GOVERNMENT OF TAMIL NADU

HIGHER SECONDARY FIRST YEAR

CHEMISTRY

VOLUME - I

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Department of School Education

Untouchability is Inhuman and a Crime

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Key features

	Scope of Chemistry	Awareness about higher education avenues in the field of Chemistry	
	Learning objectives	Describe the specific competency / performance capability acquired by the learner	
	Do you know	Additional information provided to relate the content to day-to-day life / development in the field	
	Example Problems	Model problems worked out for clear-cut comprehension by the learners	
	Evaluate yourself	To help the students to assess their own conceptual understanding	
	Q.R code	Quick access to concepts, videos, animations and tutorials	
	ICT	Opens up resources for learning; enables the learners to access, extend transform ideas / informations	
	Summary	A glance on the substance of the unit	
	Concept map	Inter relating the concepts for enabling learners to visualize the essence of the unit	
	Evaluation	To assess the level of understanding through multiple choice question,numerical problems etc.	
	Books for Reference	List of relevant books for further reading	
	Key answers	To help the learners confirm the accuracy of the answers arrived and remedy the gaps in learning	
	Glossary	Important terms are enlisted with equivalent Tamil words	
	Appendix	Comprises fundamental constants and Data tables	

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The courses offered, top colleges and competitive exams conducted for higher education after 12th in Chemistry field were summarized below.



Courses Bachelor Degree	Institution	Selection Mode	Careers in Chemistry
• B.Sc. (Chemistry) • B.Sc. (Analytical Methods in Chemistry) • B.Sc. (Applied Chemistry) • B.Sc. (Industrial Chemistry) • B.Sc. (Polymer Chemistry) • B.Sc. (Bio Chemistry)	• Arts and Science Colleges in India	Counseling based on 12th Marks in Science Subjects	• Teacher for Secondary Schools • Lab Chemist • Food Processing Firms • Paint Manufacturing Companies • Plastics Industries and Textile Industries • Agrochemical Industry • Petrochemical Industry • Water Quality and Cosmetic Chemists • Can write any type of competitive examinations such as TNPSC, Bank exams, Civil service, RRB etc.
• B.E.(Chemical Engineering)	• Indian Institute of Technologies	#JEE (Main & Advanced)	• Architectural engineering works • Resin and artificial synthetic fibers • Petroleum and coal products manufacturing • Space Fuel Processor • Biotechnology and pharmaceutical companies • Climate Change Reversal Engineer • Food Manufacturing unites, Electronics and Energy manufacturers
	• Birla Institute of Technology and Science	#BITSAT	
	• All Govt. and Private Engineering colleges in Tamilnadu	TNEA Counseling based on cut off scored in 12th std	
• B.Tech .(Rubber plastics technology)	• Madras Institute of Technology		
• B.Tech .(Petroleum Refining and Petrochemicals, Ceramic Technology(S.S), Textile Technology, Leather Technology)	• Anna University, Alagappa College of Technology, CSIR-Central Leather Research Institute and other affiliated colleges		
• B.E. / B.Tech. (Plastics Engineering / Technology)	• Central Institute of Plastics Engineering & Technology		
Diploma			
• Advanced Diploma in Technical and Analytical Chemistry (ADTAC)	• Maharashtra State Board of Technical Education (MSBTE) - Government of Maharashtra.	Counseling based on percentage scored in degree (Eligibility: Any Degree)	• Chemical, pharmaceutical, food and paint industries as Analysts, Chemists and Q.C. Chemists
• Plastics Processing & Testing	• Central Institute of Plastics Engineering & Technology	#JEE	• Plastics Industries
Masters Degree			

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Courses Bachelor Degree	Institution	Selection Mode	Careers in Chemistry
• M.Sc. (Integrated Chemistry)	• Pondicherry University	#Pondicherry University Entrance exam	• Analytical Chemist • Higher Secondary Teacher • Production Chemist • Research & Development Manager • Biomedical Chemist • Industrial Research Scientist • Materials Technologist • Quality Controller • Safety Health and Environment Specialist • Pharmaceutical Companies • Environmental Law • Space Exploration Agencies • Forensic Science Department • Ceramics Industry and Paper Industry • Military Systems Department • Patent Attorney • Nuclear engineer
	• Indian Institute of Technology (IIT Roorkee) • Indian Institute of Technology (IIT Khagarpur) • Indian Institute of Technology (IIT Bombay)	#Joint Admission Test for M.Sc. (JAM)	
	• Central University of Tamil Nadu : School of Basic and Applied Science, Thiruvarur	#CUCET entrance	
	• NISER School of Chemical Sciences, Cuttack	#NEST entrance	
	• Birla Institute of Technology and Science	#BITSAT entrance	
	• Annamalai University	#Annamalai University Entrance exam	
	• Arts and Science Colleges in India	Based on percentage scored in degree and Separate Entrance exams will be conducted by the concern institute	
• M.Sc.-General Chemistry, Analytical Chemistry, Inorganic Chemistry Organic Chemistry, Physical Chemistry, Polymer Chemistry Environmental Science NanoScience and Nanotechnology	• Government Universities like University of Madras, Alagappa University, Anna University, Annamalai University, Bharathiar University, Bharathidasan University, Madurai Kamaraj University and IISc, Bangalore, University of Delhi, etc. Arts and Sciences colleges in India	Separate Entrance exams will be conducted by the concern institute	
• M.Sc. Applied Chemistry Chemistry (Hons) Applied Chemistry(Hons) Industrial Chemistry Medicinal Chemistry Pharmaceutical Chemistry Drug Chemistry	• Anna University Andhra University Birla Institute of Technology Cochin University of Science and technology PSG College, Coimbatore Sri Venkateshwara University, Tirupati.	Separate Entrance exams will be conducted by the concern institute	• Industry related jobs • Quality Control Chemist • Production Chemist • Petrochemical industry • Food processing • Paint industry

