogen is a good reducing agent e.g. it reduces copper (II) oxide to copper

$CuO(s) + H_2(g)$ ——-> $Cu(s) + H_2O(l)$

- Reaction with Sulphur: if hydrogen is bubbled through molten sulphur, hydrogen sulphide which has a characteristics rotten egg smell is formed

$H_2(g) + N_2(g)$ ——-> $H_2S(g)$

- Hydrogen also reacts with nitrogen directly to produce ammonia gas. This involves high temperature

$3H_2(g) + N_2(g)$ ——-> $2NH_3(g)$

The Test for Hydrogen Gas, $H_{2(g)}$

Note the following characteristics when testing for hydrogen:

1. Hydrogen gas has no colour or smell.
2. Hydrogen gas has no effect on moist litmus paper or moist universal indicator paper – it is neutral.
3. Hydrogen gas burns with a characteristic ‘pop’.

Specific Test for Hydrogen Gas

The test for hydrogen is a method used to test the presence of hydrogen. This is achieved by inserting a glowing splint into the reaction test tube. If it burns with a ‘pop’ sound, then hydrogen is present. The ‘pop’ is the sound of a small explosion, hydrogen is highly flammable

Uses

1. Hydrogen was formerly used for filling balloons, airships, and other lighter-than-air craft, because it has a low density.
2. Hydrogen is used in the Haber process for the fixation of atmospheric nitrogen, in the production of methanol, and in hydrogenation of fats and oils.
3. It is also important in low-temperature research. It can be liquefied under pressure and cooled; when the pressure is released, rapid evaporation takes place and some of the hydrogen solidifies.
4. Hydrogen is used in manufacture of ammonia by Haber process
5. Hydrogen is used in the manufacture of ammonia, hydrochloric acid and methanol.
6. Hydrogen is a constituent of many gaseous fuels such as water gas and coal gas.

Hydrogen Peroxide

Hydrogen peroxide is a chemical compound of hydrogen and oxygen with the formula H_2O_2. Pure, anhydrous hydrogen peroxide is a colourless, syrupy liquid with a specific gravity of 1.44. It blisters the skin and has a metallic taste. The liquid solidifies at −0.41 °C. Concentrated solutions are unstable, and the pure liquid can explode violently if heated to a temperature above 100 °C. It is soluble in water in all proportions, and the usual commercial forms are a 3 % and a 30 % aqueous solutions. To retard the decomposition of the peroxide into water and oxygen, organic substances, such as acetanilide, are added to the solutions, and they are kept in dark bottles at low temperature.

Preparation Methods of Hydrogen Peroxide

Hydrogen peroxide is manufactured in large amounts by the electrolysis of aqueous solutions of sulfuric acid (or of potassium bisulfate or ammonium bisulfate):

$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$

On cathode On anode

$2H^+ + 2e^- \rightarrow H_2$ $2HSO_4^- - 2e^- \rightarrow H_2S_2O_8$

$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$;

$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$.

It is prepared also by the reaction of acid with other peroxides, such as those of sodium and barium:

$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$;

$BaO_2 + H_2SO_4 \rightarrow BaSO_4^- + H_2O_2$.

Chemical Properties of Hydrogen Peroxide

- Acid-base properties

Hydrogen peroxide is a week acid. In an aqueous solutions it ionizes forming hydronium-ion and peroxid-ion:

$H_2O_2 + H_2O \rightleftarrows H_3O^+ + O_2^{2-}$

- Oxidation-reduction properties

Hydrogen peroxide acts as both an oxidizing and a reducing agent.

In acidic solution it is an oxidizing agent:

$2KI + H_2O_2 + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$

However, both in basic and in a neutral solutions hydrogen peroxide can be an oxidizing agent:

$Cr_2(SO_4)_3 + 3H_2O_2 + 10NaOH \rightarrow 2Na_2CrO_4 + 3Na_2SO_4 + 8H_2SO_4$

$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

At the presence of oxidizing agent, it exhibits reduction properties in acidic, basic and neutral solutions:

$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$;

$Ag_2O + H_2O_2 \rightarrow H_2O + O_2 + 2Ag$;

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5O_2 + K_2SO_4 + 8H_2O$

- Decomposition of hydrogen peroxide

Light, heating and the heavy metals hardly accelerate the process of hydrogen peroxide decomposition:

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

Uses

1. Its oxidizing properties are used in the bleaching of substances, such as hair, ivory, feathers, and delicate fabrics, which would be destroyed by other agents.
2. It is used also medicinally, in the form of a 3 % aqueous solution, as an antiseptic and throat wash.
3. Hydrogen peroxide is used in restoring the original colors on paintings that have darkened through the conversion of the white lead used in the paintings to lead sulfide.
4. The hydrogen peroxide oxidizes the black lead sulfide to white lead sulfate.
5. It is used also as a source of oxygen in the fuel mixture for many rockets and torpedoes.

Assessment

1. An isotope of Hydrogen commonly referred to as heavy water is
   a. protium
   b. deuterium
   c. tritium
   d. basic water
2. Hydrogen is manufacture via the following methods except
   a. action of steam on iron
   b. action of steam on red hot coke
   c. action of steam on methane under nickel catalyst
   d. electrolytic method
3. All except one can displace hydrogen from water or acids
   a. Zinc
   b. Silver
   c. Potassium
   d. Heated Magnesium
4. Sodium hydride reacts with water to
   a. form an acidic solution
   b. liberate hydrogen gas
   c. form a salt
   d. liberate oxygen
   e. form a neutral solution

Answers

1. B
2. B
3. B
4. B

Week 5

Topic: Oxygen and Its Compound

Introduction

Oxygen is a colourless, odourless, tasteless gas. It is denser than air and only slightly soluble in water. A poor conductor of heat and electricity, oxygen supports combustion but does not burn. Normal atmospheric oxygen is a diatomic gas (O_2). Ozone is a highly reactive triatomic (O_3) allotrope of oxygen.

Oxygen is extremely active chemically, forming compounds with almost all of the elements except the inert gases. Oxygen unites directly with a number of other elements to form oxides. It is a constituent of many acids and of hydroxides, carbohydrates, proteins, fats and oils, alcohols, cellulose, and numerous other compounds such as the carbonates, chlorates, nitrates and nitrites, phosphates and phosphites, and sulphates and sulphites.

Discovery

Oxygen was first discovered by Scheele in 1772. But the discovery of Oxygen was credited to Priestley in 1774 two after by heating the oxide of mercury. Lavosier, another scientist was the first to describe the major properties of this gas. He called this gas – acid producer because he obtained acids by heating several non-metals in oxygen and dissolving the oxide in water.

Occurrence

Oxygen occurs in the free state as a gas, to the extent of 21 per cent by volume or 23 per cent by weight in the atmosphere.

Combined Oxygen also occurs

- In water,
- In vegetable and animal tissues,
- In nearly all rocks and

- In many minerals.
- Oxygen occurs to a larger extent in the earth's crust than any other element.

Laboratory Preparation of Oxygen

Preparation of Oxygen from Potassium Trioxochlorate(V)

The most common laboratory method of preparation of oxygen gas is by heating a mixture of potassium trioxochlorate(V), $KClO_3$, and manganese(IV) oxide, MnO_2, in a test tube. The potassium trioxochlorate(V) is decomposed in the presence of the heat to form potassium chloride, KCl, and the oxygen gas, O_2.

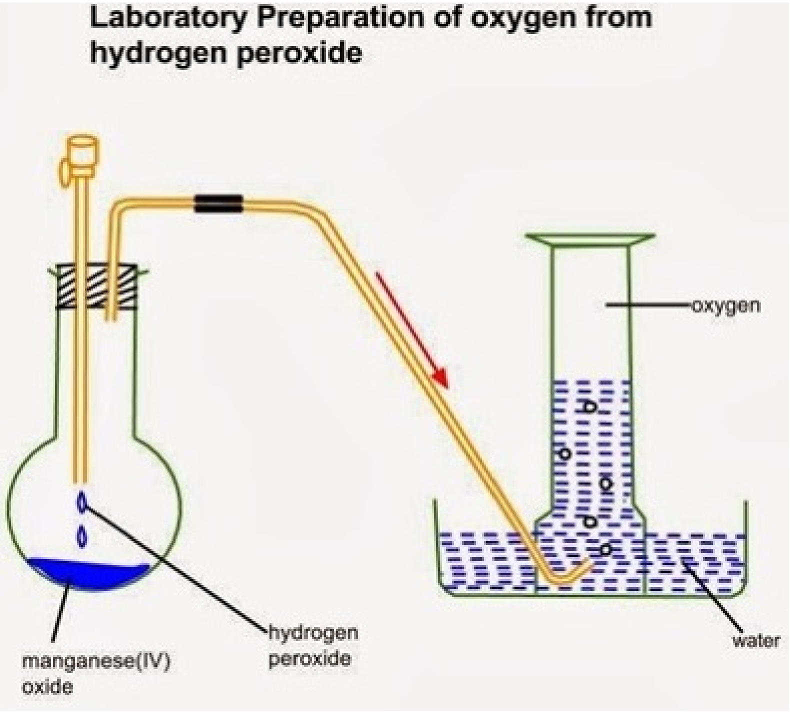
$2KClO_3(s) + \text{heat} \rightarrow 2KCl(s) + 3O_2(g)$

The oxygen formed may be collected as,

- Wet Oxygen – The oxygen is collected over water or
- Dry Oxygen – The oxygen oxygen is collected over mercury

Oxygen gas formed may be transferred to the bottom of a water trough and collected at the top of an inverted glass cylinder as wet oxygen.

The oxygen from the heated test tube may also be conveyed via a delivery tube to a U-tube containing anhydrous calcium chloride. The anhydrous calcium chloride is a drying agent that removes moisture from the oxygen gas so that dry oxygen is formed. The dry oxygen is finally delivered via another delivery tube into a glass saucer containing mercury and collected at the top of an inverted test tube on the mercury.



Another laboratory preparation of oxygen is the preparation from hydrogen peroxide in the absence of heat by,

- decomposition in the presence of manganese(IV) oxide, MnO_2, catalyst and
- oxidation in the presence of potassium tetraoxomanganate(VII), $KMnO_4$.

The decomposition of hydrogen peroxide using manganese dioxide as a catalyst also results in the production of oxygen gas.

Industrial Preparation of Oxygen

The industrial method of making oxygen involves two stages:

- liquefaction of air and
- fractional distillation of liquid air

Liquefaction of air

Gaseous air is initially passed through caustic soda to remove carbon(IV) oxide and then delivered into a compressor operating at a pressure of 200 atm where it is cooled and allowed to escape rapidly through a minute aperture into a low pressure chamber to form liquid air. The liquid air is then delivered to a fractionating column to undergo fractional distillation.

Fractional distillation of liquid air

The liquid oxygen is distilled to evolve, first, nitrogen at a boiling point of -196°C leaving behind oxygen-rich liquid. The liquid is further heated to -183°C to form gaseous oxygen which is dried, compressed and stored under pressure (at 100 atm) in a steel cylinder.

Physical Properties of Oxygen

Oxygen is

- A colourless gas, without smell or taste,
- it is slightly heavier than air,
- it is sparingly soluble in water,
- it is difficult to liquefy, boiling point -183 °C, and the liquid is pale blue in colour and is appreciably magnetic. At still lower temperatures, light-blue solid oxygen is obtained, which has a melting point of -218.4 °C.

Chemical Properties of Oxygen

- **Reaction of oxygen with air**

Oxygen gas does not react with itself or nitrogen under normal conditions. However the effect of ultraviolet light upon oxygen gas is to form the blue gas ozone, O_3, the second allotrope of oxygen. Another way to make ozone is by passing a silent electric discharge through oxygen gas. This can result in a solution containing up to 10% ozone.

- **Reaction of oxygen with water**

Oxygen gas does not react with water. It does, however, dissolve to the extent of about x g kg^{-1} at 20°C (297 K) and 1 atmosphere pressure.

- **Reaction of oxygen with the halogens**

Irradiation of a low pressure (10-20 mm Hg) mixture of oxygen, O_2, and fluorine, F_2, gases at low temperature (77 – 90 K) affords the gas dioxygen difluoride, O_2F_2.

$O_2(g) + F_2(g) \rightarrow F_2O_2(g)$

- Reaction of oxygen with acids

Oxygen gas does not react with most acids under normal conditions.

- Reaction of oxygen with bases

Oxygen gas does not react with most bases under normal conditions.

Test For Oxygen

Oxygen supports combustion so a good method of testing for oxygen is to take a glowing splint and place it in a sample of gas, if it re-ignites the gas is oxygen.

This is a simple but effective test for oxygen. There are sometimes confusions as the splint can create a pop very slightly on re-ignition, which sometimes is mistaken for hydrogen. A hydrogen pop is much more violent, sometimes enough to completely extinguish the splint.

Uses

- Oxygen is essential for life and it takes part in processes of combustion, its biological functions in respiration make it important.

- Oxygen is sparingly soluble in water, but the small quantity of dissolved oxygen in is essential to the life of fish.
- Oxygen gas is used with hydrogen or coal gas in blowpipes and with acetylene in the oxy-acetylene torch for welding and cutting metals.
- Oxygen gas is also used in a number of industrial processes.
- Medicinally, oxygen gas is used in the treatment of pneumonia and gas poisoning, and it is used as an anesthetic when mixed with nitrous oxide, ether vapour, etc.
- Carbon Dioxide is often mixed with the oxygen as this stimulates breathing, and this mixture is also used in cases of poisoning and collapse for restoring respiration.
- Liquid oxygen mixed with powdered charcoal has been used as an explosive.

Binary Compound of Oxygen (Oxide)

An oxide is a compound of Oxygen and another element (e.g. through the process of Combustion) Metals form Metal Oxides and Non-Metals form Non-Metal Oxides. Oxides can be classified as either Acidic, Basic, Amphoteric or Neutral

Types of Oxides

Based on their acid-base characteristics oxides are classified as acidic or basic. An oxide that combines with water to give an acid is termed as an acidic oxide. The oxide that gives a base in water is known as a basic oxide.

- **Acidic oxides**

Acidic oxides are the oxides of non-metals. When combined with water, they produce acids, e.g.,

$SO_2 + H_2O \longrightarrow H_2SO_3$
sulphurous acid

$CO_2 + H_2O \longrightarrow H_2CO_3$
carbonic acid

$SO_3 + H_2O \longrightarrow H_2SO_4$
sulphuric acid

Acidic oxides are, therefore, known as acid anhydrides, e.g., sulphur dioxide is sulphurous anhydride; sulphur trioxide is sulphuric anhydride.

When these oxides combine with bases, they produce salts, e.g.,

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

$SO_2 + 2NaOH \longrightarrow Na_2SO_3 + H_2O$

Examples:
SO_2, SO_3, CO_2, NO_2

Properties:

1. Do not react with acids.
2. React with bases and alkalis to form salt & water.
3. Dissolve in water to form acidic solutions.
4. Usually gases at room temp

- **Basic oxides**

Basic oxides are the oxides of metals. If soluble in water they react with water to produce hydroxides (alkalies) e.g.,

$CaO + H_2O \longrightarrow Ca(OH)_2$

$MgO + H_2O \longrightarrow Mg(OH)_2$

$Na_2O + H_2O \longrightarrow 2NaOH$

These metallic oxides are therefore, known as basic anhydrides. They react with acids to produce salts, e.g.,

$MgO + 2HCl \longrightarrow MgCl_2 + H_2O$

$Na_2O + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$

Examples:
Na_2O, CaO, MgO, FeO, CuO

Properties:
1. Do not react with bases.
2. React with acids to form salt & water.
3. Basic Oxides are usually insoluble in water. Those that dissolve in water forms alkaline solutions

- **Amphoteric oxides**

Amphoteric oxides are metallic oxides, which show both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties, e.g.,

$$ZnO + 2HCl \longrightarrow \underset{\text{zinc chloride}}{ZnCl_2} + H_2O \text{ (basic nature)}$$

$$ZnO + 2NaOH \longrightarrow \underset{\text{sodium zincate}}{Na_2ZnO_2} + H_2O \text{ (acidic nature)}$$

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O \text{ (basic nature)}$$

$$Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O \text{ (acidic nature)}$$

Examples:

ZnO, Al_2O_3, PbO,

Properties:
1. React with both acids and bases to form salt & water

- **Neutral oxides**

These are the oxides, which show neither basic nor acidic properties, that is, they do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

Examples:
CO, NO, H_2O

Properties:
1. Neutral pH

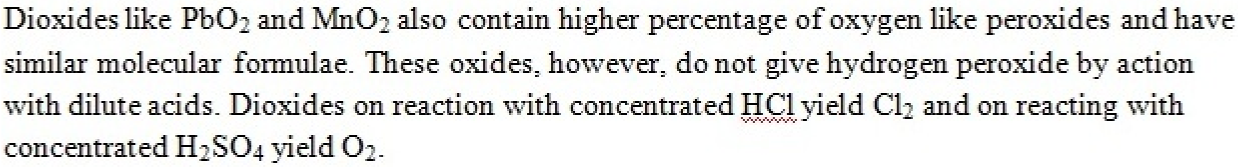
Higher Oxides

- **Peroxides and dioxides**

A peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

$$Na_2O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O_2$$



Dioxides like PbO_2 and MnO_2 also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl_2 and on reacting with concentrated H_2SO_4 yield O_2.

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$$

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O + O_2$$

- Compound oxides

Compound oxides are metallic oxides and they behave as if they are made up of two oxides, lower and higher oxides of the same metal, e.g.,

Red lead: $Pb_3O_4 = PbO_2 + 2PbO$

Ferro-ferric oxide: $Fe_3O_4 = Fe_2O_3 + FeO$

On treatment with an acid, compound oxides give a mixture of salts.

$$Fe_3O_4 + 8HCl \longrightarrow 2FeCl_3 + FeCl_2 + 4H_2O$$

$$\text{Ferro - ferric oxide} \longrightarrow \text{ferric chloride + ferrous chloride}$$

Acidic - Basic Nature of Oxides in a Period

The oxides of elements in a period become progressively more acidic as one goes from left to right in a period of the periodic table. For example, in third period, the behavior of oxides changes as follows:

$$\underbrace{Na_2O, MgO}_{\text{Basic}} \qquad \underbrace{Al_2O_3, \; SiO_2}_{\text{Amphoteric}} \qquad \underbrace{P_4O_{10}, SO_3, Cl_2O_7}_{\text{Acidic}}$$

Preparation of Oxides

Oxides can be generated via multiple reactions. Below are a few:

By direct heating of an element with oxygen

Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,

$2Mg + O_2 \xrightarrow{Heat} 2MgO$

$2Ca + O_2 \xrightarrow{Heat} 2CaO$

$S + O_2 \xrightarrow{Heat} SO_2$

$P_4 + 5O_2 \xrightarrow{Heat} 2P_2O_5$

By reaction of oxygen with compounds at higher temperatures

At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

Sulphides are usually oxidized when heated with oxygen.

$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$

$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$

When heated with oxygen, compounds containing carbon and hydrogen are oxidized.

$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O$

By thermal decomposition of certain compounds like hydroxides, carbonates, and nitrates

$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$

$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$

$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$

By oxidation of some metals with nitric acid

$2Cu + 8HNO_3 \xrightarrow{Heat} 2CuO + 8NO_2 + 4H_2O + O_2$

$Sn + 4HNO_3 \xrightarrow{Heat} SnO_2 + 4NO_2 + 2H_2O$

By oxidation of some non-metals with nitric acid

$C + 4HNO_3 \longrightarrow CO_2 + 4NO_2 + 2H_2O$

Assessment

1. The most abundant element on earth is
   a. nitrogen
   b. helium
   c. silicon
   d. oxygen
2. Which of these gases have the following physical properties? i. Diatomic gases ii. Colourless, Tasteless and Odourless iii. Slightly soluble in water iv. Liquefies easily
   a. CO
   b. O_2
   c. N_2
   d. H_2
3. Which of these reactions with oxygen is slowest?
   a. Rusting
   b. Fe + O_2
   c. Petrol + O_2
   d. Coal + O_2
4. How can Oxygen be tested?

Answers

1. D
2. B
3. A
4. Oxygen supports combustion so a good method of testing for oxygen is to take a glowing splint and place it in a sample of gas, if it re-ignites the gas is oxygen

Week 6

Topic: Halogens

Introduction

The halogens are the collective name given to the elements in group VII of the Periodic Table. There are five halogens; fluorine, chlorine, bromine, iodine and astatine. Astatine is very radioactive and cannot exist for more than a few microseconds before decaying. We will thus be concerned with the chemistry of fluorine, chlorine, bromine and iodine.

All these elements are most commonly found in the -1 oxidation state, as X^- ions. These are known as halide ions.

Halide is the name given to the ion of halogens. Table below shows the corresponding halide of the halogen

Halogen	Halide
Fluorine	Fluoride
Chlorine	Chloride
Bromine	Bromide
Iodine	Iodide

Structure

Since each atom in this group has seven valence electrons, they tend to form diatomic molecules, e.g. F_2, Cl_2, Br_2 and I_2. They are thus simple molecular, with weak intermolecular forces between the molecules.

Appearance and colour

Halogen	In pure form	In non-polar solvents	In water
Fluorine	Pale yellow gas	-	

(Reacts with solvents)-

(Reacts with water) Chlorine Pale green gas Pale green solution

Pale green solution BromineDark red liquid Orange solution

Orange solution Iodine Grey solid Purple solution –

(Insoluble)

but forms a brown solution if excess KI is present

The halogens are usually used in aqueous solution. Although iodine is insoluble in water, it is soluble if iodide ions are present (the iodine reacts with iodide ions to form triiodide ions as follows: I_2(aq) + I^-(aq) à I_3^- (aq). The triiodide ions give the solution its brown colour.

Melting and boiling points

Halogen	**Melting point /°C**	**Boiling point /°C**
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7	59
Iodine	114	184

The melting and boiling points of the halogens increase steadily down the group. This is due to the increase in strength of the Van Der Waal's forces between the molecules, which results from the increasing number of electrons in the molecule and the increasing surface area of the molecule.

Electronegativity

Electronegativity is the ability of an atom to attract electrons in a covalent bond. The electronegativity of the halogen atoms decreases down a group:

Halogen	**Electronegativity**
F	4.0
Cl	3.0
Br	2.8
I	2.5

As the number of shells increases, the shielding increases and the electrons in the covalent bond are further from (and more shielded from) the nucleus. Therefore they are less strongly attracted to the nucleus and the electronegativity decreases.

Electronic Configuration

Element	Electron arrangement of atom
Fluorine / F	2. 7
Chlorine / Cl	2.8.7
Bromine / Br	2.8.18.7
Iodine / I	2.8.18.18.7
Astatine / At	2.8.18.32.18.7

Chemical tests

- Chlorine – Turns damp litmus red, and then bleaches it.
- Bromine – Bromine also turns damp litmus red and bleaches it but slower. When sodium hydroxide is added, bromine loses its colour.

- Iodine – When starch solution is added, a blue/black colour forms

Physical properties

- Non-metals
- Insulators of electricity
- Poor conductors of heat
- Low melting point and boiling point
- Melting point and boiling point increases (going down the group) – molecular size increases / forces of attraction between molecules become stronger & more heat energy is required to overcome the stronger forces of attraction (Van der Waals' forces of attraction between molecules).
- Colour: F_2 (pale yellow gas), Cl_2 (greenish-yellow gas), Br_2 (reddish-brown liquid), I_2 (purplish-black solid) and At_2 (black solid – rarest naturally occurring element and extremely radioactive)
- Low density
- Density of element increases (going down the group) – increase in atomic mass

Chemical properties

- **Oxidation – reduction behaviour**

The halogens can act as oxidising agents by gaining electrons to form halide ions.

$X_2 + 2e^- \rightarrow 2X^-$

The oxidising ability decreases down the group with fluorine being the strongest oxidising agent. In simple terms the formation of X^- occurs in two steps.

A strong oxidising agent will readily form X^-. It will therefore, have a low bond energy and a high electron affinity. Both bond energies and electron affinities decrease down the group as the nuclear pull on the outer electrons decrease.

The change in electron affinities is most significant and so oxidising ability decreases down the group as the nuclear pull on the outer electrons decreases down the group.

Fluorine has anomalous properties due to its small size. It has a lower electron affinity than Chlorine due to electron repulsions in the overcrowded outer shell. However, it is a stronger oxidising agent than Chlorine due to its unusually low bond energy. This is due to the repulsions between outer electrons in the F_2 molecule.

Halide ions act as reducing agents by losing electrons.

$2X^- - 2e^- \rightarrow X_2$

The reducing ability increases from F^- to I^-.

In all their reactions the halogens act as oxidising agents. Hence, their reactivity decreases down the group.

- **Reaction with water**

F_2 oxidises H_2O to O_2 gas in a very exothermic reaction.

$2F_{2(g)} + 2H_2O_{(l)} \rightarrow O_{2(g)} + 4HF_{(g)}$

Cl_2 dissolves in H_2O and some hydrolysis occurs. A yellow solution of ‘chlorine water’ is formed which is a mixture of two acids. No O_2 is evolved.

$Cl_{2(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)} + HOCl_{(aq)}$

Br is only slightly soluble in H_2O and there is less hydrolysis.

$Br_{2(l)} + H_2O_{(l)} \rightarrow HBr_{(aq)} + HOBr_{(aq)}$

I_2 is virtually insoluble in H_2O. It is however soluble in KI solution due to the formation of the triiodide anion.

$I_{2(s)} + I^-_{(aq)} \rightarrow I_3^-{}_{(aq)}$

Note: All halogens are more soluble in non-polar solvents such as CCl_4. Cl_2 gives a colourless solution. Br_2 a red solution and I_2 a violet one.

- ## Displacement reactions

If a more reactive halogen is placed into a solution containing a less reactive halide a displacement reaction is seen.

For example: $Cl_{2(g)} + KI_{(aq)} \rightarrow KCl_{(aq)} + I_{2(s)}$

- F_2 will displace Cl^- Br^- I^-
- Cl_2 will displace Br^- I^-
- Br_2 will displace I^-
- I_2 will displace none
- **Reaction with alkali (NaOH solution)**

This reaction depends on the conditions:

Cold NaOH solution.