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Courses Bachelor Degree	Institution	Selection Mode	Careers in Chemistry
• M.Tech. -Polymer Science And Technology • Industrial Safety And Hazards Management	• Anna University and Alagappa College of Technology	# Tamil Nadu Common Entrance Test (TANCET)	• Industrial Safety and Hazards Management jobs in various industry
M.Phil.			
M.Phil.-Chemistry Analytical Chemistry Applied Chemistry Industrial Chemistry Crystal Science	• Universities in India • Arts and Science Colleges in India	Entrance/direct interview depending upon the College/ University	• Teaching related jobs • All industries related jobs • Technicians in imaging labs • Patent Law
Research			
• Ph.D. (Chemistry) Area: Organic Synthesis, Inorganic complexes, Computational Chemistry, Nanotechnology Electrochemistry, Material Science & Polymer Composites, Bio-sensors, Molecular modelling, chemoinformatics, Green Chemistry, Catalysts for Green Oxidation Chemistry etc.	• Indian Institute of Science, Indian Institute of Technology, Kharagpur • University of Delhi, Delhi • Indian Institute of Technology, Bombay • Tata Institute of Fundamental Research, Mumbai • Anna University, Chennai • Indian Institute of Technology, Madras • Jawaharlal Nehru Centre for Advanced Scientific Research, • University of Madras, • Bharathiar University, • Jawaharlal Nehru University, • National Institute of Technology, Annamalai University, etc.	Separate Entrance exams will be conducted by the concern institute	• Professor for Govt. colleges and Universities • Chemical scientists • Scientist posts in many central government industry • Post Doctoral Fellow • Quality control in Toxicology • Formulation Chemistry • Chemical Information Management Specialist

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Entrance Exams and Pattern

JEE-Main Paper I -3 hrs Paper II-3 hrs www.jeemain.nic.in	• Indian Institutes of Information Technology (IIITs) • Indian Institute of Engineering Science and Technology (IIEST) • National Institutes of Technology (NITs) • Indian Institute of Technology (IITs) • Government Funded Technical Institutes (GFTIs)	OMR based and Online based (choice of candidate)	Notification: 1st week of Dec Exam Date: April Negative marking: 4/-1 Total Marks:360	Physics Chemistry Mathematics Total Questions	30 30 30 90
JEE-Advanced Paper I -3 hrs Paper II-3 hrs Should qualify JEE main (paper-I) www.jeeadv.ac.in	• Indian Institutes of Information Technology (IIITs) • Indian Institute of Engineering Science and Technology (IIEST) • National Institutes of Technology (NITs) • Indian Institute of Technology (IITs) • Government Funded Technical Institutes (GFTIs)	Online	Notification: last week of April Exam Date: May second week Negative marking: 4/-1 Total Marks: 306 (Variable each year)	Physics Chemistry Mathematics Total Questions	18 18 18 54
BITSAT http://www.bitsadmission.com Time: 3 hrs	• Birla Institute of Technology and Science	Online	Notification: 2nd week of Dec Exam Date: 2nd week of May Negative marking: 3/-1 Total Marks: 450	Physics Chemistry Mathematics English Proficiency Logical Reasoning Total Questions	40 40 45 15 10 150
CUCET https://cucetexam.in Time: 2 hrs	• All Central Universities	Online	Notification: 2nd week of Feb Exam Date: April Negative marking: 1/0.25 Total Marks:175	English General Awareness Mathematical Aptitude Analytical Skill Science Total Questions	25 25 25 25 75 175
JAM http://jam.iitb.ac.in/ Time: 3 hrs	• All IITs	Online	Notification: September Exam Date: February Negative marking: 1/0.33 2/0.66 Total Marks:100	Chemistry Total Questions	60 60

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CSIR-UGC Net http://csirhrdg.res.in Time: 3 hrs	• Ph.D. admission in all Universities and Colleges	OMR	Sessions: June From out : March Exam Date: June Session: December From out : September Exam Date: December	General Science, Quantitative Reasoning & Analysis and Research Aptitude Chemistry Total Questions	60 15 75
GATE http://gate.iitg.ac.in/ Time: 3 hrs	• Ph.D. admission in all IITs	OMR	From out : September Exam Date: February Negative marking: 1/0.33 2/0.66 Total Marks:100	General Aptitude Chemistry Total Questions	10 55 65
TANCET https://www.annauniv.edu Time: 2 hrs	• Anna University Entrance exam for technology courses	Pen and Paper based exam	From out : January Exam Date: March Negative marking: 1/0.33 Total Marks:100	Engineering Mathematics Basic Engineering and Sciences Chemistry Total Questions	20 20 60 100
University of Madras http://www.unom.ac.in Time: 3 hrs	• M.Sc. Entrance exam	Pen and Paper based exam	From out : 2nd week of Feb Exam Date: April Negative marking: Nil Total Marks:100	Analytical Chemistry Inorganic Chemistry Organic Chemistry Physical Chemistry Total Questions	25 25 25 25 100
Anna University https://www.annauniv.edu Time: 1 hr	• M.Sc. Entrance exam	Online	From out : April Exam Date : May Negative marking : 1/0.25 Total Marks : 100	Chemistry Total Questions	100 100
Annamalai University http://www.annamalaiuniversity.ac.in	• M.Sc. Admission	Based on percentage scored in degree and Personal Interview.			
	• B.Sc. Admission	Counseling based on 12th Marks in Science Subjects			
Bharathiar University www. b-u.ac.in Time: 1.30 hrs	• M.Sc. Entrance exam	Pen and Paper based exam	From out : May Exam Date : Roughly July Total Marks : 60	Chemistry Total Questions	60 60
Bharathidasan University http://www.bdu.ac.in/	• M.Sc. Entrance exam	Pen and Paper based exam	From out : last week of May Exam Date : second week of June		
Madurai Kamaraj University mkuniversity.ac.in	• M.Sc. Entrance exam	Online	From out : March Exam Date : May/June		

(*Note:* All these dates are tentative and they are subjected to change every year)

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Assessment

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HIGHER SECONDARY FIRST YEAR

CHEMISTRY

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Unit 1

Basic Concepts of Chemistry and Chemical Calculations

JOY03

We think there is colour, we think there is sweet, we think there is bitter, but in reality there are atoms and a void.

– Democritus



Natural Fibre (Cotton)

Synthetic Fibre (Nylon)





Pesticide (Malathion)

Pharmaceutical (Tablets)





Refinery (Oil)

Learning Objectives

After studying this unit, students will be able to

- explain the importance of chemistry in different spheres of life.
- classify different substances into elements, compounds and mixtures.
- define atomic mass and molecular mass.
- define the amount of substance using SI unit 'mole'.
- describe Avogadro number.
- explain the relationship among mass, moles and number of atoms (or) molecules and perform calculations relating to the conversions.
- define equivalent mass and calculate equivalent mass of acid, base and oxidising/reducing agents.
- deduce empirical and molecular formula of a compound from experimental data.
- solve numerical problems based on stoichiometric calculations.
- identify the limiting reagent and calculate the amount of reactants and products in a reaction.
- define the terms oxidation, reduction, oxidant and reductant.
- predict the oxidation states of elements in various compounds.
- explain the process involved in a redox reaction and describe the electron transfer process.
- classify redox reactions into different types.
- formulate a balanced redox reaction from two half-reactions.

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1.1 Chemistry - the Centre of Life

'Unna unavu, udukka udai, irukka idam' - in Tamil classical language means food to eat, cloth to wear and place to live. These are the three basic needs of human life. Chemistry plays a major role in providing these needs and also helps us to improve the quality of life. Chemistry has produced many compounds such as fertilizers, insecticides etc. that could enhance the agricultural production. We build better and stronger buildings that sustain different weather conditions with modern cements, concrete mixtures and better quality steel. We also have better quality fabrics.

Chemistry is everywhere in the world around us. Even our body is made up of chemicals. Continuous bio-chemical reactions occurring in our body are responsible for human activities. Chemistry touches almost every aspect of our lives, culture and environment. The world in which we are living is constantly changing, and the science of chemistry continues to expand and evolve to meet the challenges of our modern world. Chemical industries manufacture a broad range of new and useful materials that are used in every day life.

Examples : polymers, dyes, alloys, life saving drugs etc.

When HIV/AIDS epidemic began in early 1980s, patients rarely lived longer than a few years. But now many effective medicines are available to fight the infection, and people with HIV infection have longer and better life.

The understanding of chemical principles enabled us to replace the non eco friendly compounds such as CFCs in refrigerators with appropriate equivalents and increasing number of green processes. There are many researchers working in different fields of chemistry to develop new drugs, environment friendly materials, synthetic polymers etc. for the betterment of the society.

As chemistry plays an important role in our day-to-day life, it becomes essential to understand the basic principles of chemistry in order to address the mounting challenges in our developing country.

1.2 Classification of Matter:

Look around your classroom. What do you see? You might see your bench, table, blackboard, window etc. What are these things made of ? They are all made of matter. Matter is defined as anything that has mass and occupies space. All matter is composed of atoms. This knowledge of matter is useful to explain the experiences that we have with our surroundings. In order to understand the properties of matter better, we need to classify them. There are different ways to classify matter. The two most commonly used methods are classification by their physical state and by chemical composition as described in the chart.

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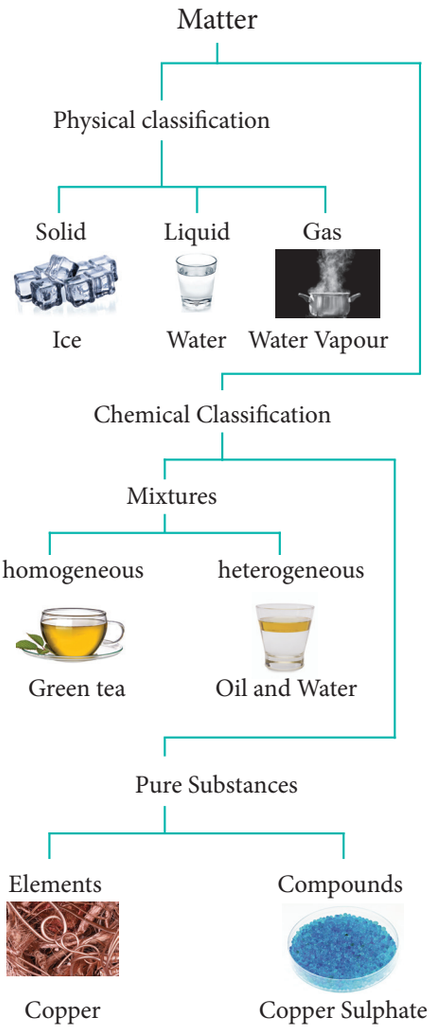

Fig. 1.1 Classification of Matter

1.2.1 Physical Classification of Matter :

Matter can be classified as solids, liquids and gases based on their physical state. The physical state of matter can be converted into one another by modifying the temperature and pressure suitably.

1.2.2 Chemical Classification :

Matter can be classified into mixtures and pure substances based on chemical compositions. Mixtures consist of more than one chemical entity present without any chemical interactions. They can be further classified as homogeneous or heterogeneous mixtures based on their physical appearance.

Pure substances are composed of simple atoms or molecules. They are further classified as elements and compounds.

Element :

An element consists of only one type of atom. We know that an atom is the smallest electrically neutral particle, being made up of fundamental particles, namely electrons, protons and neutrons.

Element can exist as monatomic or polyatomic units.

Example : **Monatomic unit** - Gold (Au), Copper (Cu); **Polyatomic unit** - Hydrogen (H_2), Phosphorous (P_4) and Sulphur (S_8)

Compound:

Compounds are made up of molecules which contain two or more atoms of different elements.

Example : Carbon dioxide (CO_2), Glucose ($C_6H_{12}O_6$), Hydrogen Sulphide (H_2S), Sodium Chloride (NaCl)

Properties of compounds are different from those of their constituent elements. For example, sodium is a shiny metal, and chlorine is an irritating gas. But the compound formed from these two elements, sodium chloride, shows different characteristics as it is a crystalline solid, vital for biological functions.

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Evaluate Yourself

1) By applying the knowledge of chemical classification, classify each of the following into elements, compounds or mixtures.
   (i) Sugar
   (ii) Sea water
   (iii) Distilled water
   (iv) Carbon dioxide
   (v) Copper wire
   (vi) Table salt
   (vii) Silver plate
   (viii) Naphthalene balls

1.3 Atomic and Molecular Masses

1.3.1 Atomic Masses

How much does an individual atom weigh? As atoms are too small with diameter of 10^{-10} m and weigh approximately 10^{-27} kg, it is not possible to measure their mass directly. Hence it is proposed to have relative scale based on a standard atom.

The C-12 atom is considered as standard by the IUPAC (International Union of Pure and Applied Chemistry), and its mass is fixed as 12 amu (or) u. The amu (or) unified atomic mass unit is defined as one twelfth of the mass of a Carbon-12 atom in its ground state.

i.e. 1 amu (or) 1u $\approx 1.6605 \times 10^{-27}$ kg.

In this scale, the relative atomic mass is defined as the ratio of the average atomic mass to the unified atomic mass unit.

$$\text{Relative atomic mass } (A_r) = \frac{\text{Average mass of the atom}}{\text{Unified atomic mass}}$$

For example,

$$\text{Relative atomic mass of hydrogen } (A_r)_H = \frac{\text{Average mass of H-atom (in kg)}}{1.6605 \times 10^{-27} \text{ kg}}$$

$$= \frac{1.6736 \times 10^{-27} \text{ kg}}{1.6605 \times 10^{-27} \text{ kg}}$$

$$= 1.0078 \approx 1.008 \text{ u.}$$

Since most of the elements consist of isotopes that differ in mass, we use average atomic mass. Average atomic mass is defined as the average of the atomic masses of all atoms in their naturally occurring isotopes. For example, chlorine consists of two naturally occurring isotopes $_{17}Cl^{35}$ and $_{17}Cl^{37}$ in the ratio 77 : 23, the average relative atomic mass of chlorine is

$$= \frac{(35 \times 77) + (37 \times 23)}{100}$$

$$= 35.46 \text{ u}$$

1.3.2 Molecular Mass

Similar to relative atomic mass, relative molecular mass is defined as the ratio of the mass of a molecule to the unified atomic mass unit. The relative molecular mass of any compound can be calculated by adding the relative atomic masses of its constituent atoms.