$2OH^-_{(aq)} + Cl_{2(g)} \rightarrow Cl^-_{(aq)} + ClO^-_{(aq)} + H_2O_{(l)}$

Hot NaOH solution.

$6OH^-_{(aq)} + Cl_{2(g)} \rightarrow 5Cl^-_{(aq)} + ClO_3^- + 3H_2O_{(l)}$

In hot solution the ClO^- ions are disproportionating

$3ClO^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + ClO_3^-{}_{(aq)}$

- ## Other Reactions of the Halogens

Reaction with hydrogen H_2

- Halogens readily combine with hydrogen to form the hydrogen halides which are colourless gaseous covalent molecules
- e.g. hydrogen + chlorine ==> hydrogen chloride
- $H_{2(g)} + Cl_{2(g)}$ ==> $2HCl_{(g)}$

- The hydrogen halides dissolve in water to form very strong acids with solutions of pH1 e.g. hydrogen chloride forms hydrochloric acid in water HCl(aq) or H^+Cl^-(aq) because they are fully ionised in aqueous solution even though the original hydrogen halides were covalent! An acid is a substance that forms H^+ ions in water.
- Bromine forms hydrogen bromide gas $HBr_{(g)}$, which dissolved in water forms hydrobromic acid $HBr_{(aq)}$. Iodine forms hydrogen iodide gas $HI_{(g)}$, which dissolved in water forms hydriodic acid $HI_{(aq)}$. Note the group formula pattern.

Reaction with Group 1 Alkali Metals Li Na K etc.

- Alkali metals burn very exothermically and vigorously when heated in chlorine to form colourless crystalline ionic salts e.g. NaCl or Na^+Cl^-. This is a very expensive way to make salt! Its much cheaper to produce it by evaporating sea water!
- e.g. sodium + chlorine ==> sodium chloride
- $2Na_{(s)} + Cl_{2(g)} \Longrightarrow 2NaCl_{(s)}$
- The sodium chloride is soluble in water to give a neutral solution pH 7, universal indicator is green. The salt is a typical ionic compound i.e. a brittle solid with a high melting point. Similarly potassium and bromine form potassium bromide KBr, or lithium and iodine form lithium iodide LiI. Again note the group formula pattern.

Reaction with other metals

- If aluminium or iron is heated strongly in a stream of chlorine (or plunge the hot metal into a gas jar of chlorine carefully in a fume cupboard) the solid chloride is formed.
- aluminium + chlorine ==> aluminium chloride$_{\text{(white solid)}}$
    - $2Al_{(s)} + 3Cl_{2(g)} \Longrightarrow 2AlCl_{3(s)}$
- iron + chlorine ==> iron(III) chloride$_{\text{(brown solid)}}$
    - $2Fe_{(s)} + 3Cl_{2(g)} \Longrightarrow 2FeCl_{3(s)}$

- If the iron is repeated with bromine the reaction is less vigorous, with iodine there is little reaction, these also illustrate the halogen reactivity series.

Chlorine

Chlorine is a greenish yellow gas which combines directly with nearly all elements. Chlorine is a respiratory irritant. The gas irritates the mucous membranes and the liquid burns the skin. Chlorine mainly occurs as rock salt ($NaCl$) Carnallite, (KCl, $MgCl_2.6H_2O$) and calcium chloride. ($CaCl_2$).

Industrial Preparation of Chlorine

Chlorine is very reactive and is not found free in nature as Cl_2 gas. It is most found as common salt $NaCl$. Chlorine is extracted from the purified molten ore of sodium chloride by use of electrolysis in the Down's Cell. During this process sodium chloride is decomposed into sodium and chlorine. When molten, the ions of sodium chloride are free to move. The Na ions are attracted to the iron cathode, and deposit as sodium metal, whilst the chlorine ions move towards the graphite anode to form chlorine gas. This gas bubbles up under the steel hood above the anode and is collected.

$2NaCl + 2H_2O$ ————————> $2Na + Cl_2$

Another industrial way of making chlorine is by the electrolysis of brine, a concentrated sodium chloride solution. A diaphragm cell is used in this process. This cell contains titanium anodes and steel cathodes separated by a porous diaphragm made of asbestos

Saturated brine is added to the anode compartment. When current flows through the cell, 50% of the chloride ions are attracted to the anode. The Cl ions lose an electron and form Cl_2 atoms. These join up to form chlorine molecules. Chlorine gas then rises to the surface and is piped away

$2NaCl + 2H_2O$ ————————> 2

$NaOH + Cl_2 + H_2$

Laboratory Preparation of Chlorine

Any of the methods listed below, can be used to prepare chlorine in the laboratory.

From concentrated hydrochloric acid by oxidation

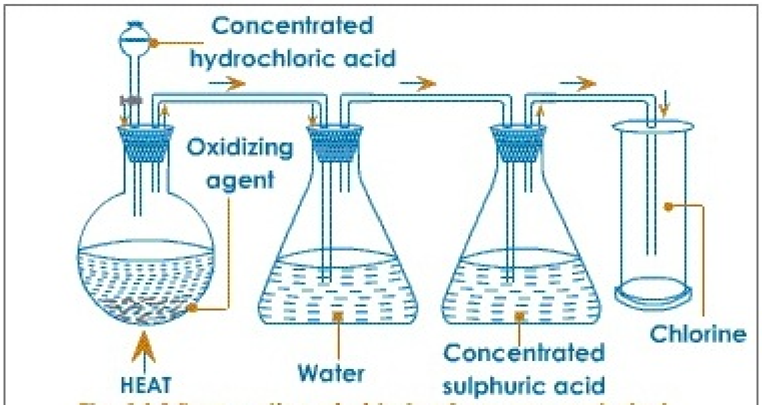


Fig. 14.3 Preparation of chlorine from concentrated hydrochloric acid with the help of oxidising agents

Chlorine can be prepared by removing the hydrogen from hydrochloric acid using an oxidizing agent. Any oxidising agent such as manganese dioxide, lead dioxide, trilead tetroxide, potassium permanganate or potassium dichromate can be used. Firstly, the oxidising agents are taken in the round bottomed flask. Concentrated hydrochloric acid is then added through a thistle funnel. This mixture is then heated. The oxygen of the oxidizing agents combines with the hydrogen of the hydrochloric acid leaving behind chlorine i.e. hydrogen is removed from hydrochloric acid. The metallic ions of the oxidising agents combine with part of chlorine to form the respective chlorides.

$$\text{Oxidising Agent} + \underset{\text{acid}}{\text{Conc. hydrochloric}} \longrightarrow \underset{\text{chloride}}{\text{Metal}} + \text{Water} + \text{Chlorine}$$

$$\underset{\text{Manganese (IV)oxide}}{MnO_2(s)} + \underset{\text{Hydrochloric acid}}{4HCl(l)} \xrightarrow{\Delta} \underset{\text{Manganese (II)chloride}}{MnCl_2(aq)} + \underset{\text{Water}}{2H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)}$$

$$\underset{\text{Lead(IV) oxide}}{PbO_2(s)} + \underset{\text{Hydrochloric acid}}{4HCl(l)} \xrightarrow{\Delta} \underset{\text{Lead (II) chloride}}{PbCl_2(aq)} + \underset{\text{Water}}{2H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)}$$

$$\underset{\text{Trilead tetroxide}}{Pb_3O_4(s)} + \underset{\text{Hydrochloric acid}}{8HCl(l)} \xrightarrow{\Delta} \underset{\text{Lead(II) chloride}}{3PbCl_2(aq)} + \underset{\text{Water}}{4H_2O(l)} + \underset{\text{Chlorine}}{Cl_2(g)}$$

$$\underset{\text{Potassium Permanganate}}{2KMnO_4(s)} + \underset{\text{Hydrochloric acid}}{16HCl(l)} \longrightarrow \underset{\text{Potassium chloride}}{2KCl(aq)} + \underset{\text{Manganese (II)chloride}}{2MnCl_2} + \underset{\text{Water}}{8H_2O(l)} + \underset{\text{Chlorine}}{5Cl_2(g)}$$

$$\underset{\text{Potassium dichromate}}{K_2Cr_2O_7(s)} + \underset{\text{Hydrochloric acid}}{14HCl(l)} \xrightarrow{\Delta} \underset{\text{Potassium chloride}}{2KCl(aq)} + \underset{\text{Chromium (III)chloride}}{2CrCl_3(aq)} + \underset{\text{Water}}{7H_2O(l)} + \underset{\text{Chlorine}}{3Cl_2(g)}$$

Note: No heating is required in when potassium permanganate is used as an oxidizing agent in the above method of preparing chlorine.

Test for Chlorine

It is a greenish-yellow gas which turns damp blue litmus red and then bleaches it.

Physical Properties

- It is a pale yellow-green gas which is denser than air
- It has a choking smell, and even in small quantities
- It is poisonous to people and animals
- This made it suitable for use in chemical warfare during World War I

Chemical Properties

- It combines with metals and non metals to form chlorides. it decomposes water forming HCl and HClO (hypochlorous acid) which is unstable and decomposes giving nascent oxygen which is responsible for oxidizing and bleaching action of chlorine.

$Cl_2 + H_2O$ ——> HCl + HClO;

HClO —> HCl + [O]

Coloured matter + O —> Colourless matter.

The bleaching action is permanent and colour is not restored on standing. However, it cannot be used for bleaching delicate articles such as straw, silk, wool etc. which are damaged by it.

- Cl_2 oxidizes Br^- and I^- ions to Br_2 and I_2 respectively.

$Cl_2 + 2X^-$ ——> $2Cl^- + X_2$ (X = Br or I).

It combines with alkalis forming hypochlorite and chlorate salts in cold and hot conditions respectively.

2NaOH (dil.) + Cl_2 ————> NaCl + NaClO + H_2O (Cold condition)

2NaOH (conc.) + $3Cl_2$ ————> 5NaCl + $NaClO_3$ + $3H_2O$ (Hot condition)

During these reactions, halogen is simultaneously reduced to X^- ion and is oxidized to either hypohalite (XO^-) or halate ($XO^-{}_3$) ion. Such reactions are called disproportionation reactions.

- With slaked lime, Cl_2 gives bleaching powder ($CaOCl_2$)

  $Ca(OH)_2 + Cl_2$ ———> $CaOCl_2 + H_2O$

- With ammonia, Cl_2 reacts as follows

  $8NH_3$ (excess) + $3Cl_2$ ———> 6 NH_4Cl + N_2

  NH_3 + $3Cl_2$(excess) ———> NCl_3 + 3HCl

- With SO_2 and CO, addition compounds are formed

  SO_2 (dry) + Cl_2 ——> SO_2Cl_2 (Sulfuryl chloride)

$CO + Cl_2 \longrightarrow COCl_2$ (Carbonyl chloride or phosgene)

Cl_2 is strong oxidizing agent. It oxidizes $FeCl_2$ to $FeCl_3$,
moist SO_2 to H_2SO_4, SO_3^{2-} to $SO^{2-}{}_4$, thiosulphate to sulphate and sulphur.

Uses

Chlorine is a major industrial chemical and it is used in:

- The extraction of metals such as titanium
- The manufacture of plastics, such as PVC
- The manufacture of solvents, such as trichloroethane
- The production of drugs, dry-cleaning fluids, weedkillers, pesticides and bleaches
- The purification of water

Hydrogen Chloride

Hydrogen chloride was discovered in 1648. It is a very useful chemical compound. It occurs in free state in volcanic gases and in gastric juices of mammals. It was first prepared in 1648 by scientist called Johann Rudolf Glauber using rock salt and concentrated sulphuric acid. In 1772, Joseph Priestley was able to obtain it in pure form.

Hydrogen chloride is a gas at room temperature. Solutions of hydrogen chloride in water are known as hydrochloric acid. Hydrogen chloride is widely used in the chemical industry as a reagent in the manufacture of other chemicals. Most of it is produced as a co-product of reactions involving chlorine

Hydrogen chloride is a colourless gas, slightly denser than air. It has a strong, irritating odour and fumes strongly in moist air forming hydrochloric acid droplets. It is very soluble in water and in fact it will undergo the fountain experiment

Industrial Preparation of Hydrogen Chloride

Hydrogen can be burnt in chlorine. This is used in industry to produce hydrogen chloride. The latter can then be used to prepare hydrochloric acid. This is done by passing hydrogen chloride gas through an absorption tower where it is dissolved in water.

$H_2(g) + Cl_2(g) \text{ —–> } 2HCl(g)$

$HCl(g) \text{—–> } HCl(aq)$

When hydrogen chloride gas dissolves in water, $H^+(aq)$ ions are formed – this is why the solution is acidic.

$HCl(aq) \text{—–> } H^+(aq) + Cl^-(aq)$

Laboratory Preparation

- Heating sodium chloride with concentrated tetraoxosulphate (VI) acid in a round-bottomed flask
- Reaction of moist hydrogen gas with chlorine in the presence of the diffused sunlight

In the laboratory, hydrogen chloride may be prepared by reacting sodium chloride with concentrated tetraoxosulphate (VI) acid. It is a reversible reaction, but as the hydrogen chloride gas is removed, the equilibrium shifts to the right

$NaCl(s) + H_2SO_4(l) \text{ —–> } NaHSO_4(s) + HCl(g)$

Physical properties

- Colourless gas
- Pungent smell
- Slightly sour taste
- Fumes in moist air
- Not combustible
- Just extinguishes a glowing splint
- Very soluble in water; solution called hydrochloric acid
- Liquefies at 10° C at 40 atmospheric pressure
- Boiling point: −83°C
- Freezing point: −113° C

Chemical properties

- It forms dense white fumes of ammonium chloride when it reacts with ammonia.

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(g)$

It also forms a white precipitate of silver chloride, AgCl, with silver nitrate ($AgNO_3$) acidified with dilute nitric acid. (All soluble chlorides give this.)

- If dry hydrogen chloride gas is passed over heated iron wire then the wire becomes coated with a green solid – iron (II) chloride.

$Fe(s) + 2 HCl(g) \longrightarrow FeCl_2(s) + H_2(g)$

- It is a typical strong acid which turns both litmus and pH paper red.
- It reacts with metals producing salt and hydrogen, e.g. magnesium reacts quite vigorously with dilute acid producing magnesium chloride and hydrogen.

$Mg(s) + 2HCl(aq) \quad MgCl_2(s) + H_2(g)$

- It will react with bases to form a salt (metal chloride) and water. E.g. it will react with an alkali such as sodium hydroxide to give sodium chloride and water.

$NaOH(aq) + HCl(aq) \quad NaCl(aq) + H_2O(l)$

- It will react with copper (II) oxide forming copper (II) chloride and water.

$CuO(s) + 2HCl(aq) \quad CuCl_2(aq) + H_2O(l)$

- It will react with carbonates forming a salt, water and carbon dioxide. E.g. It reacts with calcium carbonate to give calcium chloride, water and carbon dioxide.

$CaCO_3(s) + 2HCl(aq) \quad CaCl_2(aq) + H_2O(l) + CO_2(g)$

Uses of hydrochloric acid

It is used in the:

- Production of vinyl chloride, the monomer for PVC
- Preparation of metal surface before electroplating or galvanizing
- Manufacture of drugs where acidic conditions may be required
- Manufacture chlorine and some other chlorides.
- Saturated solution of zinc chloride in dilute hydrochloric acid is used to clean metallic surfaces before plating or soldering.

Comparison of Solubility of HCl in water and in Toluene

- HCl is a very polar molecule, and it dissociates easily in water because it is polar, and the ions become hydrated, making this dissociation energetically favourable but HCl molecules in non-polar methylbenzene, also known as toluene, will not dissociate because there are no charges in toluene to surround the dissociated ions of HCl to make this energetically favourable.

- HCl dissociates into ions in water but remains as molecules in organic solvents.
- It conducts electricity in water but not in methylbenzene
- Shows acid behaviour in water but not in methylbenzene due to presence of H+ ions.

Assessment

1. The following are physical properties of Chlorine except
   a. It cannot be liquefied
   b. it is denser than air
   c. it is sparingly soluble in water
   d. it is poisonous
2. Fluorine is prepared by
   a. reacting fluorides with chlorine gas
   b. reacting fluorides with hydrogen chloride
   c. electrolysis
   d. reacting fluorine wit concentrated Tetraoxosulphate acid
3. Bromine was discovered by
   a. Balard
   b. Scheele
   c. Courtois
   d. Cavendish
4. The bleaching action of chlorine in water is because
   a. of its reducing property
   b. of its oxidizing power
   c. it is a strong acid
   d. its ability to react with water to form oxochlorate acid
   d. it is an oxygen acceptor
5. Chlorine is a common bleaching agent. This is not true with
   a. wet litmus paper
   b. printer’s ink

c. wet pawpaw leaf
d. most wet fabric dyes

6. When chlorine water is exposed to sunlight, the products formed are
   a. hydrochloric acid and oxygen
   b. chlorine gas and oxochlorate(I) acid
   c. oxygen and oxochlorate(I) acid
   d. hydrogen and oxygen
   e. oxochlorate(I) acid and hydrogen

Answers

1. A
2. C
3. C
4. D
5. B
6. A

Week 7

Topic: Nitrogen Family

Introduction

The nitrogen family includes the following compounds: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi).

All Group 5 elements have the electron configuration ns^2np^3 in their outer shell, where n is equal to the principal quantum number. The nitrogen family is located in the p-block in Group 5, having 5 electrons in their outer energy level. As you move down the nitrogen family: atomic radius increases, ionic radius increases, ionization energy decreases, and electronegativity decreases. Nitrogen family elements often form covalent compounds, usually with the oxidation numbers +3 or +5. Nitrogen and phosphorus are non-metals, Arsenic and Antimony are metalloids, while Bismuth is a metal

Properties of Group 5 Elements

Element/Symbol	**Atomic Number**	**Mass**	**Electron Configuration**	**Covalent Radius(pm)**	**Electronegativity**	**First Ionization Energy (kJ/mol)**	**Common Physical Form(s)**
Nitrogen (N)	7	14.01	$1s^2\ 2s^2\ 2p^3$	75	3.0	1402	Colorless Gas
Phosphorus (P)	15	30.97	$[Ne]3s^2\ 3p^3$	110	2.1	1012	White Solid / Red Solid
Arsenic (As)	33	74.92	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$	121	2.0	947	Yellow Solid / Gray Solid

Antimony (Sb)	51	121.76	[Kr] $4d^{10}\ 5s^2\ 5p^3$	140	1.9	834	Yellow Solid / Silver-White Metallic Solid
Bismuth (Bi)	83	208.98	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$	155	1.9	703	Pink-White Metallic Solid

Nitrogen

Daniel Rutherford, a Scottish Physician, discovered Nitrogen in 1772. But it was Lavoisier, who proved that nitrogen is an element and that it was not a supporter of combustion and respiration. He called it ‘azote’ meaning ‘no life’. The name ‘Nitrogen’ was given to it by Jean Antoine Chaptal (1756 – 1832), in the year 1790.

Occurrence of Nitrogen

Nitrogen exists in the free state and in combined form in the atmosphere of the earth. In the free state it occurs as N_2 and occupies about 80% by volume of air. In the combined form, it is present as ammonia and all ammonium compounds, in nitric acid and in all nitrates, nitrites and in all living things in the form of proteins.

Industrial Preparation (large scale)

Industrially, Nitrogen is prepared by fractional distillation; Oxygen is obtained at the same time. Air is purified by removing gas from it. Then carbondioxide is removed and lastly water vapour. The remaining air is removed and compressed. The liquified air is allowed to evaporate. Because Nitrogen has a lower boiling point, it evaporates first leaving liquid oxygen.

Laboratory Preparation of Nitrogen

Preparation of Nitrogen from Air

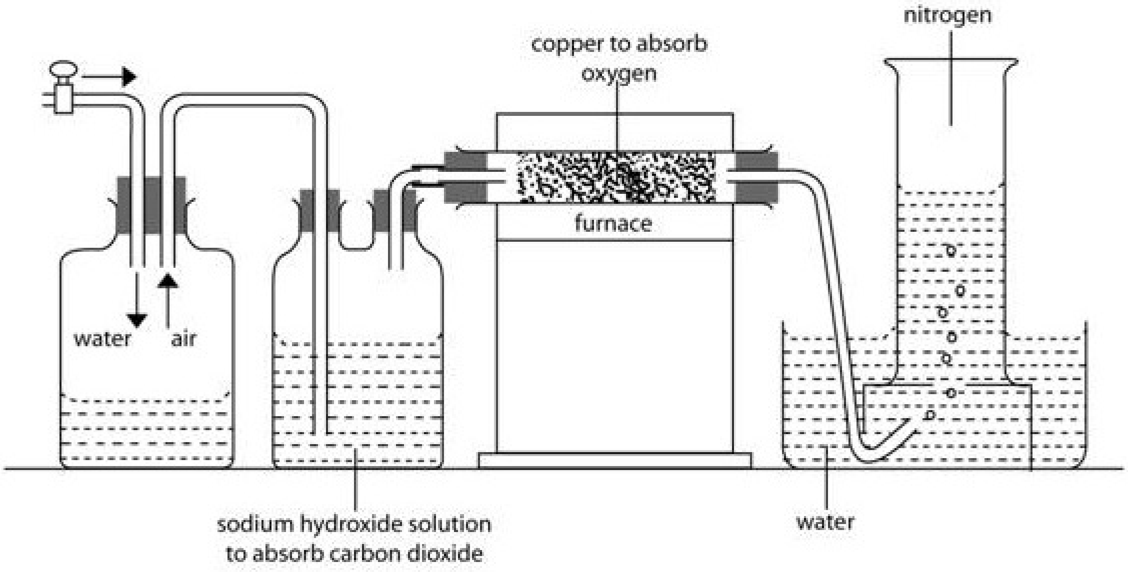
Nitrogen is prepared from the air by removing oxygen and carbon dioxide. Water is used to push air through sodium hydroxide solution (caustic soda solution) which removes carbon dioxide.

$2NaOH\ (ag) + CO_2\ (g)\ Na_2CO_3\ (g) + H_2O\ (i)$

The remaining gas is passed over heated copper turnings to remove Oxygen.

$2Cu\ (s) + O_2\ (g) 2CuO\ (s)$

Nitrogen is collected over water as it is insoluble in water.



Preparation of Nitrogen from Chemical Compounds

- By treating excess ammonia with chlorine, ammonium chloride and nitrogen are formed.
- Nitrogen can also be prepared by b heating a mixture of ammonium chloride and sodium dioxonitrate (III).

$NaNO_2\ (s) + NH_4Cl\ (s)\ NH_4NO_2\ (s) + NaCl\ (s)$

- Nitrogen is formed by decomposition of ammonium dioxonitrate (III)

$NH_4NO_2\ (s) N_2\ (g) + 2H_2O\ (i)$

Physical Properties of Nitrogen

1. it is colourless gas without smell
2. it is a reactive gas
3. it does not burn / doesn't support combustion
4. it is neither acidic nor basic
5. Density of nitrogen is 1.25 x 10^{-3} $g.cm^{-3}$ at 20°C
6. Melting point of nitrogen is -210 °C
7. Boiling point of nitrogen is -195.8 °C

Chemical Properties of Nitrogen

- Nitrogen does not easily combine with other elements under ordinary conditions. A molecule of nitrogen is diatomic. These two atoms have combined by mutually sharing three pairs of electrons.
- Nitrogen is inert unlike Oxygen, it reacts under special conditions for example, It reacts with some metals at very high temperatures forming nitrides e.g. Calcium and magnesium.

  $3Mg\ (s) + N_2(g) Mg_3N_2(s)$

$3Ca\ (s) + N_2\ (g)\ Ca_3N_2\ (s)$

- It forms nitric oxide and nitrogen dioxide with oxygen
- Its reacts with hydrogen to give ammonia

Uses of Nitrogen

1. Nitrogen is used in high temperature thermometers where mercury cannot be used.
2. Nitrogen is used in the manufacture of ammonia, trioxonitrate (V) acid, trioxonitrate (V) salt and fertilizer

3. Liquid nitrogen is used as refrigerant and also used to shrink metal parts that are to be fitted inside other parts
4. Liquid nitrogen is also used in grinding substances that are too tough or too sticky to grind at normal temperature, including drugs, cosmetics and plastics

Assessment

1. The name Nitrogen was given by ....
   a. Daniel Rutherford
   b. Lavoisier
   c. Jean Antoine Chaptal
   d. Jean Claude
2. Nitrogen combines directly with metals except
   a. Cu
   b. Mg
   c. Ca
   d. Al
3. Nitrogen combines directly with Oxygen under
   a. catalyst
   b. high voltage electric work
   c. the presence of traces of NO
   d. in vacuum
4. Hydride of Nitrogen which is capable of turning red litmus blue makes nitrogen to have an oxidation state of
   a. +2
   b. -2
   c. +3
   d. -3

Answers

1. C
2. C
3. B
4. D

Week 9

Topic: Sulphur

Introduction

Sulphur is a yellow, brittle non-conducting solid with a fairly low melting point (115°C). It is insoluble in water but soluble in other solvents such as carbon disulphide or methylbenzene. In the lab, sulphur can be found as two forms: roll sulphur and flowers of sulphur. (Note: these are not allotropes but just different forms – polymorphs. Sulphur is extracted from the earth’s crust via Frasch process.

Sulphur is found in metal ores, for example zinc blende (ZnS) and copper pyrites ($CuFeS_2$). It also occurs as the free element in sulphur beds found in Poland, Iraq, USSR and USA. These beds occur about 100-200m below ground level and in between the sulphur deposits there are layers of clay and sand. So, a special process is needed to extract this Sulphur. Sulfur is a non-metallic element, which is very important in the chemical industry.

Sources

It is found as the element in sulphur beds 200m below the ground in volcanic areas and also in metal ores such as copper pyrites (iron sulphides) and zinc blende and also in volcanic areas.

Allotropes Of Sulphur

Sulphur exists in many allotropic forms however the important three allotropic forms of sulphur are as under.

1. Rhombic Sulphur: It is an allotropic form of sulphur which is stable below 96°C one molecule of rhombic sulphur contains 8-atoms i-e 8_g. The crystal of rhombic sulphur has octahedral structure.

Preparation

Rhombic sulphur is prepared by dissolving ordinary powdered sulphur in carbon disulphide (cs_2) the saturated solution is then filtered and the filtrate is allowed to evaporate at room temperature. After evaporating Cs_2, crystals of rhombic sulphur are obtained crystal of rhombic sulphur.