For example,

i) Relative molecular mass of hydrogen molecule (H_2)

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= 2 × (relative atomic mass of hydrogen atom)

= 2 × 1.008 u

= 2.016 u.

ii) Relative molecular mass of glucose ($C_6H_{12}O_6$)

= (6 × 12) + (12 ×1.008) + (6 ×16)

= 72+12.096+96

= 180.096 u

Table 1.1 Relative atomic masses of some elements

Element	Relative atomic mass	Element	Relative atomic mass
H	1.008	Cl	35.45
C	12	K	39.10
N	14	Ca	40.08
O	16	Cr	51.99
Na	23	Mn	54.94
Mg	24.3	Fe	55.85
S	32.07	Cu	63.55

Evaluate Yourself

2) Calculate the relative molecular mass of the following.

(i) Ethanol(C_2H_5OH)

(ii) Potassium permanganate ($KMnO_4$)

(iii) Potassium dichromate ($K_2Cr_2O_7$)

(iv) Sucrose ($C_{12}H_{22}O_{11}$)

1.4 Mole Concept

Often we use special names to express the quantity of individual items for our convenience. For example, a dozen roses means 12 roses and one quire paper means 24 single sheets. We can extend this analogy to understand the concept of mole that is used for quantifying atoms and molecules in chemistry. Mole is the SI unit to represent a specific amount of a substance.

To understand the mole concept, let us calculate the total number of atoms present in 12 g of carbon -12 isotope or molecules in 158.03 g of potassium permanganate, 294.18 g of potassium dichromate and 180 g of glucose.

12 Numbers = 1 Dozen



12 Roses



12 Balls



12 Apples

1 Mole ≡ 6.023×10^{23} entities



158.03g of $KMnO_4$



294.18g of $K_2Cr_2O_7$

Fig. 1.2 Mole Concept

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Table 1.2 Calculation of number of entities in one mole of substance.

S. No.	Name of substance	Mass of the substance taken (gram)	Mass of single atom or molecule (gram) = Atomic mass or Molar mass / Avovadro Number	No. of atoms or molecules = Mass of substance ÷ Mass of single atom or molecule
	(1)	(2)	(3)	(2)÷(3)
1.	Elemental Carbon (C-12)	12	1.9926×10^{-23}	$\frac{12}{1.9926 \times 10^{-23}} = 6.022 \times 10^{23}$
2.	Glucose ($C_6H_{12}O_6$)	180	29.89×10^{-23}	$\frac{180}{29.89 \times 10^{-23}} = 6.022 \times 10^{23}$
3.	Potassium dichromate ($K_2Cr_2O_7$)	294.18	48.851×10^{-23}	$\frac{294.18}{48.851 \times 10^{-23}} = 6.022 \times 10^{23}$
4.	Potassium permanganate ($KMnO_4$)	158.03	26.242×10^{-23}	$\frac{158.03}{26.242 \times 10^{-23}} = 6.022 \times 10^{23}$

From the calculations we come to know that 12 g of carbon-12 contains 6.022×10^{23} carbon atoms and same numbers of molecules are present in 158.03 g of potassium permanganate and 294.18 g of potassium dichromate. Similar to the way we use the term 'dozen' to represent 12 entities, we can use the term 'mole' to represent 6.022×10^{23} entities (atoms or molecules or ions)

One mole is the amount of substance of a system, which contains as many elementary particles as there are atoms in 12 g of carbon-12 isotope. The elementary particles can be molecules, atoms, ions, electrons or any other specified particles.



Gastric acid and antacids:

Antacids are commonly used medicines for treating heartburn and acidity. Do you know the chemistry behind it?

Gastric acid is a digestive fluid formed in the stomach and it contains hydrochloric acid. The typical concentration of the acid in gastric acid is 0.082 M. When the concentration exceeds 0.1 M it causes the heartburn and acidity.

Antacids used to treat acidity contain mostly magnesium hydroxide or aluminium hydroxide that neutralises the excess acid. The chemical reactions are as follows.

$$3\ HCl + Al(OH)_3 \rightarrow AlCl_3 + 3\ H_2O$$

$$2\ HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2\ H_2O$$

From the above reactions we know that 1 mole of aluminium hydroxide neutralises 3 moles of HCl while 1 mole of magnesium hydroxide neutralises 2 moles of HCl.

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Let us calculate the amount of acid neutralised by an antacid that contains 250 mg of aluminium hydroxide and 250 mg of magnesium hydroxide.

Active Compound	Mass in (mg)	Molecular mass ($g\ mol^{-1}$)	No. of moles of active compound	No. of moles OH^-
$Al(OH)_3$	250	78	0.0032	0.0096
$Mg(OH)_2$	250	58	0.0043	0.0086
Total no. of moles of OH^- ion from one tablet				0.0182

One tablet of above composition will neutralise 0.0182 mole of HCl for a person with gastric acid content of 0.1 mole. One tablet can be used to neutralize the excess acid which will bring the concentration back to normal level. (0.1 – 0.018 = 0.082 M)



1.4.1 Avogadro Number:

The total number of entities present in one mole of any substance is equal to 6.022×10^{23}. This number is called Avogadro number which is named after the Italian physicist Amedeo Avogadro who proposed that equal volume of all gases under the same conditions of temperature and pressure contain equal number of molecules. Avogadro number does not have any unit.



Lorenzo Romano Amedeo Carlo Avogadro (1776-1856)

He is known for the Avogadro's hypothesis. In honour of his contributions, the number of fundamental particles in a mole of substance was named as Avogadro number. Though Avogadro didn't predict the number of particles in equal volumes of gas, his hypothesis did lead to the eventual determination of the number as 6.022×10^{23} Rudolf Clausius, with his kinetic theory of gases, provided evidence for Avogadro's law.

In a chemical reaction, atoms or molecules react in a specific ratio. Let us consider the following examples

Reaction 1 : $C + O_2 \rightarrow CO_2$

Reaction 2 : $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

In the first reaction, one carbon atom reacts with one oxygen molecule to give one carbon dioxide molecule. In the second reaction, one molecule of methane burns with two molecules of oxygen to give one molecule of carbon dioxide and two molecules of water. It is clear that the ratio of reactants is based on the number of molecules. Even though the ratio is based on the number of molecules it is practically difficult to count the number of molecules. Because of this reason it is beneficial to use **'mole'** concept rather than the actual number of molecules to quantify the reactants and the products. We can explain the first reaction as one mole of carbon reacts with one mole of oxygen to give one mole of carbon dioxide and the second reaction as one mole of methane burns with two moles of oxygen to give one mole of carbon dioxide and two moles of water. When only atoms are involved, scientists also use the term one gram atom instead of one mole.