Properties:

- It is consist of pale yellow crystals.
- It melts at 110℃.
- It is insoluble in water and soluble in carbon disulphide.
- It is stable at room temperature.
- Its specific gravity is 208g/cm3.

2. Monoclinic Sulphur: It is the allotropic form of sulphur which is stable between 96 to 119°C a molecule of monoclinic sulphur consists of eight sulphur atoms i-e 8g, but is different from rhombic sulphur in the arrangement of atoms.

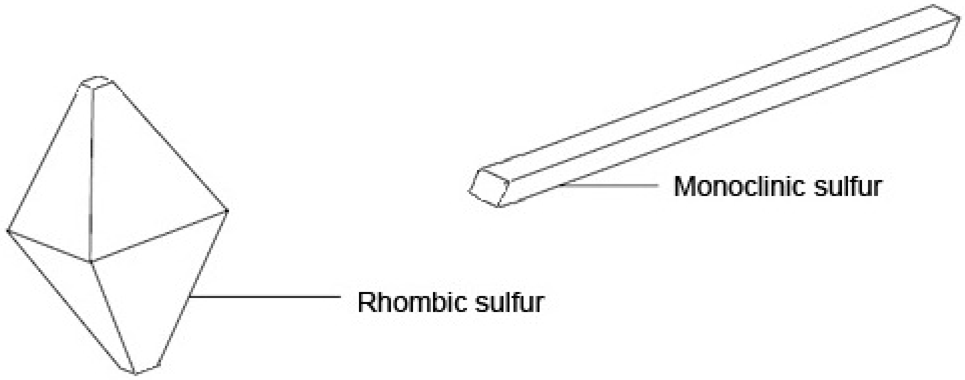
Preparation:

Ordinary sulphur is mulled in a china dish with slow heating. The molten sulphur is allowed to cool down until a crest is formed at the surface, the holes are made in the crest by glam rod and molten sulphur is powered out, the crest is also removed and at the bottom, needle shaped crystals of monoclinic sulphur are left.

Properties:

- It is stable from 96℃-119℃.
- Its melting point is 119℃.

- It is soluble in carbon disulphide.
- Its one molecule consist of 8 atoms.
- It is found as pale yellow needle shaped crystals.



3. Plastic Sulphur: It is a non crystalline allotropic form of sulphur, it can be stretched like a rubber, it is unstable and changes into rhombic sulphur on slight heating even at room temperature it also changes.

Preparation:

Heat some powdered sulphur in a test tube, it will melt into a yellow liquid, on further heating it changes into a dark red molten mars. Throw this molten maxs into cold water. On solidification the plastic sulphur is obtained.

Extraction of Sulphur

Sulphur is extracted using the Frasch Process.

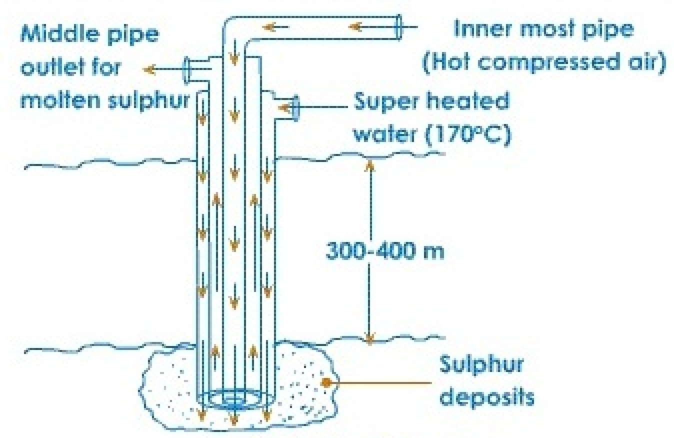


Fig. 13.21 Frasch process

Superheated water at 170°C and hot compressed air are pumped into layers of sulphur through pipes. This forces water and molten sulphur to the surface. Sulphur is insoluble in water and so the two substances emerging from the pipes are easily separated. The sulphur is about 99.5% pure and can be used directly.

Physical Properties of Sulphur

The Frasch Process, as a result of some of the following properties, extracts sulphur:

- brittle yellow solid
- melting point of 119°C and a boiling point of 444°C
- non-conductor of heat and electricity
- burns with blue flame when lit
- insoluble in water

Chemical Properties of Sulphur

- Sulphur burns readily in air forming sulphur dioxide

$S + O_2 ==> SO_2$

- Sulphur reacts with hydrogen gas when the latter is bubbles through molten sulphur near its boiling point.

$S + H_2 ==> H_2S$

- Sulphur dissolves in caustic alkali solutions forming sulphides and thiosulphates.

$4S + 6 NaOH ==> Na_2S_2O_3 + 2 Na_2S + 3H_2O$

Uses of Sulphur

- For the manufacture of sulphuric acid.
- Fruit trees are sprayed with sulphur to prevent insect and fungal attack.
- For the manufacture of calcium hydrogensulphite $Ca(HSO_3)_2$ which is in turn used to bleach wood pulp in the manufacture of paper.
- For the vulcanisation of rubber, i.e. converting soft rubber into the hard, tough substance of which motor tyres and similar substances are made of.
- In the manufacture of dyes, fireworks, matches, sulphur compounds such as CS_2 and sodium thiosulphate (Na_2S_2O3) used in photography, sulphur ointment, and tablets and drugs used in medicine.

Assessment

1. One molecule of Sulphur contains ……. atoms
   a. 8
   b. 16
   c. 4
   d. 2
2. Sulphur is a ……… coloured solid
   a. Green

   b. Greenish yellow
   c. Yellow
   d. Light yellow

3. Which of the allotropes of sulphur has amber colour with needle shape
   a. Rhombic sulphur
   b. Pastric sulphur
   c. Monoclinic sulphur
   d. Flower of sulphur

4. When sulphur is gradually heated and in limited supply of air, it develops a feature at 200°C. This feature is
   a. turns into brown vapour
   b. develops a floral pattern
   c. becomes highly viscous
   d. turns into amber-coloured liquid

5. Sulphur is extracted from the earth's crust by one of the following processes
   a. Solvay process
   b. Frasch process
   c. Contact Process
   d. Kiln process

6. Sulphur reacts with soft rubber to harden it by
   a. direct linkage
   b. polymerization
   c. cross linkage
   d. smoking

Answers

1. A
2. C
3. C

4. A
5. B
6. C

Week 10

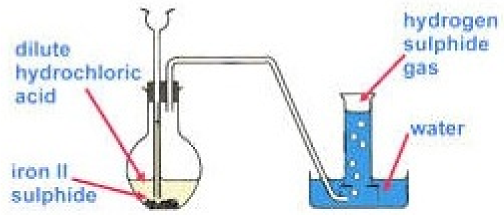
Topic: Compounds of Sulphur

Hydrogen Sulphide (H_2S)

Hydrogen Sulphide occurs naturally in petroleum deposits and is also an air pollutant. It is easily identified by its characteristic smell.

Laboratory Preparation

Hydrogen Sulphide is prepared by the action of dilute hydrochloric acid on iron (II) sulphide. The liberated gas is collected above warm water (since it readily dissolves in cold water) or by downward delivery.



SAFETY FIRST
This preparation must be carried out in a fume cupboard and only by a teacher.

Equation of reaction: $FeS_{(s)} + 2HCl_{(aq)} \longrightarrow FeCl_{2(aq)} + H_2S_{(g)}$

Test

The prepared gas can be recognized by any of the following ways:

- Smell: This gas has a characteristic rotten-egg smell;
- Action on Litmus: This gas turns litmus paper red (somehow pink);
- Action on Lead ethanoate paper: The gas turns lead ethanoate paper black.

Physical Properties

- Hydrogen sulphide is colourless gas with rotten-gas smell;
- It turns litmus paper red, somehow pinkish; because of the acidic nature of the gas;
- The gas is about 1.25 times denser than air, hence it can be collected by downward delivery

Chemical Properties

Action on water: Hydrogen sulphide can dissolve in water to form a very weak acid;

Thus: $H_2S + H_2O \longrightarrow HS^- + H_3O^+$

Acidic behaviour: The gas, when dissolved in water, shows the normal acidic properties:

- It reacts with trioxocarbonates (IV) to liberate carbon (IV) oxide gas;

$H_2S + Na_2CO_3 \longrightarrow Na_2S + H_2O + CO_2$

- It undergoes neutralization reaction to form salt (a sulphide) and water only;

$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$

- Metals higher than hydrogen in the activity series can displace the gas from the acid;

$Zn + H_2S \longrightarrow ZnS + H_2$

Action on Lead Ethanoate: Hydrogen sulphide reacts with lead ethanoate paper to from black precipitate of Lead (II) sulphide:

$(CH_3COO)_2Pb + H_2S \longrightarrow PbS + CH_3COOH$

Action on Lead trioxonitrate: In the absence of lead ethanoate, hydrogen sulphide can also form black precipitate of lead (II) sulphide with Lead (II) trioxonitrate (V) paper.

$Pb(NO_3)_2 + H_2S \longrightarrow PbS + HNO_3$

As reducing agent: H_2S acts as reducing agent by decolorizing acidified $KMnO_4$ and depositing yellow sulphur in the process.

$H_2S + 2KMnO_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + H_2O + S$

It also reduces sulphur (IV) oxide to sulphur. Thus: $2H_2S + SO_2 \rightarrow 2H_2O + 3S$

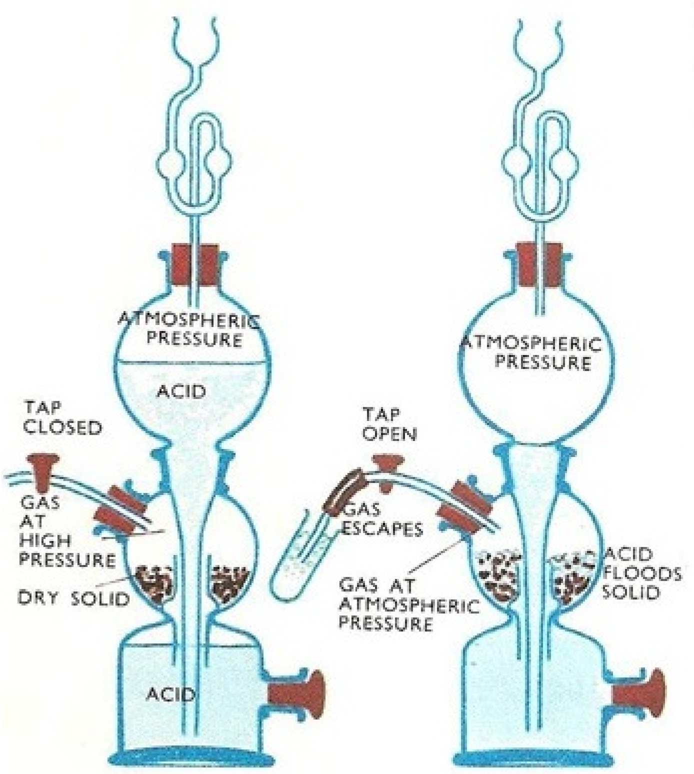
Reaction with metals: H_2S reacts with metals to form the corresponding metallic sulphide while hydrogen gas is evolved. This is, of course, with the exception of such metals that are found below hydrogen in the activity series. Thus:

$H_2S + Zn \longrightarrow ZnS + H_2$

$H_2S + Mg \longrightarrow MgS + H_2$

$H_2S + Na \longrightarrow NaS + H_2$

KIPP'S APPARATUS



This apparatus is used in the laboratory for the intermittent supply of gases prepared by the action of an aqueous solution on a solid reactant. Example of such a gas is Hydrogen Sulphide. Other gases that can be produced using the Kipp's apparatus include hydrogen and carbon (IV) oxide.

Mechanism

Kipp's Apparatus is made up of three chambers. In the intermittent preparation of H_2S gas, hydrochloric acid is poured through the thistle funnel and chamber A to the chamber C. Whenever the gas is required, the tap is opened. This causes the volume of the chamber B to increase.

In accordance with the statements of Boyle's Law, the pressure decreases. The HCl acid rises from the chamber C to the chamber B, in order to raise the pressure to be at par with the atmospheric pressure. The acid will subsequently react with the iron sulphide in the chamber B and the gas is produced.

If the gas is no longer needed, the tap is closed. Since the H_2S is still being produced for a while, there is high pressure and so the HCl acid falls back to the chamber C in order to permit the pressure to fall to the atmospheric pressure. The HCl is no longer in contact with the iron sulphide (FeS) that is in the chamber B and so the reaction ceases. There is also the consequent stop in the production of the H_2S gas.

Uses

1. In the laboratory, hydrogen sulphide acts as a reagent to detect the presence of certain anions and cations present in a given salt.
2. Hydrogen sulphide is used in the preparation of metallic sulphides.

SULPHUR (IV) OXIDE (SULPHUR DIOXIDE)

Sulphur dioxide was known from ancient times and Romans used it as a general cleansing agent. In 1770, J. Priestly prepared the gas by the action of hot concentrated sulphuric acid on mercury and called it sulphurous acid. Lavoisier studied the structure and proved that it was an oxide of sulphur.

Laboratory methods of preparing sulphur dioxide

Sulphur dioxide in the laboratory is prepared by:

- Reacting dilute hydrochloric acid or dilute tetraoxosulphate (VI) acid with sodium trioxosulphate (IV) crystals

Diagram of the apparatus used

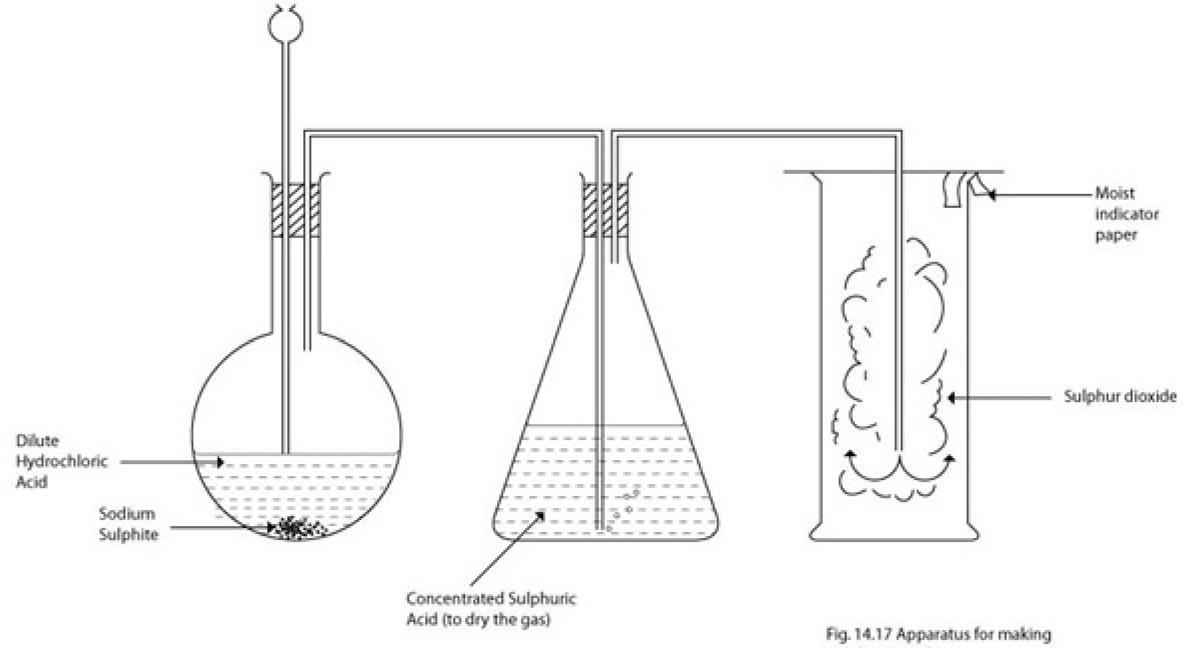


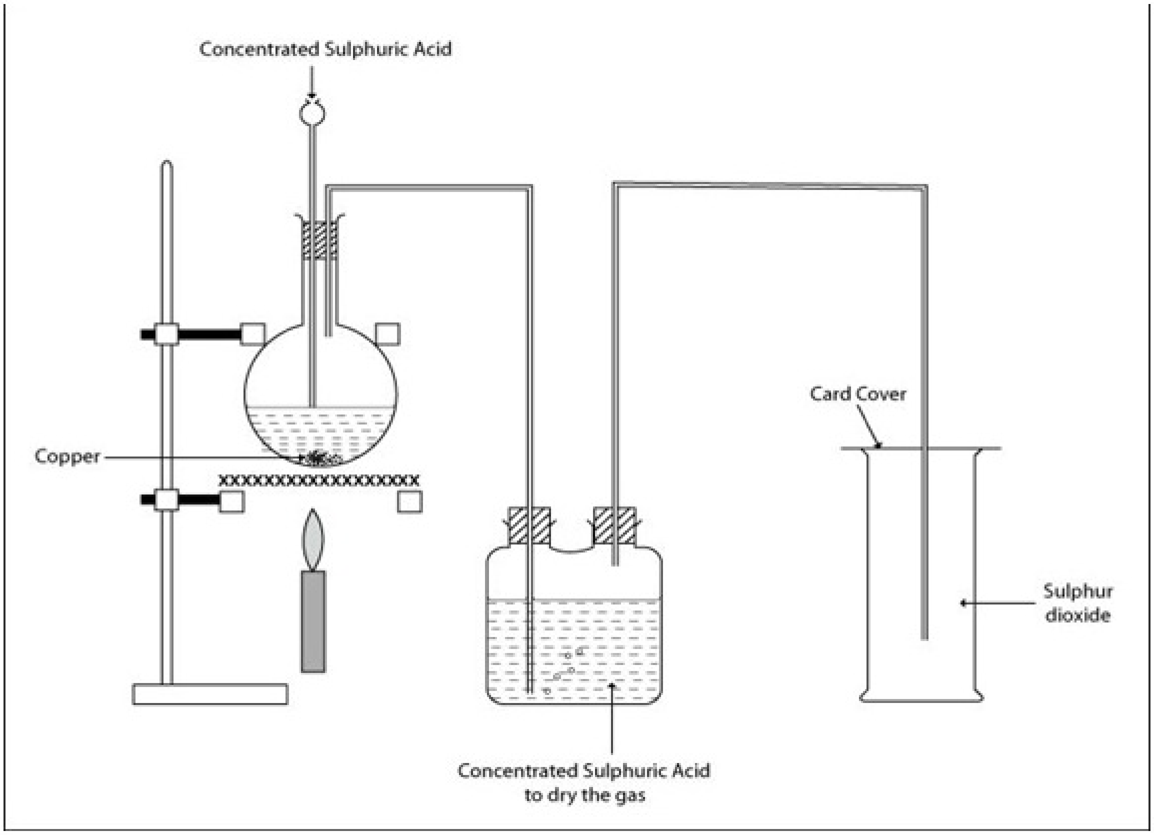
Fig. 14.17 Apparatus for making Sulphur dioxide

Equation of reaction taking place

$$Na_2SO_3(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + SO_2(g)$$

Or $Na_2SO_3(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l) + SO_2(g)$

- Heating a mixture of copper turnings and concentrated tetraoxosulphate (VI) acid (sulphuric acid). Diagram of Apparatus used is the same as the one above except a source of heat must be applied.



Equation of reaction taking place

$Cu(s) + 2H_2SO_4(aq) \longrightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(aq)$

Physical Properties of sulphur dioxide

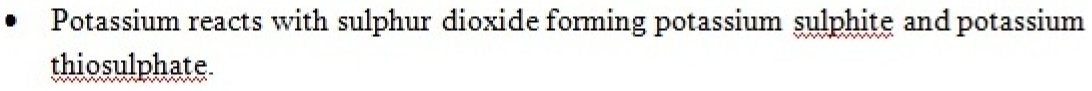
- Sulphur dioxide ‘SO_2‘ a colorless gas with a pungent and suffocating odour. It is readily soluble in cold water, sparingly soluble in hot water, and soluble in alcohol, acetic acid, and sulfuric acid.
- It can be produced by the reaction of sulphur with oxygen, by burning sulphur in air, and it is often produced during the roasting of sulfide ores, e.g, zinc smelting.
- It is a non-combustible and non-supporter of combustion.

Chemical Properties

- Magnesium burns in sulphur dioxide giving magnesium oxide and sulphur.

$$2Mg + SO_2 \longrightarrow MgO + S$$

$$3Mg + SO_2 \longrightarrow 2MgO + MgS$$



- Potassium reacts with sulphur dioxide forming potassium sulphite and potassium thiosulphate.

$$4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$$

- Sulphur dioxide reacts with alkali solution to give salt and water. [sulphites and bisulphites] When sulphur dioxide is bubbled through sodium hydroxide solution no precipitate is formed since sodium sulphite is a soluble salt. When sulphur dioxide is passed through Ca $(OH)_2$ solution, a white precipitate of insoluble calcium sulphite is formed. If excess sulphur dioxide is passed, the precipitate disappears forming soluble calcium bi sulphite.

$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$

$[Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3]$ in excess

$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$

$[CaSO_3 + H_2O + SO_2 \longrightarrow 2Ca(HSO_3)_2]$in excess

- Reacts with carbonates and liberates carbon dioxide

$K_2CO_3 + H_2O + 2\,SO_2 \longrightarrow 2KHSO_3 + CO_2$

$Na_2CO_3 + H_2O + 2SO_2 \longrightarrow 2NaHSO_3 + CO_2$

- Reacts with basic oxide to give sulphites

$Na_2O + SO_2 \longrightarrow Na_2SO_3$

$CaO + SO_2 \longrightarrow CaSO_3$

- Sulphur dioxide is a strong oxidizing agent. Oxidises magnesium to magnesium ion(Mg^{+2})

$$2Mg + SO_2 \longrightarrow 2MgO + S$$
(heated)

- Oxidises hydrogen sulphide to sulphur

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

- Sulphur dioxide is a strong reducing agent. In the presence of moisture SO_2 liberated nascent hydrogen and reduction takes place by addition of hydrogen.

$$SO_2 + 2H_2O + SO_2 \longrightarrow H_2SO_4 + 2[H]$$

Example:

$$Fe_2(SO_4)_3 + 2H_2O + SO_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

$$Cl_2 + 2H_2O + SO_2 \longrightarrow 2HCl + H_2SO_4$$

$$FeCl_3 + 2H_2O + SO_2 \longrightarrow 2FeCl_3 + H_2SO_4 + 2HCl$$

- Potassium dichromate, potassium permanganate and nitric acid are reduced by the action of SO_2 by removal of oxygen.

Example:

$$K_2Cr_2O_7 + H_2SO_4 + SO_2 \longrightarrow Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

$$2KMnO_4 + 2H_2O + 5SO_2 \longrightarrow 2MnSO_4 + 2H_2SO_4 + K_2SO_4$$

$$2HNO_3 + SO_2 \longrightarrow 2NO_2 + H_2SO_4$$

Sulphur dioxide gas exhibits bleaching properties in presence of moisture. It dissolves in water liberating nascent hydrogen. Colouring matter is bleached by reaction with nascent hydrogen. Nascent hydrogen removes oxygen atoms from the colouring matter (reduces colouring matter) and it loses its colour. This bleaching is temporary because the bleached product on exposure to atmospheric oxygen adds on oxygen atoms from air and regains its original color.

Uses of sulphur dioxide

The various uses of sulphur dioxide are:

1. In the manufacturing of sulphuric acid, sulphites, and hydrogen sulphite
2. In the sugar industry for refining and decolorizing sugar
3. For refining kerosene, and other petroleum products
4. As a disinfectant
5. As a fumigant
6. For bleaching delicate articles
7. As antichlor, to remove the excess chlorine from substances that have been bleached by chlorine
8. As a solvent for glue
9. As a refrigerant in household refrigerators
10. As a preservative for wines, meat, dry fruits etc.

SULPHUR (VI) OXIDE (SULPHUR TRIOXIDE)

Preparation of Sulphur Trioxide

Sulphur trioxide is prepared by the direct union of gaseous sulphur dioxide with ozone.

$3SO_{2(g)} + O_{3(g)} \implies 3SO_{3(g)}$

Sulphur trioxide is also prepared by passing oxygen and sulphur dioxide through concentrated sulphuric acid to dry the gases, which are then passed over a heated platinised asbestos catalyst at 450°C.

$2SO_{2(g)} + O_{2(g)} \implies 2SO_{3(g)}$

Sulphur trioxide is prepared by heating concentrated sulphuric acid with a large excess of phosphorus pentoxide, P_2O_5

$H_2SO_{4(aq)} + P_2O_{5(aq)} \implies SO_{3(g)} + 2HPO_{3(aq)}$

Properties of Sulphur Trioxide

- Sulphur trioxide is a white, crystalline, solid which is hygroscopic.
- Sulphur trioxide reacts vigorously with water to form sulphuric acid.

$SO_{3(g)} + H_2O_{(l)} ==> H_2SO_{4(aq)}$

- Sulphur trioxide reacts with water vapour in the air to form white fumes consisting of tiny droplets of sulphuric acid.
- Sulphur trioxide readily reacts with basic oxides to form sulphates.

$CaO_{(aq)} + SO_{3(g)} ==> CaSO_{4(aq)}$

- Sulphur trioxide is a planar covalent molecule with one sulphur oxygen double bond and with a bond angle of 120 degrees between the other two oxygen atoms. Sulphur trioxide has a resonance structure.

Trioxosulphate (IV) Acid

Trioxosulphate (IV) acid is the strong acid produced by dissolving sulphur dioxide in water

$SO_{2(g)} + H_2O_{(l)} ==> H_2SO_{3(g)}$

Trioxosulphate (IV) acid, H2SO3, is a weak dibasic acid, known in the form of its salts (e.g. sodium sulphite)

Preparation of Trioxosulphate (IV) Acid

Trioxosulphate (IV) acid is formed when sulphur dioxide is dissolved in water

$SO_{2(g)} + H_2O_{(l)} ==> H_2SO_{3(g)}$

Trioxosulphate (IV) acid is unstable and has never been isolated as a pure compound. It may be better represented by the following reactions

$SO_2 + H_2O ===> HSO_3^- + H^+$

HSO_3^- ===> H^+ + SO_3^-

This is known as the ionisation of Trioxosulphate (IV) acid.

Examples of the above are :

$2NaOH_{(aq)}$ + $SO_{2(g)}$ ===> $Na_2SO_{3(aq)}$ + $H_2O_{(l)}$

$Na_2SO_{3(aq)}$ + $H_2O_{(l)}$ + $SO_{2(g)}$ ===> $2NaHSO_{3\ (aq)}$

Physical Properties of Trioxosulphate (IV) Acid

- Trioxosulphate (IV) Acid, H_2SO_3, is a weak dibasic acid, known in the form of its salts
- It turns blue litmus red
- It is unstable and has never been isolated as a pure compound

Reactions of Trioxosulphate (IV) acid

- The solution when heated in a sealed tube at 150°C deposits sulphur

$3H_2SO_{3(aq)}$ ===> $2H_2SO_{4(aq)}$ + $H_2O_{(l)}$ + $S_{(s)}$

- Oxidising of Trioxosulphate (IV) acid by Oxygen

Trioxosulphate (IV) acid can be oxidised by the use of strong oxidising agents

$2H_2SO_{3(aq)}$ + $O_{2(g)}$ + $4H_2O_{(l)}$ ===> $4H_3O^+$ + $2SO_4^{2-}$

Trioxosulphate (IV) acid solution is slowly oxidised by atmospheric oxygen to sulphuric acid

- Oxidising of Trioxosulphate (IV) acid by Permanganate ions

When trioxosulphate (IV) acid is added to permanganate ion which is coloured purple, SO_2 will decolourise the MnO_4 (ion) when it is reduced to the colourless Mn (ion)

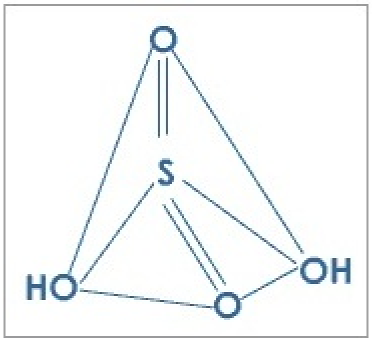
$2MnO_4^- + 5H_2SO_{3(aq)} + 4H_2O_{(l)} ===> 2Mn^{2+} + 4H_3O^+ + 5SO_4^{2-} + 3H_2O_{(l)}$

Uses of Trioxosulphate (IV) acid

- Trioxosulphate (IV) acid is a strong reducing agent
- The solution has bleaching properties : Moistened wool, straw for hats, and other materials injured by chlorine are bleached on exposure to sulphur dioxide or the fumes of burning sulphur

TETRAOXOSULPHATE (VI) ACID (SULPHURIC ACID)

Sulphuric acid, H_2SO_4 is a colourless, odourless, extremely corrosive, oily liquid. It was initially called oil of vitriol. It occurs in the free state and combined state. It is also formed near sulphide beds.



In the combined form, it occurs as salts in minerals as metallic sulphates.

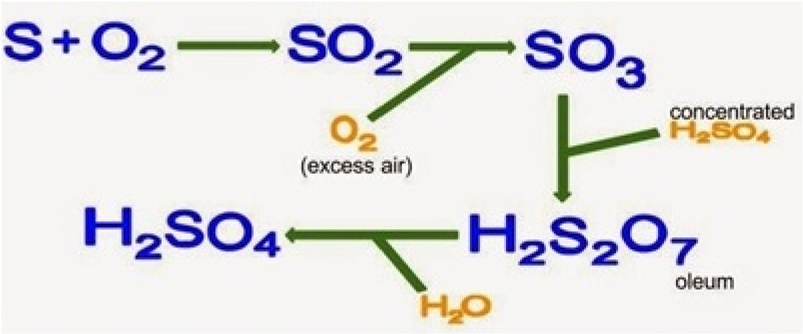
Industrial Preparation of Tetraoxosulphate(VI) Acid

Sulphuric acid is prepared by contact process all over the world. Preparation of sulphuric acid by contact process is based upon the catalytic oxidation of SO_2 to SO_3.

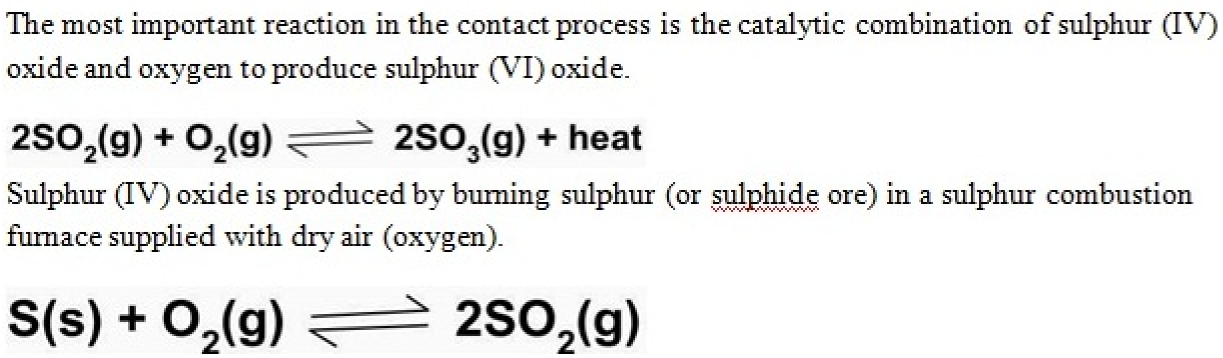
There are five steps in the manufacture of sulphuric acid by the contact process:

- Production of sulphur dioxide
- Purification of gases
- Oxidation of sulphur dioxide to sulphur trioxide
- Absorption of sulphur trioxide in sulphuric acid

- Dilution of oleum



Chemical reactions of the contact process.



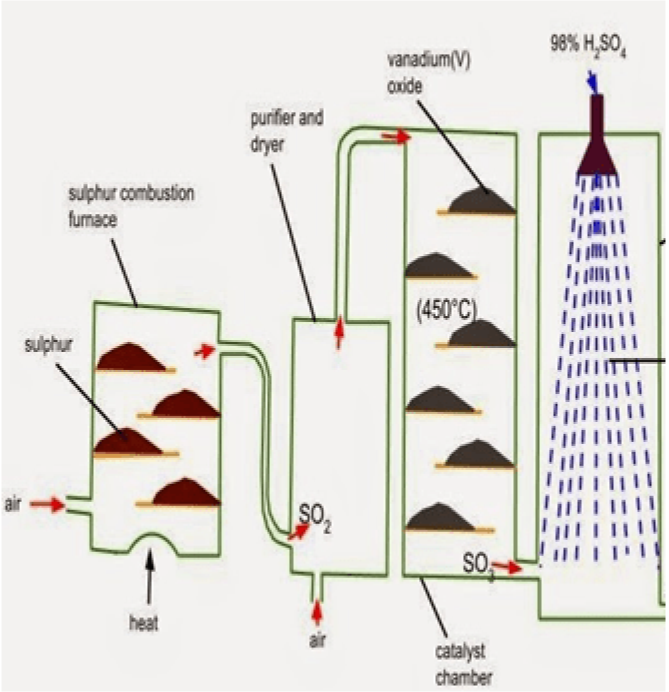
The most important reaction in the contact process is the catalytic combination of sulphur (IV) oxide and oxygen to produce sulphur (VI) oxide.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + heat$$

Sulphur (IV) oxide is produced by burning sulphur (or sulphide ore) in a sulphur combustion furnace supplied with dry air (oxygen).

$$S(s) + O_2(g) \rightleftharpoons 2SO_2(g)$$

The sulphur (IV) oxide is mixed with excess air and passed through a purifier to remove dust and other impurities. The mixture of sulphur(IV) oxide and air is passed through a dryer containing concentrated tetraoxosulphate (VI) acid, and the dry mixture is delivered into a catalyst chamber (or contact tower) where the sulphur(IV) oxide combines with the oxygen in the presence of vanadium(IV) oxide catalyst to form sulphur(VI) oxide.



Industrial preparation of tetraoxosulphate (VI) acid.

The sulphur (VI) oxide is cooled and channeled into an absorption tower where it combines with concentrated tetraoxosulphate (VI) acid to form oleum, $H_2S_2O_7$.

$SO_3(g) + H_2SO_4(aq) \rightarrow H_2S_2O_7(aq)$

Oleum is a very thick liquid which is diluted with water to produces 98% tetraoxosulphate (VI) acid.

$H_2S_2O_7(aq) + H_2O(l) \rightarrow 2H_2SO_4(aq)$

Sulphur (VI) oxide is capable of reacting with water to produce tetraoxosulphate (VI) acid. But it is not dissolve directly in water during the industrial preparation of tetraoxosulphate (VI) acid because the reaction produces large amount of heat which would cause the acid solution to boil and spill a mist of acid droplets to the surrounding.

Note:

- The mixture containing sulphur(IV) oxide and air is purified to remove impurities that might poison the vanadium(V) oxide catalyst

- Contact process is operated at a temperature of 450 – 500 °C and atmospheric pressure.

Physical Properties of Sulphuric Acid

- Sulphuric acid is a powerful protonating agent.
- It is also a moderately strong oxidizing agent.
- Sulphuric acid is also a powerful dehydrating agent and is used to remove a molecule of water from many organic compounds.
- In dilute solution, sulphuric acid is a strong dibasic acid forming two series of salts.

Note: A Dibasic Acid has two acidic hydrogen atoms in its molecules which can be ionised. Sulphuric Acid, H_2SO_4, is a dibasic acid, because it contains two hydrogens atoms which ionise in aqueous solution to become Hydrogen Ions, H(+).

H_2SO_4 ==> $2\ H^{(+)}$ + $SO_4^{(2-)}$

Reactions of Sulphuric Acid

- **Electrolysis of a Solution of dilute Sulphuric Acid**

The Electrolysis of an Aqueous Solution of dilute Sulphuric Acid is often carried out in a Hofmann Voltammeter, an apparatus in which the gases evolved at the anode and cathode can be collected in separate graduated tubes. When the solution is electrolyzed hydrogen is produced at the cathode and oxygen at the anode. These gases can be shown to be present in a 2 to 1 ratio and result from the electrolysis of water under acidic conditions.

Sulphuric acid is a strong electrolyte is fully dissociated in aqueous solution

H_2SO_4 ==> $2H^+$ + SO_4^{2-}

Water is a weak electrolyte and is only slightly dissociated

H_2O ==> H^+ + OH^-

During electrolysis, the Hydrogen Ions, H^+, migrates towards the cathode, and are discharged there (i.e. they gain an electron and are converted to hydrogen gas).

$2H^+ + 2e^- ==> H_2$

At the anode the concentration of Hydroxyl Ions, OH^-,is too low to maintain a reaction and the Sulphate Ions, SO_4^{2-} are not oxidized but remain on in solution at the end. Water molecules must be the species reacting at the anode.

$2H2O ==> O_2 + 4H^+ + 4e^-$

The overall reaction is

Cathode Reaction :

$2H^+ + 2e^- ==> H_2$ $4H^+ + 4e^- ==> 2H_2$

Anode Reaction :

$2H_2O ==> O_2 + 4H^+ + 4e^-$

Overall Cell Reaction:

$4H^+ + 2H_2O ==> 2H_2 + O_2 + 4H^+$

For every Hydrogen Ions, H(+), discharged at the anode, another hydrogen ion is formed at the cathode. The net result is that the concentration of the Sulphuric Acid, H2SO4, remains constant and this electrolysis consists of the decomposition of water with the overall reaction

$2H_2O ==> 2H_2 + O_2$

- Ferrous Sulphate, Fe_2SO_4, is the salt formed when Iron, Fe, is dissolved in Sulphuric Acid, H_2SO_4.
- Hydrogen Chloride, HCl, may be prepared in the laboratory by heating Concentrated Sulphuric Acid, H_2SO_4, with Sodium Chloride, NaCl.

- Sulphur (VI) oxide, SO_3, is prepared by heating concentrated Sulphuric Acid, H_2SO_4, with a large excess of Phosphorus Pentoxide, P_2O_5.

$NaCl + H_2SO_4 \Longrightarrow NaHSO_4 + HCl$

$H_2SO_4 + P_2O_5 \Longrightarrow SO_3 + 2\,HPO_3$

- Sulphur Dioxide, SO_2, is usually made in the laboratory by heating concentrated Sulphuric Acid, H_2SO_4, with Copper turnings, Cu.

$Cu + 2\,H2SO4 \Longrightarrow CuSO4 + SO2 + 2\,H2O$

- Hydrogen Fluoride, HF, can be prepared in the laboratory by heating Concentrated Sulphuric Acid, H_2SO_4, with Calcium Fluoride, CaF_2.

$H2SO4 + CaF2 \Longrightarrow 2\,HF + CaSO4$

- Hydrogen Iodide, HI, can be prepared by direct combination of the elements using a platinum catalyst. In the laboratory it is prepared by heating Concentrated Sulphuric Acid, H_2SO_4, with Sodium Iodide, NaI.

$H_2SO_4 + 2\,NaI \Longrightarrow 2\,HI + Na_2SO_4$

Uses of sulphuric acid

- In the manufacture of fertilizers, ammonium phosphate and calcium super phosphate.
- In the manufacture of rayon and nylon and also in the preparation of dyes and drugs from coal tar derivatives.
- In the manufacture of the explosives such as Tri-nitro toluene , Tri-nitro glycerine and picric acid.
- In the manufacture of nitric acid, hydrochloric acid and phosphoric acid.
- In the manufacture of sodium sulphate for glass industry and ferrous sulphate for ink industry.

- In the purification of petrol, kerosene, and lubricants.
- It is used in metallurgy for extraction of metals. Leaching of metallic compounds gives sulphates which on electrolysis gives the metal in pure form .It is used for pickling of metals.
- It is used in storage of batteries.
- It is used as a laboratory reagent for the preparation of iodine, carbon monoxide and hydrogen.

Tetraoxosulphate (VI) Salts

Sodium Tetraoxosulphate (VI)

Sodium tetraoxosulphate (VI), Na_2SO_4, is called different names depending on whether it is in the anhydrous or hydrated form. Anhydrous sodium tetraoxosulphate (VI), Na_2SO_4, is known as salt-cake while sodium tetraoxosulphate (VI) decahydrate, $Na_2SO_4.10H_2O$, is known as Glauber's salt . The decahydrate form is efflorescent, as such slowly loses its water of crystallization when exposed to the atmosphere.

Sodium tetraoxosulphate (VI) is prepared in the laboratory by the neutralization of dilute tetraoxosulphate (VI) acid, H_2SO_4, with sodium hydroxide, NaOH.

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

Industrial preparation of sodium tetraoxosulphate(VI) involves heating sodium chloride and concentrated tetraoxosulphate (VI) acid at a high temperature. The process involves the formation of sodium hydrogen tetraoxosulphate (VI), $NaHSO_4$, as an intermediate product with the evolution of hydrogen chloride gas, HCl.

$NaCl(s) + H_2SO_4(aq) \rightarrow NaHSO_4(aq) + HCl(g)$

Then the sodium hydrogen tetraoxosulphate(VI) reacts with more sodium chloride to form the sodium tetraoxosulphate(VI).

$NaHSO_4(aq) + NaCl(aq) \rightarrow Na_2SO_4(aq) + HCl(g)$

Sodium tetraoxosulphate(VI) is used as a purgative! It is used in the manufacture of glass, detergents and wood pulp. And finally, it is used in the production of sodium sulphide, H_2S.

Assessment

1. Sulphur (iv) oxides bleaches by
   a. oxidation
   b. reduction
   c. decomposition
   d. carboxylation
2. Sulphur(iv) oxide is used for these except
   a. germicide and fumigant
   b. refrigerant
   c. preserving liquids like orange juice
   d. used for restoring ozone layer
3. One of the following is not a use of Sulphuric acid
   a. As a coolant
   b. It is used in metallurgy for extraction of metals. .
   c. It is used in storage of batteries.
   d. It is used as a laboratory reagent for the preparation of iodine, carbon monoxide and hydrogen.
4. …….. a colorless gas with a pungent and suffocating odour
   a. Sulphur(vi)oxide
   b. Tetraoxosulphate(vi) oxide
   c. Sulphur dioxide
   d. Sulphur Trioxide
5. One of these is not a test for Hydrogen Sulphide
   a. Smell: This gas has a characteristic rotten-egg smell
   b. Action on Litmus: This gas turns litmus paper red (somehow pink)
   c. Action on Lead ethanoate paper: The gas turns lead ethanoate paper black
   d. Taste: The gas has a sweetened taste

Answers

1. B
2. D
3. A
4. C
5. D

Week 4

Topic: Hydrogen

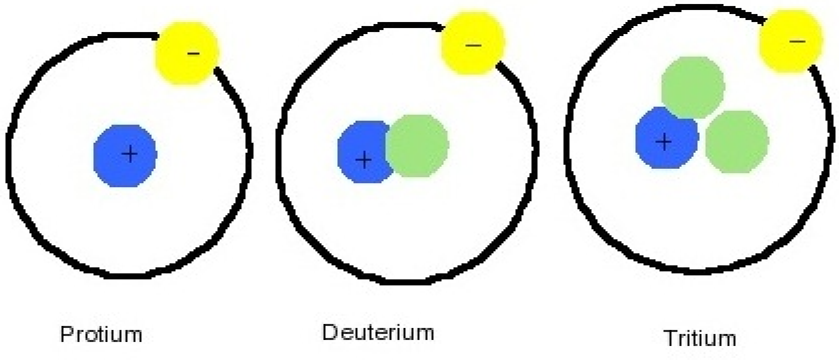
Introduction

Hydrogen was first isolated and shown to be a discrete element by Henry Cavendish in 1766. Before that, Robert Boyle and Paracelsus both used reactions of iron and acids to produce hydrogen gas. Antoine Lavoisier gave hydrogen its name because it produced water when ignited in air. Hydrogen comes from Greek meaning “water producer” (“hydro” =water and “gennao”=to make).

Hydrogen is one of the most important elements in the world. It is all around us. It is a component of water (H_2O), fats, petroleum, table sugar ($C_6H_{12}O_6$), ammonia (NH_3), and hydrogen peroxide (H_2O_2)—things essential to life, as we know it.

Atomic hydrogen, having atomic number 1 and an atomic weight 1.008 amu, is the simplest element. At ordinary temperatures and pressures it is a gas, composed of diatomic molecules, H_2 and is only very slightly soluble in water. In this form, hydrogen is a colourless, odourless, and tasteless gas. The sun and other stars are composed largely of hydrogen. Naturally occurring hydrogen is mostly composed of ^1H atoms and a very small percentage of deuterium. Hydrogen containing compounds can both be ionic and covalent in nature. Examples include acids, bases, and all organic compounds. In organic compounds, hydrogen is covalently bonded.

Isotopes



Three Hydrogen Isotopes

- **Protium (**^{1}H) is the most common isotope, consisting of 99.98% of naturally occurring hydrogen. It is a nucleus containing a single proton.
- **Deuterium** (^{2}H) is another an isotope containing a proton and neutron, consisting of only .0156% of the naturally occurring hydrogen. Commonly indicated with symbol D, D2O is called heavy water, which has a higher density, melting point, and boiling point than regular water. Replacing protium with deuterium (called deuteration) has important implications for the rate of reaction called kinetic-isotope effect.
- **Tritium** (^{3}H) is a radioactive isotope with a 12.3-year half-life, which is continuously formed in the upper atmosphere due to cosmic rays. It is can also be made in a lab from Lithium-6 in a nuclear reactor. Tritium is also used in hydrogen bombs.

Laboratory Preparation of Hydrogen

- **Preparation of hydrogen gas from water**

Water is the most common and probably most important compound of hydrogen. Hydrogen is liberated when a direct current of electricity is passed through water containing a small amount of an electrically conducting substance such as sulfuric acid, H_2SO_4. The chemical change that occurs is summarized in a chemical equation below:

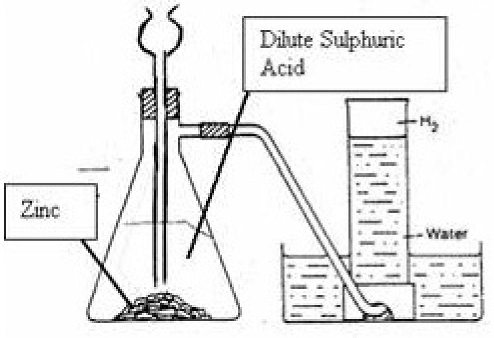
$2\ H_2O(l)$ + electrical energy ——-> $2\ H_2(g) + O_2(g)$

- Preparation of hydrogen gas from active metals

Several of the most active metals-such as lithium, sodium, potassium, rubidium, cesium, magnesium, and calcium-will react with water to produce hydrogen gas. The net chemical change is summarized in reaction below using the reaction of sodium metal with water as an example. This reaction produces hydrogen gas and sodium hydroxide.

$2Na(s) + 2\ H_2O(l)$ ——-> $2\ NaOH(aq) + H_2(g)$

- **Preparation of hydrogen gas from metals with acids**



This is the most convenient laboratory method of producing hydrogen. Several of the metals most commonly used are shown in the reactions below. In each of these reactions, the metal reacts with an acid to produce a salt and hydrogen gas. The salts produced in the reactions listed below are magnesium chloride, magnesium sulfate, and zinc phosphate, respectively.

$Mg(s) + 2\ HCl(aq)$ ——> $MgCl_2(aq) + H_2(g)$

$Mg(s) + H_2SO_4(aq)$ ——> $MgSO_4(aq) + H_2(aq)$

$3Zn(s) + 2\ H_3PO_4(aq)$ ——> $Zn_3(PO_4)_2(aq) + 3H_2(g)$

Action of Zinc on and acid

Dilute hydrochloric acid or tetraoxosulphate (vi) acid attacks metallic zinc with the liberationof hydrogen gas. No heating necessary

$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Action of Sodium on Water

Sodium liberates hydrogen from cold water. This reaction is very vigorous and should be carried out with extreme care using only a small piece of sodium

$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$

Physical properties of Hydrogen

Hydrogen is the lightest element known. It is 14.4 less dense than air

It is neutral to moist litmus paper i.e. it has no action on either red or blue litmus paper

Hydrogen is a colourless and odourless gas when pure

It is slightly soluble in water, two part dissolving in 100 parts of water by volume

Chemical Properties of Hydrogen

- Hydrogen wanting to give up its single electron causes it to act like an alkali metal:

$H(g) \rightarrow H^+(g) + e^-$

- A half-filled valence shell with one e- also causes hydrogen to act like a halogen because it wants to gain Noble gas configuration by adding an e^-:

$H(g) + e^- \rightarrow H^-(g)$

- Reactions with Active Metals: Hydrogen accepts e- from an active metal to form ionic hydrides like LiH. By forming an ion with -1 charge, the hydrogen behaves like a halogen.

$2M(s)+H_2(g) \rightarrow 2MH(s)$ M= group 1 metals

Example: $2K(s)+H_2(g) \rightarrow 2KH(s)$ $2K(s)+Cl_2(g) \rightarrow 2KCl(s)$

$M(s)+H_2(g) \rightarrow MH_2(s)$ M= group 2 metals

Example: $Ca(s)+H_2(g) \rightarrow CaH_2(s)$ $Ca(s)+Cl_2(g) \rightarrow CaCl_2(s)$

- Reactions with Non-metals: Unlike metals forming ionic bonds with nonmetals, hydrogen forms polar covalent bonds. Despite being electropositive like the active metals that form ionic bonds with nonmetals, hydrogen is much less electropositive than the active metals, and forms covalent bonds.

Hydrogen + Halogen → Hydrogen Haliden($H_2(g)+ Cl_2(g) \rightarrow HCl(g)$)

Hydrogen + Oxygen → Water ($H_2(g)+O_2(g) \rightarrow H_2O(g)$)

- Hydrogen is a good reducing agent e.g. it reduces copper (II) oxide to copper

$CuO(s) + H_2(g) \text{———>} Cu(s) + H_2O(l)$

- Reaction with Sulphur: if hydrogen is bubbled through molten sulphur, hydrogen sulphide which has a characteristics rotten egg smell is formed

$H_2(g) + N_2(g) \text{———>} H_2S(g)$

- Hydrogen also reacts with nitrogen directly to produce ammonia gas. This involves high temperature

$3H_2(g) + N_2(g) \text{———>} 2NH_3(g)$

The Test for Hydrogen Gas, $H_{2(g)}$

Note the following characteristics when testing for hydrogen:

1. Hydrogen gas has no colour or smell.
2. Hydrogen gas has no effect on moist litmus paper or moist universal indicator paper – it is neutral.
3. Hydrogen gas burns with a characteristic ‘pop’.

Specific Test for Hydrogen Gas

The test for hydrogen is a method used to test the presence of hydrogen. This is achieved by inserting a glowing splint into the reaction test tube. If it burns with a ‘pop’ sound, then hydrogen is present. The ‘pop’ is the sound of a small explosion, hydrogen is highly flammable

Uses

1. Hydrogen was formerly used for filling balloons, airships, and other lighter-than-air craft, because it has a low density.
2. Hydrogen is used in the Haber process for the fixation of atmospheric nitrogen, in the production of methanol, and in hydrogenation of fats and oils.
3. It is also important in low-temperature research. It can be liquefied under pressure and cooled; when the pressure is released, rapid evaporation takes place and some of the hydrogen solidifies.
4. Hydrogen is used in manufacture of ammonia by Haber process
5. Hydrogen is used in the manufacture of ammonia, hydrochloric acid and methanol.
6. Hydrogen is a constituent of many gaseous fuels such as water gas and coal gas.

Hydrogen Peroxide

Hydrogen peroxide is a chemical compound of hydrogen and oxygen with the formula H_2O_2. Pure, anhydrous hydrogen peroxide is a colourless, syrupy liquid with a specific gravity of 1.44. It blisters the skin and has a metallic taste. The liquid solidifies at −0.41 °C. Concentrated solutions are unstable, and the pure liquid can explode violently if heated to a temperature above 100 °C. It is soluble in water in all proportions, and the usual commercial forms are a 3 % and a 30 % aqueous solutions. To retard the decomposition of the peroxide into water and oxygen, organic substances, such as acetanilide, are added to the solutions, and they are kept in dark bottles at low temperature.