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1.4.2 Molar Mass:

Molar mass is defined as the mass of one mole of a substance. The molar mass of a compound is equal to the sum of the relative atomic masses of its constituents expressed in g mol^{-1}.

Examples:

- relative atomic mass of one hydrogen atom = 1.008 u
- molar mass of hydrogen atom = 1.008 g mol^{-1}
- relative molecular mass of glucose = 180 u
- molar mass of glucose = 180 g mol^{-1}

1.4.3 Molar Volume:

The volume occupied by one mole of any substance in the gaseous state at a given temperature and pressure is called molar volume.

Conditions	Volume occupied by one mole of any gaseous substances (in litre)
273 K and 1 bar pressure (STP)	22.71
273 K and 1 atm pressure	22.4
298 K and 1 atm pressure (Room Temperature & pressure (SATP)	24.47

Evaluate Yourself

3a) Calculate the number of moles present in 9 g of ethane.

3b) Calculate the number of molecules of oxygen gas that occupies a volume of 224 ml at 273 K and 3 atm pressure.

1.5 Gram Equivalent Concept:

Similar to mole concept gram equivalent concept is also widely used in chemistry especially in analytical chemistry. In the previous section, we have understood that mole concept is based on molecular mass. Similarly gram equivalent concept is based on equivalent mass.

Definition:

Gram equivalent mass is defined as the mass of an element (compound or ion) that combines or displaces 1.008 g hydrogen or 8 g oxygen or 35.5 g chlorine.

Consider the following reaction:

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$$

In this reaction 1 mole of zinc (i.e. 65.38 g) displaces one mole of hydrogen molecule (2.016 g).

Mass of zinc required to displace 1.008 g hydrogen is

$$= \frac{65.38}{2.016} \times 1.008$$

$$= \frac{65.38}{2}$$

The equivalent mass of zinc = 32.69

The gram equivalent mass of zinc
= 32.69 g eq^{-1}

Equivalent mass has no unit but gram equivalent mass has the unit g eq^{-1}

It is not always possible to apply the above mentioned definition which is

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based on three references namely hydrogen, oxygen and chlorine, because we can not conceive of reactions involving only with those three references. Therefore, a more useful expression used to calculate gram equivalent mass is given below.

$$\text{Gram equivalent mass} = \frac{\text{Molar mass (g mol}^{-1})}{\text{Equivalence factor (eq mol}^{-1})}$$

On the basis of the above expression, let us classify chemical entities and find out the formula for calculating equivalent mass in the table below.

1.5.1 Equivalent Mass of Acids, Bases, Salts, Oxidising Agents and Reducing Agents

Chemical entity	Equivalent Factor(n)	Formula for calculating equivalent mass (E)	Example
Acids	basicity (no. of moles of ionisable H^+ ions present in 1 mole of the acid)	$E = \frac{\text{Molar mass of the acid}}{\text{Basicity of the acid}}$	H_2SO_4 basicity = 2 eq mol^{-1} Molar mass of H_2SO_4 = $(2 \times 1) + (1 \times 32) + (4 \times 16)$ = 98 g mol^{-1} Gram equivalent mass of $H_2SO_4 = \frac{98}{2}$ = 49 g eq^{-1}
Bases	Acidity (no. of moles of ionisable OH^- ion present in 1 mole of the base)	$E = \frac{\text{Molar mass of the base}}{\text{Acidity of the base}}$	KOH acidity = 1 eq mol^{-1} Molar mass of KOH = $(1 \times 39)+(1 \times 16)+(1 \times 1)$ = 56 g mol^{-1} Gram equivalent mass of KOH = $\frac{56}{1}$ = 56 g eq^{-1}
Oxidising agent (or) reducing agent	No. of moles of electrons gained (or) lost by one mole of the reagent during redox reaction	$E = \frac{\text{Molar mass of the oxidising (or) reducing agent}}{\text{No. of moles of electrons gained or lost by one mole of the oxidising (or) reducing agent}}$	$KMnO_4$ is an oxidising agent, Molar mass of $KMnO_4$ = $(1 \times 39) +(1 \times 55) + (4 \times 16)$ = 158 g mol^{-1} In acid medium permanganate is reduced during oxidation and is given by the following equation, $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ $\therefore n = 5$ eq mol^{-1}. Gram equivalent mass of $KMnO_4 = \frac{158}{5} = 31.6$ g eq^{-1}.

Mole concept requires a balanced chemical reaction to find out the amount of reactants involved in the chemical reaction while gram equivalent concept does not

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require the same. We prefer to use mole concept for non-redox reactions and gram equivalent concept for redox reactions.

For example,

If we know the equivalent mass of $KMnO_4$ and anhydrous ferrous sulphate, without writing balanced chemical reaction we can straightaway say that 31.6 g of $KMnO_4$ reacts with 152 g of $FeSO_4$ using gram equivalent concept.

The same can also be explained on the basis of mole concept. The balanced chemical equation for the above mentioned reaction is

$$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 8H_2O$$

i.e. 2 moles ($2 \times 158 = 316$ g) of potassium permanganate reacts with 10 moles ($10 \times 152 = 1520$ g) of anhydrous ferrous sulphate.

$\therefore$ 31.6 g $KMnO_4$ reacts with

$$\frac{1520}{316} \times 31.6 = 152 \text{ g of } FeSO_4$$

Evaluate Yourself

4a) 0.456 g of a metal gives 0.606 g of its chloride. Calculate the equivalent mass of the metal.

4b) Calculate the equivalent mass of potassium dichromate. The reduction half-reaction in acid medium is,

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2\ Cr^{3+} + 7H_2O$$

1.6 Empirical Formula and Molecular Formula

Elemental analysis of a compound gives the mass percentage of atoms present in the compound. Using the mass percentage, we can determine the empirical formula of the compound. Molecular formula of the compound can be arrived at from the empirical formula using the molar mass of the compound.

Empirical formula of a compound is the formula written with the simplest ratio of the number of different atoms present in one molecule of the compound as subscript to the atomic symbol. Molecular formula of a compound is the formula written with the actual number of different atoms present in one molecule as a subscript to the atomic symbol.

Let us understand the empirical formula by considering acetic acid as an example.

The molecular formula of acetic acid is $C_2H_4O_2$

The ratio of C : H : O is 1 : 2 : 1 and hence the empirical formula is CH_2O.