Preparation Methods of Hydrogen Peroxide

Hydrogen peroxide is manufactured in large amounts by the electrolysis of aqueous solutions of sulfuric acid (or of potassium bisulfate or ammonium bisulfate):

$H_2SO_4 \rightleftarrows H^+ + HSO_4^-$

On cathode On anode

$2H^+ + 2e^- \rightarrow H_2$ $2HSO_4^- - 2e^- \rightarrow H_2S_2O_8$

$2H_2SO_4 \rightarrow H_2S_2O_8 + 2H^+ + 2e^-$;

$H_2S_2O_8 + 2H_2O \rightarrow 2H_2SO_4 + H_2O_2$.

It is prepared also by the reaction of acid with other peroxides, such as those of sodium and barium:

$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$;

$BaO_2 + H_2SO_4 \rightarrow BaSO_4^- + H_2O_2$.

Chemical Properties of Hydrogen Peroxide

- Acid-base properties

Hydrogen peroxide is a week acid. In an aqueous solution it ionizes forming hydronium-ion and peroxid-ion:

$H_2O_2 + H_2O \rightleftarrows H_3O^+ + O_2^{2-}$

- Oxidation-reduction properties

Hydrogen peroxide acts as both an oxidizing and a reducing agent.

In acidic solution it is an oxidizing agent:

$2KI + H_2O_2 + H_2SO_4 \rightarrow I_2 + K_2SO_4 + 2H_2O$

However both in basic and in a neutral solutions hydrogen peroxide can be an oxidizing agent:

$Cr_2(SO_4)_3 + 3H_2O_2 + 10NaOH \rightarrow 2Na_2CrO_4 + 3Na_2SO_4 + 8H_2SO_4$

$PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$

At the presence of oxidizing agent it exhibits reduction properties in acidic, basic and neutral solutions:

$Cl_2 + H_2O_2 \rightarrow 2HCl + O_2$;

$Ag_2O + H_2O_2 \rightarrow H_2O + O_2 + 2Ag$;

$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + 5O_2 + K_2SO_4 + 8H_2O$

- Decomposition of hydrogen peroxide

Light, heating and the heavy metals hardly accelerate the process of hydrogen peroxide decomposition:

$$2H_2O_2 \xrightarrow{MnO_2} 2H_2O + O_2$$

Uses

1. Its oxidizing properties are used in the bleaching of substances, such as hair, ivory, feathers, and delicate fabrics, which would be destroyed by other agents.
2. It is used also medicinally, in the form of a 3 % aqueous solution, as an antiseptic and throat wash.
3. Hydrogen peroxide is used in restoring the original colors on paintings that have darkened through the conversion of the white lead used in the paintings to lead sulfide.
4. The hydrogen peroxide oxidizes the black lead sulfide to white lead sulfate.
5. It is used also as a source of oxygen in the fuel mixture for many rockets and torpedoes.

Assessment

1. An isotope of Hydrogen commonly referred to as heavy water is
   a. protium
   b. deuterium
   c. tritium
   d. basic water
2. Hydrogen is manufacture via the following methods except
   a. action of steam on iron
   b. action of steam on red hot coke
   c. action of steam on methane under nickel catalyst
   d. electrolytic method
3. All except one can displace hydrogen from water or acids
   a. Zinc
   b. Silver
   c. Potassium
   d. Heated Magnesium
4. Sodium hydride reacts with water to
   a. form an acidic solution
   b. liberate hydrogen gas
   c. form a salt
   d. liberate oxygen
   e. form a neutral solution

Answers

1. B
2. B
3. B
4. B

THIRD TERM NOTES ON CHEMISTRY

Week 1

Topic: Water

Content

- **Sources of Water**
- **Types of Water**
- **Water Pollution**
- **Uses of Water**

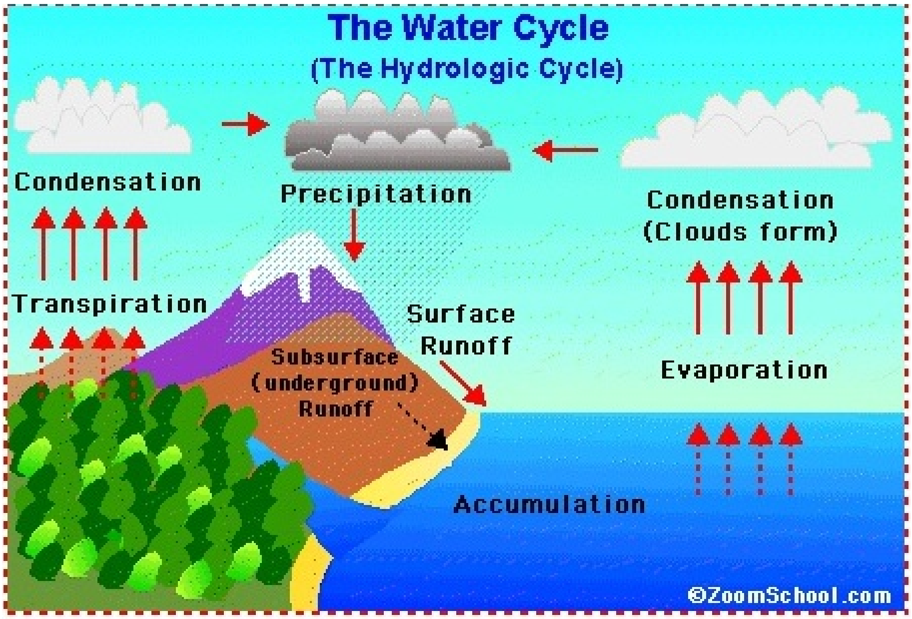
Introduction

We live on a planet that is dominated by water. More than 70% of the Earth’s surface is covered with this simple molecule. Scientists estimate that the hydrosphere contains about 1.36 billion cubic kilometers of this substance mostly in the form of a liquid (water) that occupies topographic depressions on the Earth. Water is also essential for life. Water is the major constituent of almost all life forms. Most animals and plants contain more than 60% water by volume. Without water life would probably never have developed on our planet.

Water has a very simple atomic structure. This structure consists of two hydrogen atoms bonded to one oxygen atom. The nature of the atomic structure of water causes its molecules to have unique electrochemical properties. The hydrogen side of the water molecule has a slight positive charge. On the other side of the molecule a negative charge exists. This molecular polarity causes water to be a powerful solvent and is responsible for its strong surface tension

Water Cycle

The Water Cycle (also known as the hydrologic cycle) is the journey water takes as it circulates from the land to the sky and back again.



The Sun's heat provides energy to evaporate water from the Earth's surface (oceans, lakes, etc.). Plants also lose water to the air (this is called transpiration). The water vapour eventually condenses, forming tiny droplets in clouds. When the clouds meet cool air over land, precipitation (rain, sleet, or snow) is triggered, and water returns to the land (or sea). Some of the precipitation soaks into the ground. Some of the underground water is trapped between rock or clay layers; this is called groundwater. But most of the water flows downhill as runoff (underground), eventually returning to the seas as slightly salty water.

Sources of Water

- Rain water
- Spring water
- Well water
- River water
- Lake water
- Tap water
- Sea water

Types of Natural Water

There are four major types of natural water:

Rain Water: This is the purest form of natural water because it is formed as a result of the condensation of water vapour in the atmosphere. Rain water contains small impurities like gases such as CO_2 from the air and also dust particles present in the air. Dissolved oxygen and nitrogen will always be present in rain water.

River Water: Rivers are used extensively for sewage disposal. River water contains a lot of dissolved air, mineral salts, bacteria and organic remains. It is dirty and needs to be purified especially before drinking.

Spring Water: Spring water is purer than river water. It contains a considerable amount of mineral salts but very little suspended impurities such as dust and bacteria. It is good for drinking

Sea Water: This is the most impure form of water because impure water is constantly flowing into it and at the same time, pure water is constantly leaving it by evaporation. The main inorganic metallic salt present in sea water is sodium chloride, but magnesium, calcium and potassium salts are also present. Of all the solid impurities in sea water, the most important ones are calcium tetraoxosulphate (VI) and calcium hydrogentrioxocarbonate (IV)

Types of Water

Water is of two types namely hard and soft water

Hard Water – Hard water will not lather readily with soap. It contains a numbe rof dissolved salts, the most being calcium tetraoxosulphate (vi), magnesium tetraoxosulphate (vi). **Hard water** is formed when **water** percolates through deposits of limestone and chalk which are largely made up of calcium and magnesium carbonates.

Advantages of Hard Water

- It has dissolved mineral contents
- The calcium salt present in hard water, when taken by animals can help build strong bones
- Hard water helps animals such as snails to make their shells
- Hard water can be supplied in pipes made of lead and it wont dissolve the lead.

Disadvantages

- It requires lots of soap for washing. It wastes soap
- It causes furring in Kettles and broilers
- It cannot be used in dyeing and tanning as the salts in it interfere with the modes of actions of the processes

Soft Water

Soft water is **water** which has relatively low concentration of calcium carbonate and other ions . The **water** that lathers with soap easily is called or known as **soft water**. It describes type of **water** that contain few or no minerals like calcium (Ca) or magnesium (Mg) ions.

Uses of Water

- Domestic Purposes – cooking. drinking. bathing. washing.
- Agricultural Purposes – farming, gardening, fisheries, irrigation
- Industrial Purposes – manufacturing.
- Recreation- swimming, rafting, boating.
- Hydropower generation.

- For building construction
- For the generation of steam for industrial use and electricity generation
- For the manufacture of hydrogen, oxygen and water gas
- As a solvent.

What makes water a universal solvent

The following properties of water make it a universal solvent

(i) Water is a polar molecule

(ii) Water can form hydrogen bonds with other polar compounds.

(iii) Water dissolves many substances by reacting with them chemically.

(iv) Water is cheap and easily available everywhere.

Water Pollution

Water pollution has been extensively documented as a contributor to health problems in humans and marine animal ecosystems. It has a huge impact on our lives, and if we do our part by not throwing trash or chemicals into our water supplies and drains, we can contribute to the improvement of aquatic life and of our health in general.

What is water pollution?

Water pollution is any chemical, physical or biological change in the quality of water that has a harmful effect on any living thing that drinks or uses or lives (in) it.

In other words, water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, aquifers and groundwater), very often by human activities.

It has been suggested that it is the leading worldwide cause of deaths and diseases and that it accounts for the deaths of more than 14,000 people daily.

Water covers 70% of the Earth's surface and makes up over 60% of the human body. Water pollution affects marine ecosystems, wildlife health, and human well-being. The answer to solving pollution is to make changes in our daily habits and pay more attention to the types of products we consume. The following lists display causes of water pollution and the effects it has on human health and the environment.

Types of water pollution

There are many types of water pollution because water comes from many sources. Here are a few types of water pollution:

1. **Nutrients Pollution**
Some waste water, fertilizers and sewage contain high levels of nutrients. If they end up in water bodies, they encourage algae and weed growth in the water. This will make the water undrinkable, and even clog filters. Too much algae will also use up all the oxygen in the water, and other water organisms in the water will die out of oxygen from starvation.

2. **Surface water pollution**
Surface water includes natural water found on the earth's surface, like rivers, lakes, lagoons and oceans. Hazardous substances coming into contact with this surface water, dissolving or mixing physically with the water can be called surface water pollution.

3. **Oxygen Depleting**
Water bodies have micro-organisms. These include aerobic and anaerobic organisms. When to much biodegradable matter (things that easily decay) end up in water, it encourages more microorganism growth, and they use up more oxygen in the water. If oxygen is depleted, aerobic organisms die, and anaerobic organism grow more to produce harmful toxins such as ammonia and sulphides.

4. **Ground water pollution**
When humans apply pesticides and chemicals to soils, they are washed

deep into the ground by rain water. This gets to underground water, causing pollution underground. This means when we dig wells and bore holes to get water from underground, it needs to be checked for ground water pollution.

5. Microbiological

In many communities in the world, people drink untreated water (straight from a river or stream). Sometimes there is natural pollution caused by microorganisms like viruses, bacteria and protozoa. This natural pollution can cause fishes and other water life to die. They can also cause serious illness to humans who drink from such waters.

6**. Suspended Matter**

Some pollutants (substances, particles and chemicals) do not easily dissolve in water. This kind of material is called particulate matter. Some suspended pollutants later settle under the water body. This can harm and even kill aquatic life that live at the floor of water bodies.

7. **Chemical Water Pollution**

Many industries and farmers work with chemicals that end up in water. These include chemicals that are used to control weeds, insects and pests. Metals and solvents from industries can pollute water bodies. These are poisonous to many forms of aquatic life and may slow their development, make them infertile and kill them.

8. **Oil Spillage**

Oil spills usually have only a localized affect on wildlife but can spread for miles. The oil can cause the death of many fish and stick to the feathers of seabirds causing them to lose the ability to fly.

In BP Oil spill in 2010, Over 1,000 animals (birds, turtles, mammals) were reported dead, including many already on the endangered species list. Of the animals affected by the spill that are still alive only about 6% have been reported cleaned, but many biologists and other scientists predict they will die too from the stress caused by the pollution

GLOBAL WATER POLLUTION

Global warming is also imparting additional heat to the oceans. Estimates suggest that nearly 1.5 billion people lack safe drinking water and that at least 5 million deaths per year can be attributed to waterborne diseases.

Fighting Global Warming

In terms of water pollution, there are two main threats from global warming:

- Ocean Acidification
- Ocean Temperature

Causes of Water Pollution

- Sewage from domestic households, factories and commercial buildings Sewage that is treated in water treatment plants is often disposed into the sea. Sewage can be more problematic when people flush chemicals and pharmaceutical substances down the toilet.

- Dumping solid wastes and littering by humans in rivers, lakes and oceans. Littering items include cardboard, Styrofoam, aluminum, plastic and glass.
- Industrial waste from factories, which use freshwater to carry waste from the plant into rivers, contaminates waters with pollutants such as asbestos, lead, mercury and petrochemicals.
- Oil Pollution caused by oil spills from tankers and oil from ship travel. Oil does not dissolve in water and forms a thick sludge.
- Burning fossil fuels into the air causes the formation of acidic particles in the atmosphere. When these particles mix with water vapor, the result is acid rain.
- An increase in water temperature is caused by global warming and thermal plants that use lakes and rivers to cool down mechanical equipment.

Effects of Water Pollution

- Groundwater contamination from pesticides causes reproductive damage within wildlife in ecosystems.
- Sewage, fertilizer, and agricultural run-off contain organic materials that when discharged into waters, increase the growth of algae, which causes the depletion of oxygen. The low oxygen levels are not able to support most indigenous organisms in the area and therefore upset the natural ecological balance in rivers and lakes.
- Swimming in and drinking contaminated water causes skin rashes and health problems like cancer, reproductive problems, typhoid fever and stomach sickness in humans. Which is why it's very important to make sure that your water is clean and safe to drink.
- Industrial chemicals and agricultural pesticides that end up in aquatic environments can accumulate in fish that are later eaten by

humans. Fish are easily poisoned with metals that are also later consumed by humans. Mercury is particularly poisonous to small children and women. Mercury has been found to interfere with the development of the nervous system in fetuses and young children.

- Ecosystems are destroyed by the rising temperature in the water, as coral reefs are affected by the bleaching effect due to warmer temperatures. Additionally, the warm water forces indigenous water species to seek cooler water in other areas, causing an ecological damaging shift of the affected area.
- Human-produced litter of items such as plastic bags and 6-pack rings can get aquatic animals caught and killed from suffocation.
- Water pollution causes flooding due to the accumulation of solid waste and soil erosion in streams and rivers.
- Oil spills in the water causes animal to die when they ingest it or encounter it. Oil does not dissolve in water so it causes suffocation in fish and birds.

Prevention of water pollution

Dealing with water pollution is something that everyone (including governments and local councils) needs to get involved with. Here are a few things you can do to help.

- Never throw rubbish away anyhow. Always look for the correct waste bin. If there is none around, please take it home and put it in your trash can. This includes places like the beach, riverside and water bodies.
- Use water wisely. Do not keep the tap running when not in use. Also, you can reduce the amount of water you use in washing and bathing. If we all do this, we can significantly prevent water shortages and reduces the amount of dirty water that needs treatment.

- Do not throw chemicals, oils, paints and medicines down the sink drain, or the toilet. In many cities, your local environment office can help with the disposal of medicines and chemicals. Check with your local authorities if there is a chemical disposal plan for local residents.
- Buy more environmentally safe cleaning liquids for the use at home and other public places. They are less dangerous to the environment.
- If you use chemicals and pesticides for your gardens and farms, be mindful not to overuse pesticides and fertilizers. This will reduce runoffs of the material into nearby water sources. Start looking at options of composting and using organic manure instead.If you live close to a water body, try to plants lots of trees and flowers around your home, so that when it rains, chemicals from your home does not easily drain into the water.
- Governments, local councils and laws
  Many governments have very strict laws that help minimize water pollution. These laws are usually directed to industries, hospitals, schools and market areas on how to dispose, treat and manage sewage. Do you know the laws in your country? This is the time to find out.
- In many developed cities, waste or sewage treatment is very efficient, and designed to minimise pollution of water bodies. Click on the button below to see an example of how a good sewage (wastewater) treatment works.

Solution

A solution is a homogenous mixture of two or more substances that exist in a single phase. There are two main parts to any solution.

- The solute is the component of a solution that is dissolved in the solvent; it is usually present in a smaller amount than the solvent.

- The solvent is the component into which the solute is dissolved, and it is usually present in greater concentration.

For example, in a solution of salt water, salt is the solute and water is the solvent. In solutions where water is the solvent, the solution is referred to as an aqueous solution.

A solution does not have to involve liquids. For instance, air is a solution that consists of nitrogen, oxygen, carbon dioxide, and other trace gases, and solder is a solution of lead and tin. The general rule of thumb for solutions is the idea that like dissolves like. Polar, ionic substances are soluble in polar solvents, while non-polar solutes are soluble in non-polar solvents. For example, alcohol and water, which are both polar, can form a solution and iodine and carbon tetrachloride, which are both non-polar, make a solution. However, iodine will not readily dissolve in polar water.

Types of Solutions

At the molecular level, molecules and ions of a solute are completely mixed with and interact with those of the solvent when a solute dissolves in a solvent. This type of mixing is homogeneous because no boundary is visible in the entire solution. In a mixture, differences may exist between regions or parts of the whole system.

Material exists in three states: solid, liquid, and gas. Solutions exist in all these states:

1. Gaseous mixtures are usually homogeneous and all gases mixtures are gas-gas solutions. The air is a natural gas solution, but its water and carbon dioxide contents may vary depends on the temperature and places.
2. When molecules of gas, solid or liquid are dispersed and mixed with those of liquid, the homogeneous (uniform) states are called liquid solutions. Solid, liquid and gas dissolve in liquid to form liquid solutions. In general, the terms solution and liquid solution are synonymous. Gases and liquid solutions have attracted the attention of most chemists, while material scientists and engineers

are more interested in the manufacture and properties of solid solutions.

3. Many alloys, ceramics, and polymer blends are solid solutions. Within certain range, copper and zinc dissolve in each other and harden to give solid solutions called brass. Silver, gold, and copper form many different alloys with unique colours and appearances. Alloys and solid solutions are important in the world of materials. The research, development, manufacture, and production of these material are big business.

True Solutions and Colloidal Solution

When solute particles dissolve such that they are able to get in between the solvent particles, the resultant homogenous mixture is called true solution. The solute particles, which are simple molecules or ions, are too small to be seen by naked eye and are called crystalloids. Example of true solutions are aqueous solutions of sodium chloride and copper (II) tetraoxosulphate (VI).

In false solutions or colloidal solutions, the individual solute particles are larger than the particles of the true solution, but not large enough to be seen by naked eye. Some examples of colloids are addition of starch to water. Milk is also a colloidal solution of fat in a watery liquid.

Suspension

A suspension is a heterogenous mixture of undissolved particles in a given medium. The particles are usually large enough to be seen without the aid of an instrument, and they eventually settle down if left standing.

The slow settling at the bottom of the particles is known as sedimentation. A suspension can be separated by filtration or centrifuge. The muddy water is a typical example of suspension. The muddy water will settle after a time, if left undisturbed, leaving a brown residue on the bottom of the containing vessel and clear water above.

Assessment

1. One of the following is a disadvantage of Hard water
   a. It has dissolved mineral contents
   b. The calcium salt present in hard water, when taken by animals can help build strong bones
   c. It requires lots of soap for washing
   d. Hard water helps animals such as snails to make their shells
2. One of the following does not make water a universal solvent
   a. Water is a polar molecule
   b. Water can form hydrogen bonds with other polar compounds.
   c. Water dissolves many substances by reacting with them chemically.
   d. Water has bipolar nature
3. The **water** that lathers with soap easily is called or known as ....
   a. Soft water
   b. Hard water
   c. Rain water
   d. Pure water
4. .... water is the purest form of natural water because it is formed as a result of the condensation of water vapour in the atmosphere
   a. Rain
   b. River
   c. Lake
   d. Spring
5. Water is temporarily hard because it contains
   a. Chlorine
   b. $CaSO_4$
   c. $Ca(HCO_3)_3$
   d. $CuSO_4$

Answers

1. C
2. D
3. A
4. A
5. B

Week 2

Topic: Water

Contents

- **Structure of Water**
- **Causes and Removal of Hardness of Water**
- **Water Purification**
- **Distilled Water**

Introduction

Water is a transparent and nearly colorless chemical substance that is the main constituent of Earth's streams, lakes, and oceans, and the fluids of most living organisms.

Density: 1 g/cm³

Molar mass: 18.01528 g/mol

Melting point: 0 °C

Boiling point: 99.98 °C

IUPAC ID: Water, Oxidane

Structure of Water

1. A water molecule is composed of two hydrogen atoms and one oxygen atom

2. Two lone-pair electrons from the oxygen atom make two lobes of negative density in the overall molecule
3. Large dipole moment—gives 33% ionic character to O-H bonds

4. Large polarizability
5. The H-O-H angle is 104.3 degree

The structure of water contributes tremendously to its unique properties. Water has two Hydrogen atoms attached to an Oxygen atom give it some partial charges due to Oxygen's great electro-negativity. These partial charges are what make it possible for water to form hydrogen bonds.

It is also due to its bent shape, due to the two lone pairs of electrons, which allow it to have this dipole moment. If it was linear, then it would not contain a dipole because both individual dipole's would be pulling against each other, thus canceling. Thanks to the electron pairs and their repulsions, water is in a bent shape, and the polarity is allowed to exist.

Test for Water

When a few drops of water are added to:

- white anhydrous copper (II) tetraoxosulphate (VI), it turns blue
- blue cobalt (II) chloride, it turns pink

Hardness of Water

Hard water contains dissolved magnesium and calcium ions. These make it more difficult for the water to form lather with soap.

Hardness in water is caused by dissolved magnesium ions and calcium ions. These can get into the water when it comes into contact with limestone and other rocks that contain calcium compounds. This can happen, for example, when rainwater flows over these rocks on its way to a reservoir.

Types of Hardness of Water

There are two types of hardness: temporary hardness and permanent hardness

- Temporary hardness

Temporary hardness is caused by dissolved calcium hydrogentrioxocarbonate (IV), $Ca(HCO_3)_2$.

Rainwater is naturally acidic because it contains dissolved carbon dioxide from the air. It reacts with calcium carbonate in rocks to form calcium hydrogentrioxocarbonate (IV) (which is soluble):

calcium carbonate + water + carbon dioxide → calcium hydrogentrioxocarbonate(IV)

Temporary hardness is removed by boiling the water. When this happens, the soluble calcium hydrogentrioxocarbonate(IV) decomposes (breaks down) to form calcium carbonate (which is insoluble), water and carbon dioxide:

calcium hydrogentrioxocarbonate(IV) → calcium carbonate + water + carbon dioxide

$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$

The insoluble calcium carbonate forms a layer of limescale. This may coat the heating element in kettles and irons (furring of kettle and boilers), for example, making it less efficient. Limescale is unsightly and it clogs up hot water pipes and boilers.

- Permanent hardness

Permanent hardness is caused by dissolved magnesium or calcium tetraoxosulphate(VI). Unlike temporary hardness, it is not removed by boiling the water.

Softening water (removal of water hardness)

Hardness can be removed by adding sodium carbonate (washing soda) or by passing the water through an ion-exchange column.

- Washing soda

Sodium carbonate (Na_2CO_3), also known as washing soda, can soften both temporary and permanent hard water. It is soluble in water and adds a large amount of carbonate ions to the water. These react with dissolved calcium ions, forming a precipitate of calcium carbonate:

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

Remember: the calcium ions come from the hard water and the carbonate ions from the washing soda.

- Ion-exchange

Ion-exchange resins can also soften both temporary and permanent hard water. The resin is made into small balls around 1–2 mm in diameter, which are packed into a tube or ‘column’. The ion-exchange resin starts with sodium ions stuck to it.

As the hard water passes through the column, sodium ions come off the resin and go into the water, while calcium ions come out of the water and stick to the resin. In effect, calcium ions that do cause hardness are swapped for sodium ions that do not cause hardness.

Dish washing machines contain ion-exchange resin to soften the water used to wash the dishes. The resin needs recharging with dishwasher salt (sodium chloride) once it becomes full of calcium ions.

Purification of Water

Purification is the act of removing pollutants from water so that it is fit for drinking. This can be achieved by a number of methods including filtration, sedimentation, chlorination and other chemical treatments.

Filtration: It is one of the methods to purify water through the use of filter paper but , the water might not be good for drinking, as it can still contain germs. Filtration would make the water clear, and can be done in laboratory in small quantity.

Sedimentation: For drinking purposes the clear water obtained by filtration is not pure enough and particles which are not retained by the filter beds have to be removed. This is done by adding powdered potash alum. This will coagulate all the particles to settle at the bottom of the container.

Chlorination: The clear water from the above method may still contain harmful bacteria and other microbes. These germs can be killed by boiling the water if we need small quantity of water. For a large scale water supply chlorine is added to the water to kill harmful germs.

General Properties of Water

Water has several other unique physical properties. These properties are:

- Water has a high specific heat. Specific heat is the amount of energy required to change the temperature of a substance. Because water has a high specific heat, it can absorb large amounts of heat energy before it begins to get hot. It also means that water releases heat energy slowly when situations cause it to cool. Water's high specific heat allows for the moderation of the Earth's climate and helps organisms regulate their body temperature more effectively.
- Water in a pure state has a neutral pH. As a result, pure water is neither acidic nor basic. Water changes its pH when substances are dissolved in it. Rain has a naturally acidic pH of about 5.6 because it contains natural derived carbon dioxide and sulphur dioxide.
- Water conducts heat more easily than any liquid except mercury. This fact causes large bodies of liquid water like lakes and oceans to have essentially a uniform vertical temperature profile.
- Water molecules exist in liquid form over an important range of temperature from 0 – 100° Celsius. This range allows water molecules to exist as a liquid in most places on our planet.
- Water is a universal solvent. It is able to dissolve a large number of different chemical compounds. This feature also enables water to carry solvent nutrients in runoff, infiltration, groundwater flow, and living organisms.
- Water has a high surface tension. In other words, water is adhesive and elastic, and tends to aggregate in drops rather than spread out

over a surface as a thin film. This phenomenon also causes water to stick to the sides of vertical structures despite gravity's downward pull. Water's high surface tension allows for the formation of water droplets and waves, allows plants to move water (and dissolved nutrients) from their roots to their leaves, and the movement of blood through tiny vessels in the bodies of some animals.

- Water molecules are the only substance on Earth that exist in all three physical states of matter: solid, liquid, and gas. Incorporated in the changes of state are massive amounts of heat exchange. This feature plays an important role in the redistribution of heat energy in the Earth's atmosphere. In terms of heat being transferred into the atmosphere, approximately 3/4's of this process is accomplished by the evaporation and condensation of water.
- The freezing of water molecules causes their mass to occupy a larger volume. When water freezes it expands rapidly adding about 9% by volume. Fresh water has a maximum density at around 4° Celsius (see Table 8a-1). Water is the only substance on this planet where the maximum density of its mass does not occur when it becomes solidified.

Physical Properties of Pure Water

1. It freezes at 0°C
2. It is clear and colourless
3. It has no smell and has insipid taste
4. It boils at 100°C
5. It is neutral to litmus
6. Its maximum density is 1g cm^{-3} at 4°C
7. It turns anhydrous copper (II) tetraoxosulphate (VI) blue. (This test denotes merely the presence of water).

Chemical Properties of Water

1. Water reacts with metals in a number of ways, with the degree of reactivity depending on the position of the metal in the electrochemical series.

- Sodium, potassium and calcium react with cold water to form alkalis and liberate hydrogen
- Magnesium and zinc react only with steam to liberate hydrogen and form oxides
- Iron reacts only with excess steam at red heat
- Copper, gold, silver and mercury do not react with water in any form

2. Non-metals like chlorine, oxygen and silicon also react with water
3. Oxides of alkaline metals readily form strong alkalis or hydroxides with water. Calcium oxide partially dissolve in water to form calcium hydroxide or slaked lime
4. Certain oxides of non-metals like carbon, sulphur and nitrogen form acids with water.
5. Water reacts with organic and inorganic compounds. Such reactions are generally described as hydrolysis.

For example, Al_2S_3 (s) + $6H_2O$ (l) ——-> $2Al(OH)_3$ (s) + $3H_2S$ (g)

Distilled Water

Distilled water is chemically pure water. It is prepared by condensing steam using Liebig condenser. Water prepared using exchange resin is called deionized water.

Distilled water is used in

- the laboratory for preparing reagents and analytical work
- industrial processes
- preparation of drugs

- car batteries

Assessment

1. Temporary hardness of water is removed by the use of the following except
   a. boiling
   b. use of $Ca(OH)_2$
   c. use of slake lime
   d. use of alum
2. Distilled water is different from deionized water because
   a. distilled water is a product of condensed steam while deionized water is filtered laboratory water
   b. distilled water is always pure and sold in packs while deionized water is not packaged for consumption
   c. distilled water is a product of condensed steam while deionized water is produced using exchange resins which absorbed undesired ions
   d. distilled water is man made while deionized water is natural and artificial
3. One of the following is not a physical property of water
   a. It is clear and colourless
   b. It has no smell and has insipid taste
   c. It boils at 0°C
   d. It is neutral to litmus
4. Water in a pure state has a .... pH.
   a. Neutral
   b. Acidic
   c. Basic
   d. Alkaline
5. Test for water: When few drops of water is added to blue cobalt (II) chloride, it turns ......
   a. red
   b. pink

c. orange
d. remains blue

Answers

1. D
2. C
3. C
4. A
5. B

Week 3

Topic: Solubility

Introduction

The term solubility refers to the maximum amount of material that will dissolve in a given amount of solvent at a given temperature to produce a stable solution.

Saturated and Unsaturated Solution

A saturated solution of a solute at a particular temperature is one which contains as much solute as it can dissolve at that temperature in the presence of undissolved solute particles.

A given volume of water can only dissolve a certain amount of salt in it at room temperature. If more salt is added to such a solution, the salt will remain undissolved. Such a salt solution is said to be saturated. On the other hand, an unsaturated solution can continue to dissolve more solutes, if added, until the solution becomes saturated. In a saturated solution, the dissolved solutes and the undissolved solutes are in equilibrium at a particular temperature.

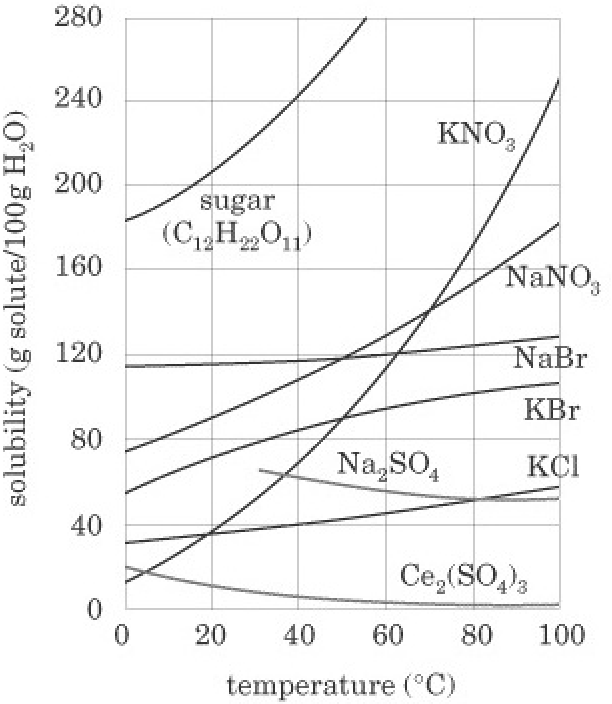
Supersaturated solution

A supersaturated solution is one which contains more of the solute than it can normally hold at that temperature. Supersaturated solution is unstable and the excess solute will separate out if the solution is disturbed slightly by shaking or even a dust particle is dropped into it.

Solubility graphs or curves

If the solubilities of a solute in a given solvent are plotted against their respective temperatures, a solubility graph or curve showing the effect of temperature on the solubility of the substance will be obtained.

By looking at the plot of solubilities below, you can see that most solids increase in solubility with an increase in temperature.



Gases, however, decrease in solubility with an increase in temperature.

Degrees of Saturation

When referring to solutions, there are three degrees of saturation—unsaturated, saturated, and supersaturated. If a solution is unsaturated, the solvent is capable of dissolving more solute. When the solution is saturated, the solvent has dissolved the maximum amount of solute that it can at the given temperature. At this point we say that the solution is in a state of dynamic equilibrium—the processes of dissolving and precipitation are happening at the same rate. A supersaturated solution is one in which the solvent contains more solute than it can theoretically hold at a given temperature. Supersaturated solutions are often formed by heating a solution and dissolving more solute, then cooling the solution down slowly. These solutions are unstable and crystallize readily.

Concentration Terms

Solutions are often referred to as being concentrated or dilute. These two terms are very general. While concentrated indicates that there is a lot of solute dissolved in the solvent (perhaps the solution is near to being saturated) and dilute indicates that a small amount of solute is dissolved in the solvent.

Molarity (M)

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

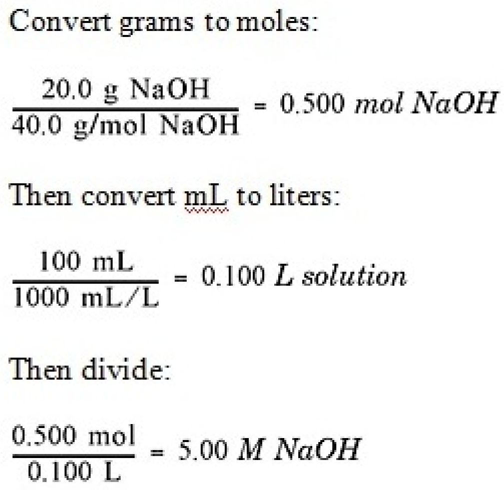
The molarity of a solution is a measure of the number of moles of solute per liter of solution. For instance,

[NaCl] = 0.75

This means that 0.75 mole of NaCl is dissolved per 1.00 L of solution. The brackets around the number indicate that the concentration is expressed in terms of molarity.

Example 1: Calculate the molarity of a solution prepared by dissolving 20.0 g of solid NaOH in enough water to make 100 mL of solution.

Solution:



Convert grams to moles:

$$\frac{20.0\ \text{g NaOH}}{40.0\ \text{g/mol NaOH}} = 0.500\ mol\ NaOH$$

Then convert mL to liters:

$$\frac{100\ \text{mL}}{1000\ \text{mL/L}} = 0.100\ L\ solution$$

Then divide:

$$\frac{0.500\ \text{mol}}{0.100\ \text{L}} = 5.00\ M\ NaOH$$

Dilution

Dilution is the process of taking a more concentrated solution and adding water to make it less concentrated. The concentration of the diluted solution using the equation below:

$M_1V_1 = M_2V_2$

where M is molarity and V is the volume, in liters, of the solution.

Example 1:

What volume of 6.0 M sulfuric acid (H_2SO_4) must be used to prepare 2.0 L of a 0.10 M H_2SO_4 solution?

Solution:

$M_1V_1 = M_2V_2$

(6.0 M) (V_1) = (0.10 M) (2.0 L)

V_1 = 0.033 L

or 33 mL should be measured out and then diluted by adding enough water to make 2.00 L total volume.

Calculations on Solubility

Examples 1: If 12.2 g of lead(II) trioxonitrate(V) were dissolved in 21 g of distilled water at 20°C, calculate the solubility of the solute in mol dm^{-3}.

Solution:

Molar mass of $Pb(NO_3)_2$ = 331 g

12.2 g of $Pb(NO_3)_2$ = 12.2/331 = 0.037 mole

21 g of water at 20°C dissolved 0.037 mole of $Pb(NO_3)_2$

1000 cm3 of water at 20 °C dissolved 1000 x 0.037 / 21

= 1.76 moles of $Pb(NO_3)_2$

At 20°C, the solubility of $Pb(NO_3)_2$ in water is 1.76 mol dm^{-3}

Using formula Method

Solubility = mass/molar mass x 1000/vol

= 12.2/331 x 1000/21

= 1.7751 mol dm^{-3}

= 1.76 mol dm^{-3}

Example 2: The solubility of potassium trioxonitrate (V) is exactly 1800 g per 1000 g water at 83°C and 700 g per 1000 g water at 40°C. Calculate the mass of potassium trioxonitrate (V) that will crystallize out of solution if 155 g of the saturated solution at 83 °C is cooled to 40°C.

Solution:

	Solvents	+	Solution	= Solution
Masses involved at 83°C	1000 g		1800 g	= 2800 g
Masses involved at 40°C	1000 g		700 g	= 1700 g

Solute deposited on cooling from 83°C to 40°C = 2800 – 1700 = 1100 g

On cooling from 83°C to 40°C,

2800 g of saturated solution deposit 1100 g of solute

155 g of saturated solution will deposit = 1100 x 155 / 2800

= 60.89 g of solute

Application of Solubility Curves

1. Solubility curves enable pharmacists to determine the amounts of solid drugs that must be dissolved in a given quantity of solvent to give a prescribed drug mixture
2. The curves also enable chemists and research workers to determine the most suitable solvents to be used at various temperatures for the extraction of essential chemicals from various natural sources.
3. With the help of solubility curves, a given mixture of solutes can be separated or purified by fractional crystallization.

Assessment

1. A supersaturated solution is one which contains more of the …….. than it normally holds at that temperature
   a. solute
   b. solvent
   c. solution
   d. none of the above
2. The solubility of Calcium trioxocarbonate is exactly 1500 g per 500 g water at 79°C and 400 g per 500 g water at 30°C. Calculate the mass of Calcium trioxocarbonate that will crystallize out of solution if 280 g of the saturated solution at 79 °C is cooled to 30°C.
3. What volume of 8.0 M sulfuric acid (H_2SO_4) must be used to prepare 5.0 L of a 0.20 M H_2SO_4 solution? (Hint – M1V1 = M2V2)
4. A saturated solution of a solute at a particular temperature is one which contains as much solvents as it can dissolve at that

temperature in the presence of undissolved solute particles.
True/False

Answers

1. A
2.
3.
4. False

Week 4

Topic: Mass and Volume Relationships

Mass and Volume

Mass is the amount of 'stuff' inside an object; the more stuff there is, the more mass.

Matter is made up of atoms and molecules, and the more of them we have, the greater the mass of an object is. We measure mass in units like kilograms, ounces, and pounds. In science, we prefer kilograms, which are the SI (Standard International) unit of mass. Your bathroom scale is calibrated to tell you your mass, but it only works properly on Earth. If you took it to the moon, the weight on the scale would change, but of course, your mass would not.

Volume is how much space something takes up. The standard unit of volume is meters cubed (or cubic meters). The classic question people ask to show the difference between mass and volume is, Which has the greatest mass, a pound of feathers or a pound of nails? Well, it's a pound of each, so they both have the same mass. It's just that a pound of feathers will take up a huge amount of space; it has a greater volume.

QUANTITY	SYMBOL	UNITS
Mass	m	g or Kg
Molar Mass	M	g mol^{-1}
Volume	V	cm^3, dm^3
Molar volume	Vm	dm^3 mol^{-1}
Amount	n	mol
Molar concentration	c	mol $dm-^3$
Mass concentration	p	g mol^{-1}

Avogadro's constant	L	mol^{-1}
Number	N	–
Molar mass	M	$g\ mol^{-1}$

Relationships between Quantities

M = m/n Molar volume = Mass/amount

Molar volume = Number/Amount

Avogadro's constant = L = N/A = Number /Amount

A mole is the amount of substance containing Avogadro's number of formular units

Mole Ratios and Mass Relationships

A mole is the amount of substance which contains as many elementary particles as there are carbon atoms in 0.012kg of carbon -12. The numerical coefficients of a balanced equation represent the numbers of moles of reactants and products. From these coefficients, we get the mole ratio of the reactants and products in a reaction. A balanced equation of a chemical reaction tells us the relationship of the amounts of reactants to one another and to the products. Their relationship between the amounts of reactants and products is known as the stoichiometry of the reaction.

Amount = reacting mass/Molar mass

Examples

1. Calculate the number of moles of calcium chloride $CaCl_2$ that can be obtained from 25g of limestone, $CaCO_3$, in the presence of excess hydrogen chloride, HCl. (Ca = 40, C = 12, O = 16, H = 1, Cl=35.5)
   Equation of Reaction
   $CaCO_{3(s)} + 2HCl \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$
   From the equation
   1 mole of $CaCO_3$ yields 1 mole of $CaCl_2$

Number of moles of $CaCO_3$ reacted
$\frac{\text{Reacting Mass}}{\text{Molar Mass}}$ = 25g/100 $gmol_{-1}$ = 0.25mol
0.25 mole $CaCO_3$ of yields 0.25 mole of $CaCl_2$

2. Determine the mass of Carbon(iv)oxide CO_2 produced on burning of 104g of ethyne, C_2H_2 (C=12, O = 16, H=1)
   Equation of Reaction $2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(g)}$
   Molar Mass: 26g 44g 2mol 4mol
   Amount of C_2H_2 reacted = $n = \frac{m}{M} = \frac{104g}{26\ g\ mol{-1}} = 4mol$ From the equation,2 moles of C_2H_2 produce 4 moles of CO_2

4 moles of C_2H_2 produce 4/2 x 4 = 8 moles of CO_2

8 x 44 = 352g of CO_2

352g of CO_2 are produced by burning 104g of C_2H_2

3. Calculate the volume of carbon dioxide formed at STP in 'ml' by the complete thermal decomposition of 3.125 g of pure calcium carbonate (Relative atomic mass of Ca=40, C=12, O=16)As per the equation, $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2\ (g)$ 40 + 12 + (16 x 3) 1 mole100g 22.4 litres100 g 24400 mlVolume of carbon dioxide formed from 100 g of $CaCO_3$ = 22400 ml

Volume of carbon dioxide from 3.125 g of $CaCO_3$ = ?

$CaCO_3$: CO_2

100 g : 22400 ml

3.125 g : x

$$x = \frac{3.125 \times 22400}{100} = 700\,ml$$

Volume of carbon dioxide formed = 700 ml.

Volume Volume Relationship

4. Calculate the approximate volume of air needed at STP, to oxidize 4480 litres of ammonia to nitric oxide in the Ostwald's process.

Solution:

As per the equation,

$$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(vap)$$

4 vols. : 5 vols.

4 x 22.4 litres : 5 x 22.4 litres

89.6 litres : 112 litres

Volume of oxygen required to oxidize 89.6 litres of ammonia = 122 litres

Volume of oxygen required to oxidize 4480 litres of ammonia =?

NH_3 : O_2

89.6 : 112

4480 : x

$$x = \frac{4480 \times 112}{89.6} = 5600 \text{ litres}$$

But oxygen forms only $\frac{1}{5}$th the volume of air.

Hence volume of air needed = 5600 x 5 = 28000 litres

Volume of air = 28000 litres.

Example

6. About 560 ml of carbon monoxide is mixed with 500 ml of oxygen and ignited. Calculate the volume of carbon dioxide formed, and the volume of oxygen left behind in excess.

Solution:

As per the equation,

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

2 vols. : 1 vol. 2 vol.

2 x 22400 ml : 22400 ml 2 x 22400 ml

44800 ml : 22400 ml 44800 ml

Volume of CO_2 formed by burning 2 volumes of CO = 2 volumes

Therefore, by igniting 560 ml of CO the volume of CO_2 formed = 560 ml

Volume of O_2 needed to burn 2 volumes of CO = 1 vol.

Volume of O_2 needed to burn 560 ml of CO = ?

2CO : O_2

2 vol. : 1 vol

560 ml : x

$$x = \frac{560 \times 1}{2} = 280\,ml$$

Hence volume of excess oxygen = 500 – 280 = 220 ml

Volume of carbon dioxide formed = 560 ml

Volume of excess oxygen = 220 ml.

1. Equal volumes of gases at a given temperature and pressure contain the same number of molecules. We can calculate the volumes of gases from a balanced chemical equation provided that the gases are under the same conditions of temperature and pressure. The coefficients of gaseous reactants and products in a balanced equation give the mole relations as well as the volume relations among the gases.$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$4 vol 5 vol 4 vol 6vol4 mol 5 mol 4 mol 6 mol4 volumes of ammonia reacts with 5 volumes of oxygen to yield 4 volumes of nitrogen (ii) oxide and 6 volumes of water vapour.Example

In the industrial preparation of hydrogen trioxonitrate (v) acid, ammonia gas NH3 is burned in Oxygen O2 in the presence of a catalyst according to the following equation.

$4NH_{3(g)} + 5O_{2(g)} \rightarrow 4NO_{(g)} + 6H_2O_{(g)}$

If 260cm^3 of NH_3 are burned completely, what volume of (a) O_2 is used up (b) NO is produced.

Equation of Reaction

$4NH_{3(g)} + \quad 5O_{2(g)} \rightarrow \quad 4NO_{(g)} + 6H_2O_{(g)}$

4 mol   5 mol   4 mol   6 mol

1 mol $\frac{5}{4}$ mol $\frac{4}{4}$ mol $\frac{6}{4}$ mol

260cm^3 of NH_3 will use up $\frac{5}{4}$ mol x 260 = 325cm^3 O_2

260cm^3 of NH_3 will use up $\frac{4}{4}$ mol x 260 = 260cm^3 NO

Study of Stoichiometry

This is the art of measuring chemical elements in quantitative relationship in chemical reactions. It is ordinary chemical arithmetic

Experiments can be designed to study the Stoichiometry of reactions. The type of reactions that are commonly studied are

- precipitation reactions
- displacement of hydrogen from acids
- displacement of metallic ions
- synthesis of metallic oxides
- reduction of metallic oxides

Ideal gas Law

The ideal gas law, PV=nRT, must be used to finish this problem. The variable P represents pressure, and must be in atm. The variable V is the volume, and is what we are solving for. The variable n represents moles, and 0.4764 will be substituted into the equation here. The variable R is the gas law constant and has a value of 0.0821. Its units are atm • L • mol-1 • K-1; note how the unit incorporates the units of all the other variables. It is for this reason that pressure must be in atmospheres. The temperature T must be in kelvin. First, let's make the necessary conversions for temperature and pressure.

For temperature, to convert degrees Celsius to kelvin, add 273.15. Therefore, 35.5 + 273.15 = 308.65 K. For pressure we must setup a set of proportions using the conversion factor 1 atm = 760 torr.

Assessment

1. $Fe_2O_3(s) + 3\ CO(g) \longrightarrow 2\ Fe(s) + 3\ CO_2(g)$
   Determine the volume of carbon dioxide gas that will be produced from 112.5 grams of iron at STP.

2. $2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + H_2O + 2NH_3$
   Calculate the volume of ammonia formed at STP in 'ml' by treating 2.675 g of ammonium chloride with excess of calcium hydroxide (Relative Atomic Mass of N=14, O=16, H=1, Cl=35.5, Ca=40).

3. $Cu(s) + 2H_2SO_4(aq) \longrightarrow CuSO_4(aq) + 2H_2O(l) + SO_2(g)$
   Calculate the volume of sulphur dioxide formed at STP in 'ml', by treating 4.8 g of copper with excess of hot concentrated sulphuric acid. (Relative atomic mass of Cu=64, H=1, S=32, O=16).

4. Calcium oxide is used to remove sulfur dioxide generated in coal-burning power plants according to the following reaction. 2CaO(s)+2SO2(g)+O2(g)→2CaSO4(s)2CaO(s)+2SO2(g)+O2(g)→2CaSO4(s)

What mass of calcium oxide is required to react completely with 1.4×103L1.4×103L of sulfur dioxide?

5. $4NH_3\ (g)+3O_2\ (g)\longrightarrow 2N_2\ (g)+6H_2O\ (g)$

   What is the volume of ammonia gas will react with 22.5 L of oxygen gas?

Week 5

Topic: Acid base Reactions

Acid – Base Titrations

During a titration, there is a change in pH as the acid is added to the alkali. This change in pH may be studied using a pH meter or by using an indicator (a universal indicator). The change in pH during the course of the titration depends on the strength of the acid and alkali used.

An **acid–base titration** is the determination of the concentration of an **acid** or **base** by exactly neutralizing the **acid** or **base** with an **acid** or **base** of known concentration. This allows for quantitative analysis of the concentration of an unknown **acid** or **base** solution.

Titration is a technique *to determine the concentration of an unknown solution*. A solution of known concentration (*titrant*) is used to determine the concentration of an unknown solution (*titrand or analyte*).

Typically, the titrant (the solution of known concentration) is added through a burette to a known volume of the analyte (the solution of unknown concentration) until the reaction is complete. Knowing the volume of titrant added allows us to determine the concentration of the unknown analyte. Often, an *indicator* is used to signal the end of the reaction, the *endpoint*. Titrant and analyte is a pair of acid and base. *Acid-base titrations are monitored by the change of pH as titration progresses.*

Let us be clear about some terminologies before we get into the discussion of titration curves.

- **Titrant**: solution of a known concentration, which is added to another solution whose concentration has to be determined.
- **Titrand or analyte**: the solution whose concentration has to be determined.

- **Equivalence point**: point in titration at which the amount of titrant added is just enough to completely neutralize the analyte solution. *At the equivalence point in an acid-base titration, moles of base = moles of acid and the solution only contains salt and water.*

Equipment used

The key equipment used in a titration are:

- Burette
- White tile – used to see a colour change in the solution
- Pipette
- pH indicator (the one used varies depending on the reactants)
- Erlenmeyer flask / Conical flask
- Titrant or titrator (a standard solution of known concentration, a common one is aqueous sodium carbonate)
- Analyte or titrand (solution of unknown concentration)

The pH of a weak acid solution being titrated with a strong base solution can be found at different points along the way. These points fall into one of four categories:[2]

1. initial pH
2. pH before the equivalence point
3. pH at the equivalence point
4. pH after the equivalence point

The equations and methods below assume that the concentration of the acid and base are at least 1000 times greater than the {\displaystyle

K_{a}} of the acid. If not, a more rigorous calculation using an RICE chart is required. In fact the equations below are a simplification of the RICE chart.

1. The initial pH is approximated for a weak acid solution in water using the equation

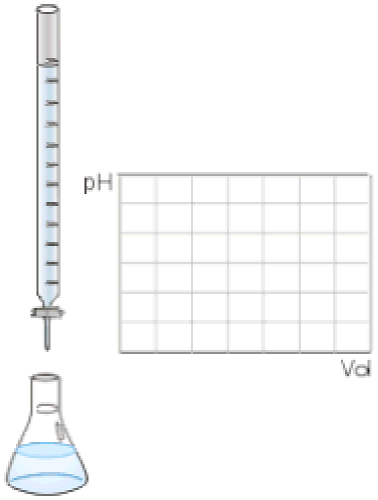
where is the dissociation constant and is the concentration of the acid.

2. The pH before the equivalence point depends on the amount of weak acid remaining and the amount of conjugate base formed. The pH can be calculated by the following formula (which is a variation of the Henderson-Hasselbalch equation):

where:

- is the negative log of the acid dissociation constant of the weak acid.
- is the number of moles of added strong base in the solution.
- is the number of moles the weak acid initially present.

When the numerator of the log term equals the denominator), then the ratio goes to 1 and the log term goes to zero. Thus the pH will equal the pK_a which occurs half-way to the equivalence point.