1.6.1 Determination of Empirical Formula from Elemental Analysis Data :

Step 1: Since the composition is expressed in percentage, we can consider the total mass of the compound as 100 g and the percentage values of individual elements as mass in grams.

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Step 2: Divide the mass of each element by its atomic mass. This gives the relative number of moles of various elements in the compound.

Step 3: Divide the value of relative number of moles obtained in the step 2 by the smallest number of them to get the simplest ratio.

Step 4: (only if necessary) in case the simplest ratios obtained in the step 3 are not whole numbers then they may be converted into whole number by multiplying by a suitable smallest number.

Example:

1. An acid found in Tamarind on analysis shows the following percentage composition: 32 % Carbon; 4 % Hydrogen; 64 % Oxygen. Find the empirical formula of the compound.

Element	Percentage	molar mass	Relative no. of moles	Simplest ratio	Simplest ratio (in whole nos)
C	32	12	$\frac{32}{12} = 2.66$	$\frac{2.66}{2.66} = 1$	2
H	4	1	$\frac{4}{1} = 4$	$\frac{4}{2.66} = 1.5$	3
O	64	16	$\frac{64}{16} = 4$	$\frac{4}{2.66} = 1.5$	3

The empirical formula is $C_2H_3O_3$

2. An organic compound present in vinegar has 40 % carbon, 6.6 % hydrogen and 53.4 % oxygen. Find the empirical formula of the compound.

Element	Percentage	Atomic Mass	Relative no. of moles	Simplest ratio	Simplest ratio (in whole no)
C	40	12	$\frac{40}{12} = 3.3$	$\frac{3.3}{3.3} = 1$	1
H	6.6	1	$\frac{6.6}{1} = 6.6$	$\frac{6.6}{3.3} = 2$	2
O	53.4	16	$\frac{53.4}{16} = 3.3$	$\frac{3.3}{3.3} = 1$	1

The empirical formula is CH_2O

Evaluate Yourself

5) A Compound on analysis gave the following percentage composition C=54.55%, H=9.09%, O=36.36%. Determine the empirical formula of the compound.

Molecular formula of a compound is a whole number multiple of the empirical formula. The whole number can be calculated from the molar mass of the compound using the following expression

$$\text{Whole number (n)} = \frac{\text{Molar mass of the compound}}{\text{Calculated empirical formula mass}}$$

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1.6.2 Calculation of Molecular Formula from Empirical Formula:

Compound	Empirical Formula	Molar mass	Empirical Formula mass	Whole number (n)	Molecular formula
Acetic acid	CH_2O	60	30	$\frac{60}{30} = 2$	$(CH_2O) \times 2$ $C_2H_4O_2$
Hydrogen Peroxide	HO	34	17	$\frac{34}{17} = 2$	$(HO) \times 2$ H_2O_2
Lactic acid	CH_2O	90	30	$\frac{90}{30} = 3$	$(CH_2O) \times 3$ $C_3H_6O_3$
Tartaric acid	$C_2H_3O_3$	150	75	$\frac{150}{75} = 2$	$(C_2H_3O_3) \times 2$ $C_4H_6O_6$
Benzene	CH	78	13	$\frac{78}{13} = 6$	$(CH) \times 6$ C_6H_6

Let us understand the calculations of molecular formula from the following example.

Two organic compounds, one present in vinegar (molar mass: 60 g mol^{-1}), another one present in sour milk (molar mass : 90 g mol^{-1}) have the following mass percentage composition. C-40%, H-6.6% ; O-53.4%. Find their molecular formula.

Since both compounds have same mass percentage composition, their empirical formula are the same as worked out in the example **problem no 2** . Empirical formula is CH_2O. Calculated empirical formula mass (CH_2O) = 12 + (2×1) + 16 = 30 g mol^{-1}.

Formula for the compound present in vinegar

$$n = \frac{\text{Molar mass}}{\text{calculated empirical formula mass}} = \frac{60}{30} = 2$$

$\therefore$ Molecular formula $= (CH_2O)_2$

$= C_2H_4O_2$

(acitic acid)

Calculation of molecular formula for the compound present in sour milk.

$$n = \frac{\text{Molar mass}}{30} = \frac{90}{30} = 3$$

Molecular formula $= (CH_2O)_3$

$= C_3H_6O_3$

(lactic acid)

Evaluate Yourself

6) Experimental analysis of a compound containing the elements x,y,z on analysis gave the following data. x = 32 %, y = 24 %, z = 44 %. The relative number of atoms of x, y and z are 2, 1 and 0.5, respectively. (Molecular mass of the compound is 400 g) Find out.

i) The atomic masses of the element x,y,z.

ii) Empirical formula of the compound and

iii) Molecular formula of the compound.

1.7 Stoichiometry

Have you ever noticed the preparation of *kesari* at your home? In one of the popular methods for the preparation of *kesari*, the required ingredients to prepare six cups of *kesari* are as follows.

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1) Rava - 1 cup

2) Sugar - 2 cups

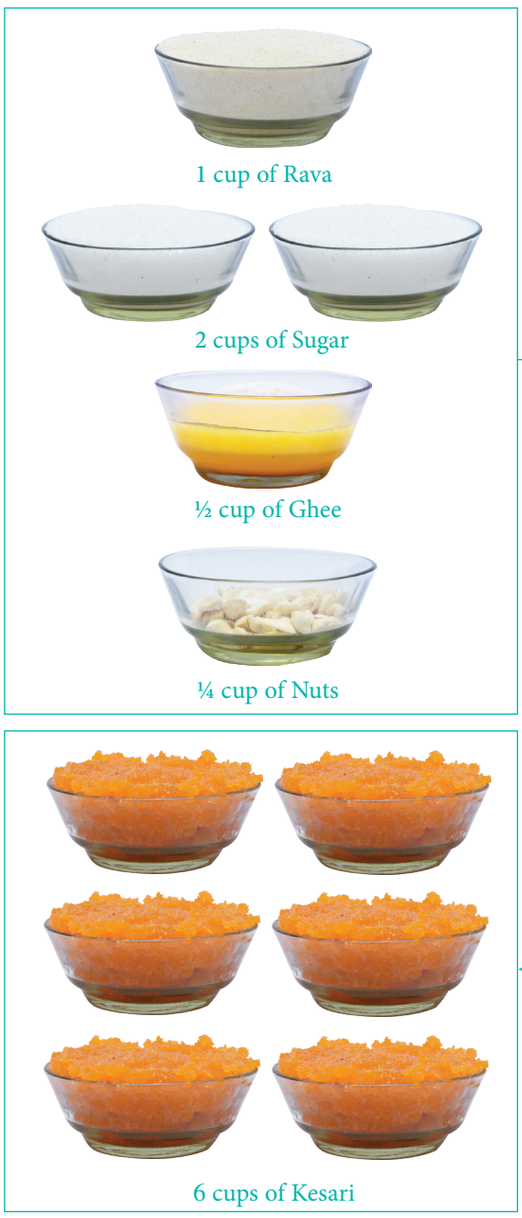
3) Ghee - $\frac{1}{2}$ cup

4) Nuts and Dry fruits - $\frac{1}{4}$ cup

Otherwise,

1 cup rava + 2 cups sugar + $\frac{1}{2}$ cup ghee + $\frac{1}{4}$ cup nuts and dry fruits → 6 cups kesari.

From the above information, we will be able to calculate the amount of ingredients that are required for the preparation of 3 cups of kesari as follows



$$\frac{1 \text{ cup rava}}{6 \text{ cups kesari}} \times 3 \text{ cups kesari} = \frac{1}{2} \text{ cup rava}$$

Alternatively, we can calculate the amount of kesari obtained from 3 cups rava as below.

$$\frac{6 \text{ cups kesari}}{1 \text{ cup rava}} \times 3 \text{ cups rava} = 18 \text{ cups kesari}$$

Similarly, we can calculate the required quantity of other ingredients too.

We can extend this concept to perform stoichiometric calculations for a chemical reaction. In Greek, *stoicheion* means element and *metron* means measure that is, **stoichiometry gives the numerical relationship between chemical quantities in a balanced chemical equation**. By applying the concept of stoichiometry, we can calculate the amount of reactants required to prepare a specific amount of a product and vice versa using balanced chemical equation.

Let us consider the following chemical reaction.

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

From this equation, we learnt that 1 mole of carbon reacts with 1 mole of oxygen molecule to form 1 mole of carbon dioxide.

$$1 \text{ mole of C} \equiv 1 \text{ mole of } O_2$$

$$\equiv 1 \text{ mole of } CO_2$$

The **symbol** '≡' means **'stoichiometrically equal to'**

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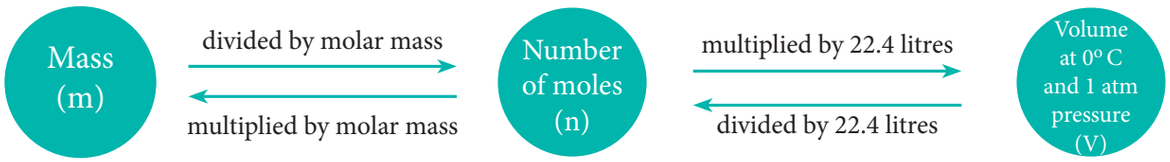
1.7.1 Stoichiometric Calculations:

Stoichiometry is the quantitative relationship between reactants and products in a balanced chemical equation in moles. The quantity of reactants and products can be expressed in moles or in terms of mass unit or as volume. These three units are inter convertible.



Let us explain these conversions by considering the combustion reaction of methane as an example. The balanced chemical equation is,

$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O(g)$

$CH_4\,(g) + 2\,O_2\,(g) \rightarrow CO_2\,(g) + 2\,H_2O(g)$				
Content	**Reactants**		**Products**	
	$CH_4\,(g)$	$O_2\,(g)$	$CO_2\,(g)$	$H_2O\,(g)$
Stoichiometric coefficients	1	2	1	2
Mole-mole relationship	1 mole	2 moles	1 mole	2 moles
Mass-mass relationship = no. of mole × molar mass	1 mol × 16 g mol^{-1} **16 g**	2 mol × 32 g mol^{-1} **64 g**	1 mol × 44 g mol^{-1} **44 g**	2 mol × 18 g mol^{-1} **36 g**
mass - volume relationship mass of reactants = No. of moles × molar mass of reactants Volume of product (1 mole of any gas occupy a volume of 22.4 litre at 273 K and 1 atm pressure)	16 g	64 g	22. 4 L	44.8 L
Volume - volume relationship	1 × 22.4 L 22.4 L	2 × 22.4 L 44.8 L	1 × 22.4 L 22. 4 L	2 × 22.4 L 44. 8 L

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Calculations based on Stoichiometry

1. How many moles of hydrogen is required to produce 10 moles of ammonia ?

   The balanced stoichiometric equation for the formation of ammonia is

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

   As per the stoichiometric equation,

   to produce 2 moles of ammonia, 3 moles of hydrogen are required

   ∴ to produce 10 moles of ammonia,

   $$\frac{3 \text{ moles of } H_2}{\cancel{2 \text{ moles of } NH_3}} \times \overset{5}{\cancel{10 \text{ moles of } NH_3}}$$

   = 15 moles of hydrogen are required.

2. Calculate the amount of water produced by the combustion of 32 g of methane.

   $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

   As per the stoichiometric equation,

   Combustion of 1 mole (16 g) CH_4 produces 2 moles (2 × 18 = 36 g) of water.

   CH_4

   $(12) + (4 \times 1) = 16\ g\ mol^{-1}$

   H_2O

   $(2 \times 1) + (1 \times 16) = 18\ g\ mol^{-1}$

   Combustion of 32 g CH_4 produces

   $$\frac{36 \text{ g } H_2O}{\cancel{16 \text{ g } CH_4}} \times \overset{2}{\cancel{32 \text{ g } CH_4}} = 72 \text{ g of water}$$

3. How much volume of carbon dioxide is produced when 50 g of calcium carbonate is heated completely under standard conditions?

   The balanced chemical equation is,

   $$CaCO_{3\,(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2\,(g)}$$

   As per the stoichiometric equation,

   1 mole (100g) $CaCO_3$ on heating produces 1 mole CO_2

   $CaCO_3$

   $(40) + (12) + (3 \times 16) = 100\ g\ mol^{-1}$

   At STP, 1 mole of CO_2 occupies a volume of 22.7 litres

   ∴ At STP, 50 g of $CaCO_3$ on heating produces,

   $$\frac{22.7 \text{ litres } of\ CO_2}{100 \text{g } \cancel{CaCO_3}} \times \overset{2}{\cancel{50 \text{ g } CaCO_3}}$$

   = 11.35 litres of CO_2

4. How much volume of chlorine is required to form 11.2 L of HCl at 273 K and 1 atm pressure ?

   The balanced equation for the formation of HCl is

   $H_2\ (g) + Cl_2\ (g) \rightarrow 2\ HCl\ (g)$

   As per the stoichiometric equation,

   under given conditions,

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To produce 2 moles of HCl, 1 mole of chlorine gas is required

To produce 44.8 litres of HCl, 22.4 litres of chlorine gas are required.