Animation of titration with base titrant

3. At the equivalence point, the weak acid is consumed and converted to its conjugate base. The pH will be greater than 7 and can be calculated from an equation derived from the following relationships:

1.
2.
3. at equivalence

The previous 3 relationships are used to generate the equivalence point pH formula below:

- = concentration of acid and = concentration of base
- = dissociation constant for water and = dissociation constant for the acid

Note that when an acid neutralizes a base, the pH may or may not be neutral (pH = 7). The pH depends on the strengths of the acid and base.

4. After the equivalence point, the solution will contain two bases: the conjugate base of the acid and the strong base of the titrant. However, the base of the titrant is stronger than the conjugate base of the acid. Therefore, the pH in this region is controlled by the strong base. As such the pH can be found using the following:

Single formula. More accurately, a single formula that describes the titration of a weak acid with a strong base from start to finish is given below:

}

- = fraction of completion of the titration (φ < 1 is before the equivalence point, φ = 1 is the equivalence point, and φ > 1 is after the equivalence point)
- = the concentrations of the acid and base respectively
- = the volumes of the acid and base respectively
- = the fraction of the weak acid that is ionized
- = the dissociation constant for the acid
- = concentrations of the H^+ and OH^- ions respectively

This formula is somewhat cumbersome, but does describe the titration curve as a single equation.

Indicator: For the purposes of this tutorial, it’s good enough to know that an indicator is a weak acid or base that is added to the analyte solution, and it changes color when the equivalence point is reached i.e. the point at which the amount of titrant added is just enough to completely neutralize the analyte solution. The point at which the indicator changes color is called the endpoint. So the addition of an indicator to the analyte solution helps us to visually spot the equivalence point in an acid-base titration.

Endpoint: refers to the point at which the indicator changes color in an acid-base titration.

- In an acid-base titration, a known volume of either the acid or the base (of unknown concentration) is placed in a conical flask.
- The second reagent (of known concentration) is placed in a burette.
- The reagent from the burette is slowly added to the reagent in the conical flask.
- A titration curve is a plot showing the change in pH of the solution in the conical flask as the reagent is added from the burette.
- A titration curve can be used to determine:

1) The equivalence point of an acid-base reaction (the point at which the amounts of acid and of base are just sufficient to cause complete neutralization).

2) The pH of the solution at equivalence point is dependent on the strength of the acid and strength of the base used in the titration.

— For strong acid-strong base titration, pH = 7 at equivalence point
— For weak acid-strong base titration, pH > 7 at equivalence point
— For strong acid-weak base titration, pH < 7 at equivalence point

Calculations at the Equivalence Point of an Acid-Base Titration

A titration is performed to determine the concentration of a reactant, this reactant may be either an acid or a base.
You can follow these 7 steps to calculate the concentration of an acid or base at the equivalence point of an acid-base titration:

1. Write the balanced chemical equation for the reaction

2. Extract all the relevant data from the question
3. Check that data for consistency:

For example, concentrations are usually given in M or mol L^{-1} but volumes are often given in mL.
You will need to convert the mL to L for consistency. The easiest way to do this is to multiply the volume in mL x 10^{-3} (which is the same as dividing the volume in mL by 1000)

4. Calculate the moles of reactant (n) for which you have both the volume (V) and concentration in mol L^{-1} (c)

moles = concentration (mol L^{-1}) x volume (L)
$n = c \times V$

5. Use the balanced chemical equation to determine the stoichiometric (mole) ratio of acid to base:

n(acid):n(base)

6. Use the stoichiometric (mole) ratio to calculate the moles of the unknown reactant
7. From the volume (V) of unknown reactant and its previously calculated moles (n), calculate its concentration (c) in mol L^{-1}:

concentration (mol L^{-1}) = moles ÷ volume (L)
$c = n \div V$

EXAMPLE: Calculating Molarity from Titration Data

Titration reveals that 11.6 mL of 3.0 M sulfuric acid are required to neutralize the sodium hydroxide in 25.00 mL of NaOH solution. What is the molarity of the NaOH solution?

Solution:

$H_2SO_4(aq) + 2NaOH(aq) \rightarrow 2H_2O(l) + Na_2SO_4(aq)$

$$\frac{?\ \text{mol NaOH}}{1\ \text{L NaOH soln}} = \frac{11.6\ \cancel{\text{mL H}_2\text{SO}_4\ \text{soln}}}{25.00\ \cancel{\text{mL}}\ \text{NaOH soln}}\left(\frac{10^3\ \cancel{\text{mL}}}{1\ \text{L}}\right)\left(\frac{3.0\ \cancel{\text{mol H}_2\text{SO}_4}}{10^3\ \cancel{\text{mL H}_2\text{SO}_4\ \text{soln}}}\right)\left(\frac{2\ \text{mol NaOH}}{1\ \cancel{\text{mol H}_2\text{SO}_4}}\right)$$

$$= \mathbf{2.8\ M\ NaOH}$$

Acid Base Indicators

Acid – base **indicators** (also known as **pH indicators**) are substances which change color with **pH**. They are usually weak acids or bases. Consider an **indicator** which is a weak acid, with the formula HIn. At equilibrium, the following chemical equation is established.

pH Range	**Indicator**
0.2 (red) – 1.8 (yellow) and 7.2 (yellow) – 8.8 (red)	Cresol Red
1.2 (red) – 2.8 (yellow) and 7.4 (yellow) – 9.0 (purple)	Cresolphthalein (meta)
1.2 (red) – 2.8 (yellow) and 7.4 (yellow) – 9.0 (purple)	Cresol Purple
1.2 (red) – 2.8 (yellow)	Thymol Blue
2.9 (purple) – 4.6 (green)	Methyl Orange – Xylene Cyanol
3.0 (yellow) – 4.6 (blue)	Bromophenol Blue
3.0 (blue) – 5.0 (red)	Congo Red
3.0 (red) – 6.3 (yellow)	Methyl Orange
4.0 (red) – 5.6 (yellow)	Alizarin Red S
4.0 (yellow) – 5.6 (blue)	Bromocresol Green
4.0 (colorless) – 6.6 (green)	Dichlorofluorescein
4.2 (pink) – 6.2 (yellow)	Methyl Red

4.6 (pink) – 5.2 (blue/green)	Bromocresol Green / Methyl Red
5.2 (yellow) – 6.6 (purple)	Bromocresol Purple
5.2 (yellow) – 6.8 (red)	Chlorophenol Red
6.0 (yellow) – 7.6 (blue)	Bromothymol Blue
6.8 (yellow) – 8.2 (red)	Phenol Red
7.3 (colorless/reddish) – 8.7 (blue/green)	Naphtholphthalein (alpha)
8.0 (colorless) – 10 (pink)	Phenolphthalein
8.2 (colorless) – 9.8 (violet/red)	Cresolphthalein (ortho)
8.8 (colorless) – 10.5 (blue)	Thymolthalein
11.6 (blue) – 14.0 (yellow)	Indigo Carmine

Assessment

1. The concentration of NaOH is 0.5 M, if 20 ml is needed to titrate 35 mL of acid, what is the concentration of the acid?
   A. 0.875 M of acid
   B. 0.0029 M of the acid
   C. 0.29 M of the acid
   D. 0.00875 M of acid
2. A 15.5 mL sample of 0.215 M KOH was titrated with a weak acid. It took 21.2 mL of the acid to reach the equivalence point. What is the molarity of the acid?
   A. 0.157 M acid
   B. 0.29 M acid
   C. 0.0157 M acid
   D. 0.029 M acid
3. If 20.0 mL of 0.100 M HCl are titrated with 19.5 mL of an NaOH solution. What is the molarity of the NaOH solution?
   A. 0.0975 M NaOH

B. 0.0103 M NaOH
C. 0.103 M NaOH
D. 0.975 M NaOH

4. Calculate the molarity of a HCl solution if 25.0 mL of the solution is neutralized by 15.5 mL of 0.800 *M* NaOH:
   A. 0.248 M

B. 0.496 M

C. 1.29 M

D. 0.645 M

WEEK 6

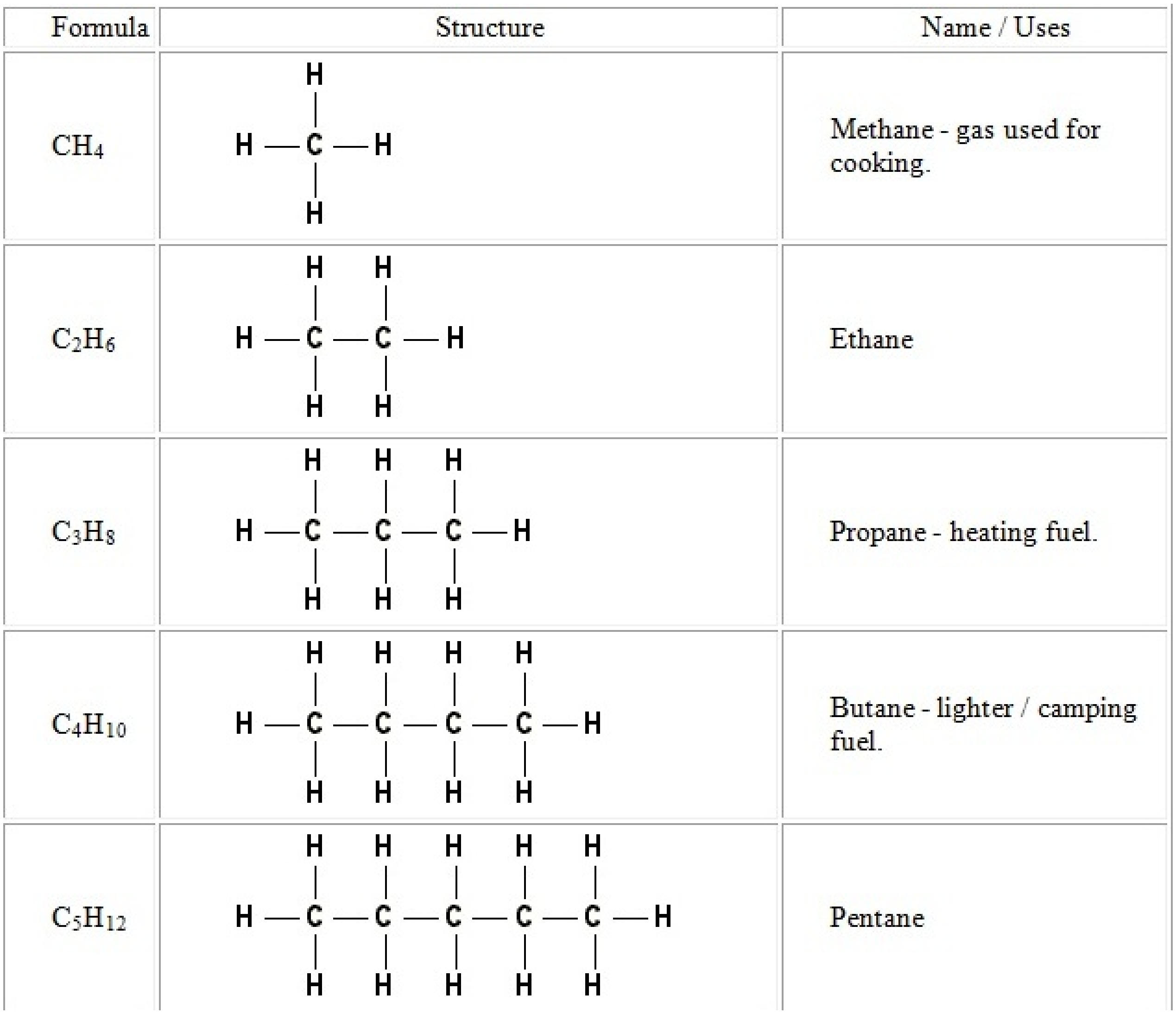
Alkanes

The alkanes are aliphatic hydrocarbons. They form a homologous series of saturated hydrocarbons which can be represented by the general molecular formula C_nH_{2n+2}. In each alkane number, all the carbon atoms are tetrahedrally bonded to the hydrogen and other carbon atoms. These hydrocarbons contain only C-C single bonds in their molecules are called alkanes. These include open chain as well as closed chain (cyclic) hydrocarbons. For example, ethane, propane cyclopentane.

Alkanes are further divided into:

- Open chain or acyclic (simple alkanes not having any closed chains). They have the general formula C_nH_{2n+2}. Examples are methane (CH_4), propane (C_3H_8) and butane (C_4H_{10}).
- Cycloalkanes or cyclic alkanes (having a closed chain or rings in their molecules). They have the general formula C_nH_{2n}. Examples are cyclopropane (C_3H_6) and cyclobutane (C_4H_8)

The simplest Hydrocarbon is methane, CH_4. This is the simplest member of a series of hydrocarbons. Each successive member of the series has one more Carbon atom than the preceding member. This is shown in the table below.



Formula	Structure	Name / Uses
CH_4	$H-\overset{H}{\underset{H}{C}}-H$	Methane - gas used for cooking.
C_2H_6	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	Ethane
C_3H_8	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	Propane - heating fuel.
C_4H_{10}	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	Butane - lighter / camping fuel.
C_5H_{12}	$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H$	Pentane

Methane

The simplest compound in the alkane series with the molecular formula of CH_4. Besides being a component of petroleum gas, it is the major constituent of natural gas. Methane is produced during the decomposition of plant matter in the absence of air.

Laboratory preparation

Methane is usually prepared by heating anhydrous sodium ethanoate with an alkali, usually soda lime (quick lime slaked with a concentrated solution of NaOH). Anhydrous sodium ethanoate is ground with an equal mass of soda lime and then heated in a hard glass test tube. Methane is given off and can be collected over water.

$CH_3COONa_{(s)} + NaOH_{(s)} \rightarrow Na_2CO_{3(s)} + CH_{4(g)}$

Physical properties

1. Methane is a colourless and odourless gas
2. It is only slightly soluble in water
3. It is less dense than air
4. It has no action on litmus

Chemical Properties

Combustion: Methane burns in air or oxygen with a pale non-luminous flame to produce steam, carbon(iv) oxide and a lot of heat

$CH_{4\,(g)} + 2O_{2(s)}\ 2H_2O_{(g)} + CO_{2(g)}$

A mixture of methane and air may explode violently when ignited

Chlorination

Methane reacts with chlorine in the presence of ultra violet light to yield a mixture of products. These products are formed by successive replacement of hydrogen

$CH_4 + Cl \rightarrow HCl + CH_3$

$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$

$CH_3Cl + Cl \rightarrow CH_2Cl + HCl$

Uses of Methane

1. Mainly used as fuel
2. Used for making hydrogen, carbon black, sulphide alkynes and tricholoromethane.

Assessment

1. One of the following is not a physical property of methane
   a. Methane is a colourless and odourless gas
   b. It is not soluble in water
   c. It is less dense than air
   d. It has no action on litmus
2. Methane reacts with chlorine in the presence of ultra violet light to yield a mixture of products by successive replacement of
   a. Hydrogen
   b. Carbon
   c. Oxygen
   d. Nitrogen
3. Methane burns in air or oxygen with a pale non-luminous flame to produce steam, carbon(iv) oxide and ……
   a. hydrogen
   b. carbon
   c. heat
   d. oxygen
4. Molecular formular of Methane
   a. CH_3
   b. CH_4
   c. CH_2
   d. CH_3OH

Answers

1. B
2. A
3. C
4. B

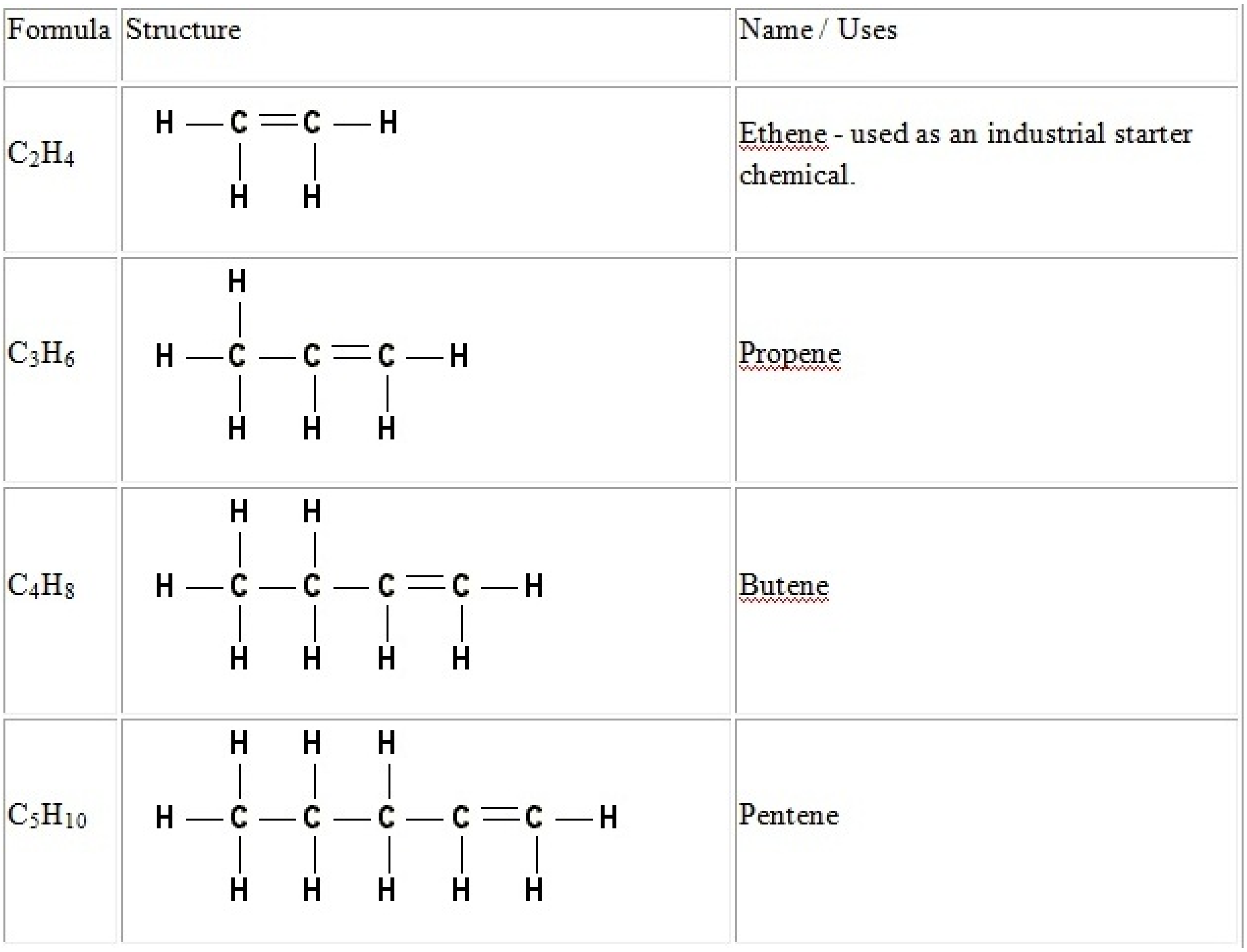
Week 7

Topic: Unsaturated Hydrocarbon – Alkenes

Alkenes

These are hydrocarbons that contain at least one carbon-carbon double bond C=C. Another series of compounds is called the alkenes. They have a general formula: C_nH_{2n} where n is a positive whole number whic is equal or greater than 2

Alkenes have fewer hydrogen atoms than the alkanes. The extra valencies left over occur as double bonds between a pair of carbon atoms. The double bonds are more reactive than single bonds making the alkenes chemically more reactive. They contain 2 hydrogen atoms lesser than the alkanes. Ethene, propene, but-1-ene and but-2-ene are colourless gases at ordinary temperatures and pressures, the next thirteen (C_5H_{10} to $C_{17}H_{34}$) are liquids while he higher ones are solid. Alkenes tend to burn with a more luminous and smoky flame than alkanes. The availability of double bonds also make them more chemically active.



Formula	Structure	Name / Uses
C_2H_4		Ethene - used as an industrial starter chemical.
C_3H_6		Propene
C_4H_8		Butene
C_5H_{10}		Pentene

Ethene

The most important alkene. One of the main products of cracking of gas oil fraction of petroleum.

Formula: C_2H_4

Density: 1.18 kg/m^3

Molar mass: 28.05 g/mol

Structure and properties: Refractive index (n), Dielectric constant (ε_r), etc

Auto-ignition temperature: 542.8 °C (1,009.0 °F; 815.9 K)

Molecular shape: D_{2h}

Solubility in diethyl ether: good

Physical Properties

1. Colourless gas with a faint sweetish smell
2. It is only sparingly soluble in water
3. It is slightly less dense than air
4. No action on litmus

Laboratory Preparation

Ethene is prepared by heating ethanol with excess concentrated tetraoxosulphate(vi) acid at 170°C. The reaction occurs in two stages.

$C_2H_5OH_{(aq)} + H_2SO_{4(aq)} \rightarrow C_2H_5HSO_{4(aq)} + H_2O_{(l)}$

On heating the ethyl hydrogen tetraoxosulphate(vi) decomposes in the presence of excess tetraoxsulphate (vi) acid to produce ethene.

$C_2H_5HSO_{4(aq)} \rightarrow C_2H_{4(g)} + H_2SO_{4(aq)}$

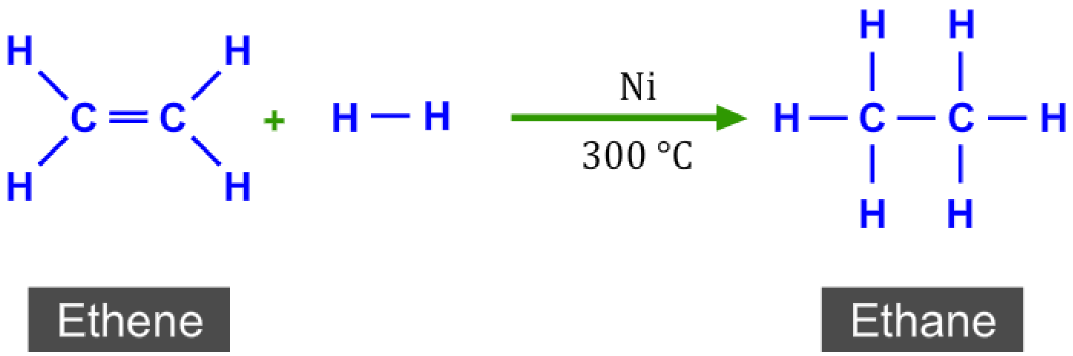
Chemical Properties

Combustion: Ethene on combustion produce carbon dioxide, water and heat.
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ + Heat.

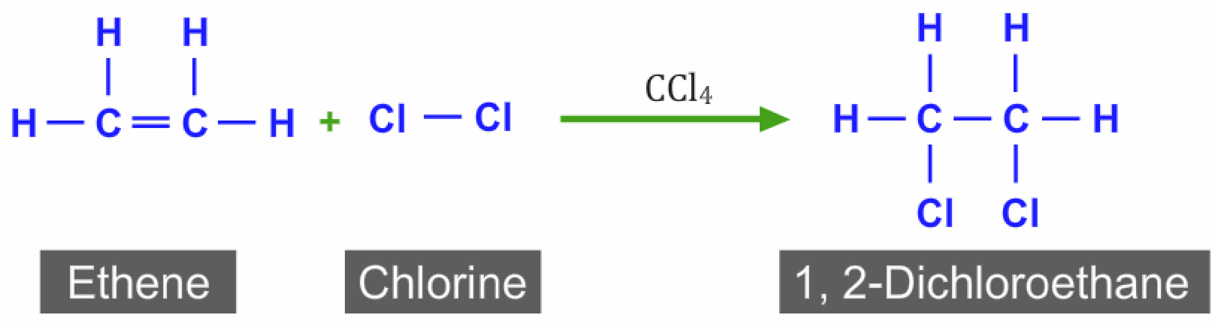
Reactivity: Ethene is more reactive than ethane and methane, as it has a double bond. The double bond is weaker than single bond. Hence, it can be readily attacked any other reactant. The typical reactions of alkenes involve the breaking of the double bond to form two single bonds. Such reactions are called addition reactions.

Addition reaction: A chemical reaction is said to be an addition reaction if two substances combine and form a third substance. In general unsaturated hydrocarbons like alkenes and alkynes prefers to undergo addition reactions.
In addition reactions molecules add across double bond or triple bond.

Addition of hydrogen to ethene: Gives ethane after catalytic hydrogenation in presence of nickel.



Addition of chlorine: When treated with halogens, forms 1, 2, dihalo ethanes.



Polymerisation: Polymerisation is a process in which large number of unsaturated hydrocarbons join together to form a big molecule. The big molecule formed in this process is called a polymer.

The polymer polythene is formed by the polymerisation of ethene at high temperature and pressure.

With Chlorine and Bromine Water – Chlorine water contains oxochlorate (i) acid which combines with ethene to form 2-chloroethanol

Uses of Ethene

1. Ethene is the main source of important organic compounds such as ethane, ethanol, ethanoic acid, epoxyethane etc
2. Ethene is the raw materials used for making many important plastics such as poly ethene, poly cholorethene, PVC (chloride), poly phenylethene or polystyrene.

3. Ethene is used to produce synthetic rubber
4. Fruit ripening

Assessment

1. One of the following is not a physical property of Ethene
   a. Colourless gas with a faint sweetish smell
   b. It is only sparingly soluble in water
   c. It is slightly less dense than air
   d. Turns red litmus to blue
2. ………. is a process in which large number of unsaturated hydrocarbons join together to form a big molecule.
   a. Polymerization
   b. Cantenation
   c. Ripening
   d. None of the above
3. Ethene on combustion produce carbon dioxide and …….
   a. OH
   b. H
   c. H_2O
   d. O

Answers

1. D
2. A
3. C

Week 8

Topic: Unsaturated Hydrocarbon – Alkynes

ALKYNES

An alkyne is a molecule made up entirely of carbon and hydrogen where on or more carbon atoms are connected by triple bonds. The general formula for an alkyne is C_nH_{2n-2} where n is the number of carbon atoms in the molecule. Alkynes are named by adding the the -yne suffix to the prefix associated with the number of carbon atoms present in the molecule.

The first three are:

C_2H_2 – Ethyne

C_3H_4 – Propyne

C_4H_6 – Butyne

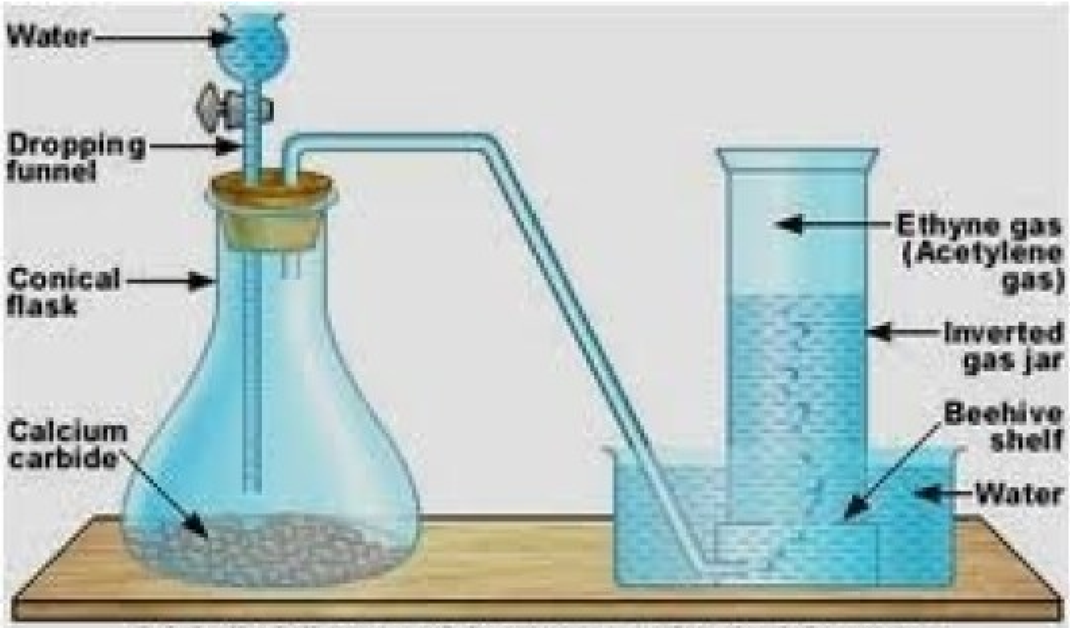
Ethyne is the first member of the alkyne series with a molecular formular C_2H_2 – and a structural formular $CH\equiv CH$.

Laboratory Preparation of Ethyne (Acetylene)

Acetylene is prepared in laboratory by the action of cold water on calcium carbide. The gas evolved is passed through an acidified coppe(II) tetraoxosulphate (vi) solution to remove and phosphine present as an impurity.

$$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$$

The air of the flask in which acetylene is to be prepared is displaced with oil gas as acetylene forms an explosive mixture with air. Acetylene evolved is collected over water. The acetylene so prepared is contaminated with small amounts of impurities such as PH_3, H_2S, AsH_3 and NH_3 which are removed by passing the mixture through $CuSO_4$ solution before its collection over water.



A labelled diagram of the apparatus for the laboratory preparation of ethyne or acetylene.

Physical Properties of Alkynes

1. Lower members (C_2 to C_4) are gases; middle one (C_5 to C_{12}) are liquids; higher are solids.
2. The boiling and melting point of alkynes show a regular increase with increase in molecular weight; however less volatile than alkene.
3. All are colourless & pure ethyne is a sweet smelling gas, however C_2H_2 has garlic odour due to the impurities of PH_3, H_2S etc.
4. Soluble in organic solvents like acetone, alcohol & sparingly soluble in water.
5. It is slightly lighter than air

Chemical Properties of Ethyne

COMBUSTION REACTION: Ethyne burns in air to give a very smoky flame and luminous flame owing to its high carbon content. A mixture of ethyne in air or oxygen may explode violently upon ignition.

$2C_2H_2 + 5O_2 \quad 4CO_2 + 2H_2O + \text{heat}$

ADDITION REACTIONS: Ethyne is highly unsaturated, containing carbon carbon triple bond in its structure. It can readily form addition products combining with a maximum of four univalent atoms or radicals per molecule. These reactions take place in 2 stages:

- the first stage yields a product with a carbon carbon double bond.
- the second stage converts this into a fully saturated compound with only carbon carbon single bond

Addition of Hydrogen:
$C_2H_2 + CH_2{=}CH_2 \rightarrow C_2H_6$
Addition of Halogen:
$C_2H_2 + Cl_2 \rightarrow Cl{-}CH{=}CH{-}Cl \rightarrow Cl_2CH{-}CHCl_2$
Addition of Hydrogen Halide:
$C_2H_2 + HBr \rightarrow CH2{=}CH{-}Br + HBr \rightarrow CH3{-}CHBr_2$
Addition of HCN:
$C_2H_2 + HCN \rightarrow CN{-}CH{=}CH{-}CN$
Addition of Water:
$C_2H_2 + H_2O \rightarrow CH_2{=}CH{-}OH$ [rearrangement] CH_3CHO (Ethanal)
Oxidation of Ethyne:
In cold solution
$C_2H_2 + H_2O + 3[O] \rightarrow 2HCOOH$ (Formic acid)
In hot solution,
$C_2H_2 + 4[O] \rightarrow (COOH)_2$ (Oxalic acid)

Uses of Alkyne

- Acetylene is used in the form of oxy-acetylene flame in welding and cutting tools .
- Used in the preparation of vinyl plastics .
- Used in the preparation of several carbon compounds like acetaldehyde , acetic acid , ethyl alcohol , benzene etc .
- Used in the preparation of solvents acetylene tetrachloride or trichloroethylene

- Used in Hawker's lamp and in light houses for illumination purposes. Also used as fuel in miner's lamp.
- Ethyne is mixed in oxygen to produce a very hot and easily controllable flame knowm as oxy-ethyne flame which is used for cutting and welding metals.
- Polymerization of ethyne and its derivatives leads to the synthesis of products such as chloroethane (plastic), propenonitrile (synthetic fibre) and neoprene (artificial rubber)

Assessment

1. Molecular formular of Ethyne
   a. C_2H_2
   b. C_3H_4
   c. C_4H_6
   d. C_5H8
2. Ethyne reacts with water to form
   a. Ethanol
   b. Ethene
   c. Ethanal
   d. Ethane
3. Ethyne burns in air to give a very ……
   a. wild flame
   b. smoky flame
   c. blue flame
   d. sweet scent
4. One of these is not a use of Ethyne
   a. Acetylene is used in the form of oxy-acetylene flame in welding and cutting tools .
   b. Used in the preparation of vinyl plastics .
   c. Used in Hawker's lamp and in light houses for illumination purposes
   d. Fruit ripening

5. Ethyne structure has a Carbon – Carbon ……. bond
   a. single
   b. triple
   c. double
   d. no

Answers

1. A
2. C
3. B
4. D
5. B

ALKYNES

An alkyne is a molecule made up entirely of carbon and hydrogen where on or more carbon atoms are connected by triple bonds. The general formula for an alkyne is C_nH_{2n-2} where n is the number of carbon atoms in the molecule. Alkynes are named by adding the the -yne suffix to the prefix associated with the number of carbon atoms present in the molecule.

The first three are:

C_2H_2 – Ethyne

C_3H_4 – Propyne

C_4H_6 – Butyne

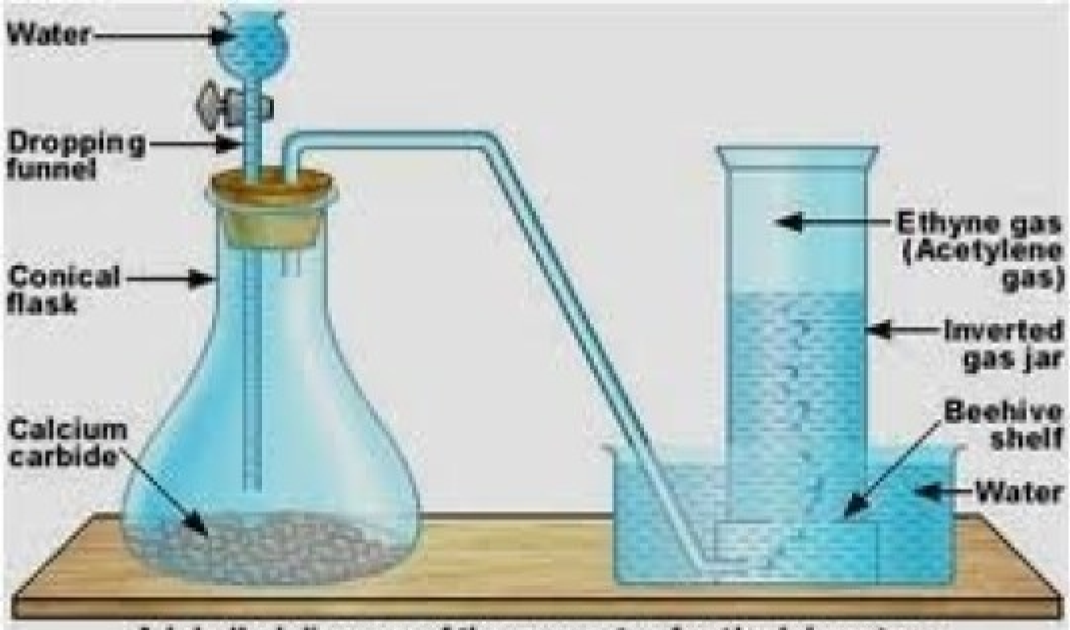
Ethyne is the first member of the alkyne series with a molecular formular C_2H_2 – and a structural formular $CH{\equiv}CH$.

Laboratory Preparation of Ethyne (Acetylene)

Acetylene is prepared in laboratory by the action of cold water on calcium carbide. The gas evolved is passed through an acidified coppe(II) tetraoxosulphate (vi) solution to remove and phosphine present as an impurity.

$CaC_{2(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + C_2H_{2(g)}$

The air of the flask in which acetylene is to be prepared is displaced with oil gas as acetylene forms an explosive mixture with air. Acetylene evolved is collected over water. The acetylene so prepared is contaminated with small amounts of impurities such as PH_3, H_2S, AsH_3 and NH_3 which are removed by passing the mixture through $CuSO_4$ solution before its collection over water.



A labelled diagram of the apparatus for the laboratory preparation of ethyne or acetylene.

Physical Properties of Alkynes

1. Lower members (C_2 to C_4) are gases; middle one (C_5 to C_{12}) are liquids; higher are solids.
2. The boiling and melting point of alkynes show a regular increase with increase in molecular weight; however less volatile than alkene.

3. All are colourless & pure ethyne is a sweet smelling gas, however C_2H_2 has garlic odour due to the impurities of PH_3, H_2S etc.
4. Soluble in organic solvents like acetone, alcohol & sparingly soluble in water.
5. It is slightly lighter than air

Chemical Properties of Ethyne

COMBUSTION REACTION: Ethyne burns in air to give a very smoky flame and luminous flame owing to its high carbon content. A mixture of ethyne in air or oxygen may explode violently upon ignition.

$2C_2H_2 + 5O_2\ 4CO_2 + 2H_2O$ + heat

ADDITION REACTIONS: Ethyne is highly unsaturated, containing carbon carbon triple bond in its structure. It can readily form addition products combining with a maximum of four univalent atoms or radicals per molecule. These reactions take place in 2 stages:

- the first stage yields a product with a carbon carbon double bond.
- the second stage converts this into a fully saturated compound with only carbon carbon single bond

Addition of Hydrogen:
$C_2H_2 + CH_2{=}CH_2 \rightarrow C_2H_6$
Addition of Halogen:
$C_2H_2 + Cl_2 \rightarrow Cl\text{-}CH{=}CH\text{-}Cl \rightarrow Cl_2CH\text{-}CHCl_2$
Addition of Hydrogen Halide:
$C_2H_2 + HBr \rightarrow CH2{=}CH\text{-}Br + HBr \rightarrow CH3\text{-}CHBr_2$
Addition of HCN:
$C_2H_2 + HCN \rightarrow CN\text{-}CH{=}CH\text{-}CN$
Addition of Water:
$C_2H_2 + H_2O \rightarrow CH_2{=}CH\text{-}OH$ [rearrangement] CH_3CHO (Ethanal)
Oxidation of Ethyne:
In cold solution

$C_2H_2 + H_2O + 3[O] \rightarrow 2HCOOH$ (Formic acid)
In hot solution,
$C_2H_2 + 4[O] \rightarrow (COOH)_2$ (Oxalic acid)

Uses of Alkyne

- Acetylene is used in the form of oxy-acetylene flame in welding and cutting tools .
- Used in the preparation of vinyl plastics .
- Used in the preparation of several carbon compounds like acetaldehyde , acetic acid , ethyl alcohol , benzene etc .
- Used in the preparation of solvents acetylene tetrachloride or trichloroethylene
- Used in Hawker's lamp and in light houses for illumination purposes. Also used as fuel in miner's lamp.
- Ethyne is mixed in oxygen to produce a very hot and easily controllable flame knowm as oxy-ethyne flame which is used for cutting and welding metals.
- Polymerization of ethyne and its derivatives leads to the synthesis of products such as chloroethane (plastic), propenonitrile (synthetic fibre) and neoprene (artificial rubber)

Assessment

1. Molecular formular of Ethyne
   a. C_2H_2
   b. C_3H_4
   c. C_4H_6
   d. C_5H8
2. Ethyne reacts with water to form
   a. Ethanol
   b. Ethene

   c. Ethanal
   d. Ethane

3. Ethyne burns in air to give a very ……
   a. wild flame
   b. smoky flame
   c. blue flame
   d. sweet scent
4. One of these is not a use of Ethyne
   a. Acetylene is used in the form of oxy-acetylene flame in welding and cutting tools .
   b. Used in the preparation of vinyl plastics .
   c. Used in Hawker’s lamp and in light houses for illumination purposes
   d. Fruit ripening
5. Ethyne structure has a Carbon – Carbon ……. bond
   a. single
   b. triple
   c. double
   d. no

Answers

1. A
2. C
3. B
4. D
5. B

Week: 9

Topic: Alkanols

Alkanols (or alcohols) are a homologous series of organic compounds with the general formula $C_nH_{2n+1}OH$ or simply ROH. Their molecules consist of a functional group — the hydroxyl group (—OH) joined to an alkyl group (R—). They can be used to fuel cars as they are flammable. Unlike alkanes, alkenes and alkynes, alkanols are not hydrocarbons as, in addition to carbon and hydrogen atoms, they contain oxygen atoms.

The two simplest alkanols are methanol and ethanol.

Other members of the alkanol family:

Name	Molecular Formula	Shortened structural formula
Methanol	CH_3OH	CH_3OH
Ethanol	C_2H_5OH	CH_3CH_2OH
Propanol	C_3H_7OH	$CH_3CH_2CH_2OH$
Butanol	C_4H_9OH	$CH_3CH_2CH_2CH_2OH$
Pentanol	$C_5H_{11}OH$	$CH_3CH_2CH_2CH_2CH_2OH$

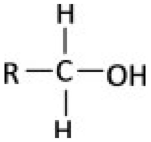
Classification of Alkanols

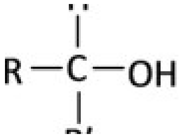
In naming the alkanols, the position of the hydroxyl group is given from the number of the carbon nearest it. The isomers of alcohols are numerous but they all fall into one of three groups Primary, Secondary or Tertiary.

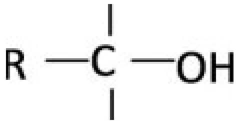
A *primary alcohol* is one that contains two hydrogen atoms and one alkyl group bonded to the carbon atom that contains the alcohol group.

A *secondary alcohol* is one that contains one hydrogen atom and two alkyl groups bonded to the carbon atom containing the alcohol group.

A *tertiary alcohol* is one that contains three alkyl groups and no hydrogen atoms bonded to the carbon atom containing the alcohol group.

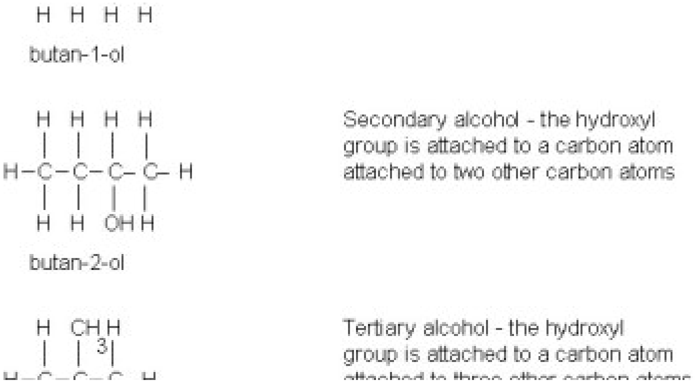






Primary alcohol. Secondary alcohol Tertiary alcohol

Examples:



Secondary alcohol - the hydroxyl group is attached to a carbon atom attached to two other carbon atoms

Tertiary alcohol - the hydroxyl group is attached to a carbon atom

Nomenclature (Naming Alkanol)

Alkanols are similar in structure to alkanes, however one hydrogen has been replaced by an OH (hydroxyl) group. However, the ane is replaced with anol. The rules is as follow:

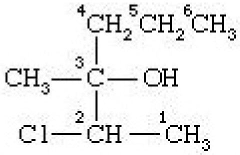
1. Determine the parent chain. The parent chain must be the longest that includes the carbon holding the OH group.

2. Number according to the end closest to the -OH group regardless of where alkyl substituents are.

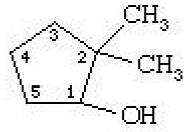
3. The format is as follows: (location of branch)-(branch name)-(location of OH group)-(parent chain)

4. Change the parent chain -e ending and replace it with an -ol.

Examples:



2-chloro-3-methyl-3-hexanol



2,2-dimethylcyclopentanol

Note: Alchohols containing more than one hydroxyl group are also called polyalcohols. Polyalcohols are named similarly to alcohols, with the exception of the prefix di-, tri-, etc before the -ol ending.

METHANOL

Methanol, otherwise known as wood spirit or methyl alcohol, is manufactured by the destructive distillation of wood in limited supply of air or derived from the refining of crude oil (Petroleum). It is the first member of the alkanol series with the molecular formula, CH_3OH

Physical Properties

1. Methanol is a colourless liquid with a boiling point of 65° C (149° F).
2. It mixes completely with water and with other short-chain alkanol.
3. It is very poisonous and toxic if drunk and small quantities of the alkanol could cause blindness while larger ones, death.
4. Methylated spirits consists of ethanol to which about 10 per cent methanol has been added (along with a blue dye called pyridine) to make it undrinkable.

Reactions of Methanol

The chemical reactions of methanol include:

Oxidation to methanal and then methanoic acid;

$CH_3OH + [O] \longrightarrow HCHO + [O] \longrightarrow HCOOH$

Formation of esters with alkanoic acids;
$CH_3OH + HCOOH \rightarrow HCOOCH_3 + H_2O$

Uses

1. Methanol is used as a solvent,
2. a fuel and additive for vehicle fuels, and
3. to make methanal, from which plastics such as Bakelite are made

ETHANOL

Sometimes called ethyl alcohol, Ethanol has the molecular formula C_2H_5OH. Often when the layman calls a substance alcohol, ethanol is being referred to. This is because ethanol, though the second member, is the most typical of the properties of alkanols (or alcohols).

Laboratory Preparation

Preparation by the Hydration of Ethene

Ethanol could be prepared in the laboratory by the hydrolysis of ethene. This is done by passing a mixture of ethene and steam over H_2SO_4 acid serving as catalyst at a temperature of above 500°C and pressure of 100 atm.

$C_2H_4 (g) + H_2O(l) \longrightarrow C_2H_5OH(l)$

Preparation by Fermentation

Fermentation is the slow breaking down of large molecules of starch to smaller molecules of alcohol by the enzymatic action of micro-organisms (usually yeast).

Ethanol can be prepared by extracting starch granules obtained by crushing starchy foodstuffs and then leaving it for some hours after inoculating with suitable enzymes(also found in yeasts).

The following reactions will take place with the gradual conversion of the starch to ethanol:

1. Starch is hydrolyzed to maltose by the action of diastase (also called invertase)
2. In the second reaction, maltose is hydrolyzed, by the action of maltase to glucose

iii. Lastly, glucose is converted to ethanol with carbon (IV) oxide gas given off by zymase enzyme

Physical Properties

1. Ethanol is a colourless, volatile liquid with a characteristics taste and smell
2. It is readily soluble in water in all proportions (due to the presence of the hydroxyl group)
3. It has a boiling point of $78^{O}C$
4. It has no action on litmus

Chemical properties:

Combustion
Alcohols burns in oxygen to produce carbon dioxide and water. Alcohols burn clearly and easily, and do not produce soot. It becomes increasingly more difficult to burn alcohols as the molecules get bigger.
e.g. combustion of ethanol: C_2H_5OH (l) + 3 O_2 (g) → 2 CO_2 (g) + 3 H_2O (g); ($\Delta H_c = -1371$ kJ/mol)

Dehydration- alcohol to alkene
Dehydration of alcohols is done by heating with concentrated sulfuric acid, which acts as the dehydrating agent, at 180°C. This reaction uses alcohols to produce corresponding alkenes and water as byproduct.
e.g. dehydration of ethanol:

Oxidation – alcohol to carboxylic acid
Alcohols can be oxidized into carboxylic acids.

e.g. oxidation of ethanol:

$C_2H_5OH + [O] \rightarrow CH_3COOH + H_2O$

Oxidation can be done by using oxidizing agents such as acidified potassium dichromate (VI), acidified potassium manganate (VII). Or, if left exposed to atmospheric air, it can oxidize and become ethanoic acid. An example is wine turning sour as the alcohol content, which is ethanol, is oxidized by atmospheric oxygen.

Esterification

Alcohols can be reacted with carboxylic acid to form esters.

Uses

1. Ethanol is an important solvent used to dissolve resins, varnishes, lacquer, soaps, perfumes, dyes, drugs and flavouring extracts
2. It is used as a fuel, either by itself or mixed with petrol, in racing cars and in rockets
3. Ethanol is present in many alcoholic beverages such as beers, wines and spirits (e.g. whisky, gin, brandy, etc.)
4. It is sometime used as an anti-freeze in automobile radiators.

Test for Alkanols

- To detect the presence of the OH group regardless there are several simple tests that can be done, however they all have the disadvantage of interference by water.
  A small piece of sodium metal can be placed in the alcohol and a steady stream of hydrogen bubbles gives a positive indication. Remember that the presence of water will also cause hydrogen to be evolved.
- To differentiate between the three classes of alcohol, it is possible to use oxidation with sodium dichromate in dilute sulphuric acid and heat.
  The 1^o alcohol oxidizes to an aldehyde (alkanal) and then to a carboxylic acid (alkanoic acid)

The 2° alcohol oxidizes to a ketone (alkanone) and stops there.
The 3° alcohol cannot be oxidized under these conditions.

- Another test is Lucas' test for 1°, 2°, 3° alcohols.
  It involves shaking the alcohol with $ZnCl_2$ and dilute HCl. The 3° alcohol goes cloudy almost at once, the 2° alcohol goes cloudy after a few minutes whereas the 1° alcohol needs concentrated HCl to go cloudy. The cloudiness is due to the formation of the haloalkane that is immiscible with the aqueous solution of the zinc chloride and forms tiny droplets of an organic phase within the aqueous phase.

Oxidation – alcohol to carboxylic acid
Alcohols can be oxidized into carboxylic acids.
e.g. oxidation of ethanol:
$C_2H_5OH + [O] \rightarrow CH_3COOH + H_2O$
Oxidation can be done by using oxidizing agents such as acidified potassium dichromate (VI), acidified potassium manganate (VII). Or, if left exposed to atmospheric air, it can oxidize and become ethanoic acid. An example is wine turning sour as the alcohol content, which is ethanol, is oxidized by atmospheric oxygen.
Esterification
Alcohols can be reacted with carboxylic acid to form esters.

Uses

1. Ethanol is an important solvent used to dissolve resins, varnishes, lacquer, soaps, perfumes, dyes, drugs and flavouring extracts
2. It is used as a fuel, either by itself or mixed with petrol, in racing cars and in rockets
3. Ethanol is present in many alcoholic beverages such as beers, wines and spirits (e.g. whisky, gin, brandy, etc.)
4. It is sometime used as an anti-freeze in automobile radiators.

Test for Alkanols

- To detect the presence of the OH group regardless there are several simple tests that can be done, however they all have the

disadvantage of interference by water.
A small piece of sodium metal can be placed in the alcohol and a steady stream of hydrogen bubbles gives a positive indication. Remember that the presence of water will also cause hydrogen to be evolved.

- To differentiate between the three classes of alcohol, it is possible to use oxidation with sodium dichromate in dilute sulphuric acid and heat.
  The 1° alcohol oxidizes to an aldehyde (alkanal) and then to a carboxylic acid (alkanoic acid)
  The 2° alcohol oxidizes to a ketone (alkanone) and stops there.
  The 3° alcohol cannot be oxidized under these conditions.
- Another test is Lucas' test for 1°, 2°, 3° alcohols.
  It involves shaking the alcohol with $ZnCl_2$ and dilute HCl. The 3° alcohol goes cloudy almost at once, the 2° alcohol goes cloudy after a few minutes whereas the 1° alcohol needs concentrated HCl to go cloudy. The cloudiness is due to the formation of the haloalkane that is immiscible with the aqueous solution of the zinc chloride and forms tiny droplets of an organic phase within the aqueous phase.

Assessment

1. One of these is not a laboratory preparation of Ethanol
   a. Hydration of Ethene
   b. by Fermentation
   c. Break down of starch granules
   d. Dehydration of Ethane
2. Ethanol can be used for the following except
   a. Ethanol is an important solvent used to dissolve resins, varnishes, lacquer, soaps, perfumes, dyes, drugs and flavouring extracts
   b. It is used as a fuel, either by itself or mixed with petrol, in racing cars and in rockets
   c. Ethanol is present in many alcoholic beverages such as beers,

wines and spirits
d. It is sometime used as a coolant in automobile radiators.

3. Give the IUPAC names of the following compounds
   - C_3H_7OH
   - $CH_3COOC_2H_5$
   - CH_3CHO
   - $CH_3CH(OH)CH_3$

Answers

1. D
2. D