∴ To produce 11.2 litres of HCl,

$$\frac{22.4 \text{ L } Cl_2}{\frac{44.8 \text{ L of HCl}}{4}} \times 11.2 \text{ L of HCl}$$

= 5.6 litres of chlorine are required.

5. Calculate the percentage composition of the elements present in magnesium carbonate. How many kilogram of CO_2 can be obtained by heating 1 kg of 90 % pure magnesium carbonate.

The balanced chemical equation is

$$MgCO_3 \xrightarrow{\Delta} MgO + CO_2$$

Molar mass of $MgCO_3$ is 84 g mol^{-1}.

84 g $MgCO_3$ contain 24 g of Magnesium.

∴ 100 g of $MgCO_3$ contain

$$\frac{24 \text{ g Mg}}{84 \text{ g } MgCO_3} \times \frac{1.19}{100 \text{ g } MgCO_3}$$

= 28.57 g Mg.

i.e. percentage of magnesium

= 28.57 %.

84 g $MgCO_3$ contain 12 g of carbon

$MgCO_3$

$(24) + (12) + (3 \times 16) = 84 \text{ g mol}^{-1}$

∴ 100 g $MgCO_3$ contain

$$\frac{12 \text{ g C}}{84 \text{ g } MgCO_3} \times \frac{1.19}{100 \text{ g } MgCO_3}$$

= 14.29 g of carbon.

∴ Percentage of carbon

= 14.29 %.

84 g $MgCO_3$ contain 48 g of oxygen

∴ 100 g $MgCO_3$ contains

$$\frac{48 \text{ g O}}{84 \text{ g } MgCO_3} \times \frac{1.19}{100 \text{ g } MgCO_3}$$

= 57.14 g of oxygen.

∴ Percentage of oxygen

= 57.14 %.

As per the stoichiometric equation,

84 g of 100 % pure $MgCO_3$ on heating gives 44 g of CO_2.

∴ 1000 g of 90 % pure $MgCO_3$ gives

$$= \frac{44 \text{ g}}{84 \text{ g} \times 100 \%} \times 90 \% \times 1000 \text{ g}$$

= 471.43 g of CO_2

= 0.471 kg of CO_2

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1.7.2 Limiting Reagents:

Earlier, we learnt that the stoichiometry concept is useful in predicting the amount of product formed in a given chemical reaction. If the reaction is carried out with stoichiometric quantities of reactants, then all the reactants will be converted into products. On the other hand, when a reaction is carried out using non-stoichiometric quantities of the reactants, the product yield will be determined by the reactant that is completely consumed. It limits the further reaction from taking place and is called as the limiting reagent. The other reagents which are in excess are called the excess reagents.

Recall the analogy that we used in stoichiometry concept i.e. kesari preparation,

As per the recipe requirement, 2 cups of sugar are needed for every cup of rava. Consider a situation where 8 cups of sugar and 3 cups of rava are available (all other ingredients are in excess), as per the cooking recipe, we require 3 cups of rava and 6 cups of sugar to prepare 18 cups of kesari. Even though we have 2 more cups of sugar left, we cannot make any more quantity of Kesari as there is no rava available and hence rava limits the quantity of Kesari in this case. Extending this analogy for the chemical reaction in which three moles of sulphur are allowed to react with twelve moles of fluorine to give sulfur hexafluoride.

The balanced equation for this reaction is, $S + 3F_2 \rightarrow SF_6$

Evaluate Yourself

7) The balanced equation for a reaction is given below

$$2x+3y \rightarrow 4l + m$$

When 8 moles of x react with 15 moles of y, then

i) Which is the limiting reagent?

ii) Calculate the amount of products formed.

iii) Calculate the amount of excess reactant left at the end of the reaction.

As per the stoichiometry,

1 mole of sulphur reacts with 3 moles of fluorine to form 1 mole of sulphur hexafluoride and therefore 3 moles of sulphur reacts with 9 moles of fluorine to form 3 moles of sulphur hexafluoride. In this case, all available sulphur gets consumed and therefore it limits the further reaction. Hence sulphur is the limiting reagent and fluorine is the excess reagent. The remaining three moles of fluorine are in excess and do not react.

Urea, a commonly used nitrogen based fertilizer, is prepared by the reaction between ammonia and carbon dioxide as follows.

$$2\,NH_3\,(g) + CO_2\,(g) \rightarrow \underset{\text{Urea}}{H_2N\text{–}\overset{\overset{O}{\|}}{C}\text{–}NH_2}\,(aq) + H_2O(l)$$

In a process, 646 g of ammonia is allowed to react with 1.144 kg of CO_2 to form urea.

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1) If the entire quantity of all the reactants is not consumed in the reaction

which is the limiting reagent ?

2) Calculate the quantity of urea formed and unreacted quantity of the excess reagent.

The balanced equation is

$$2\,NH_3 + CO_2$$
$$\downarrow$$
$$H_2NCONH_2 + H_2O$$

Answer :

1. The entire quantity of ammonia is consumed in the reaction. So ammonia is the limiting reagent. Some quantity of CO_2 remains unreacted, so CO_2 is the excess reagent.

2) Quantity of urea formed

= number of moles of urea formed × molar mass of urea
= 19 moles × 60 g mol^{-1}
= 1140 g = 1.14 kg

Excess reagent leftover at the end of the reaction is carbon dioxide.

Amount of carbon dioxide leftover

= number of moles of CO_2 left over × molar mass of CO_2
= 7 moles × 44 g mol^{-1}
= 308 g.

	Reactants		Products	
	NH_3	CO_2	Urea	H_2O
Stoichiometric coefficients	2	1	1	1
Number of moles of reactants allowed to react $n = \frac{\text{Mass}}{\text{Molar mass}}$	$\frac{646}{17}$ = 38 moles	$\frac{1144}{44}$ = 26 moles	–	–
Actual number of moles consumed during reaction Ratio (2 : 1)	38 moles	19 moles	–	–
No. of moles of product thus formed	–	–	19 moles	19 moles
No. of moles of reactant left at the end of the reaction	–	7 moles	–	–

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1.8 Redox Reactions

When an apple is cut, it turns brown after sometime. Do you know the reason behind this colour change? It is because of a chemical reaction called oxidation. We come across oxidation reactions in our daily life. For example 1) burning of LPG gas 2) rusting of iron



Fig. 1.4 Oxidation reactions in daily life

3) Oxidation of carbohydrates, lipids, etc. into CO_2 and H_2O to produce energy in the living organisms.

All oxidation reactions are accompanied by reduction reactions and vice versa. Such reactions are called redox reactions. As per the classical concept, addition of oxygen (or) removal of hydrogen is called oxidation and the reverse is called reduction.

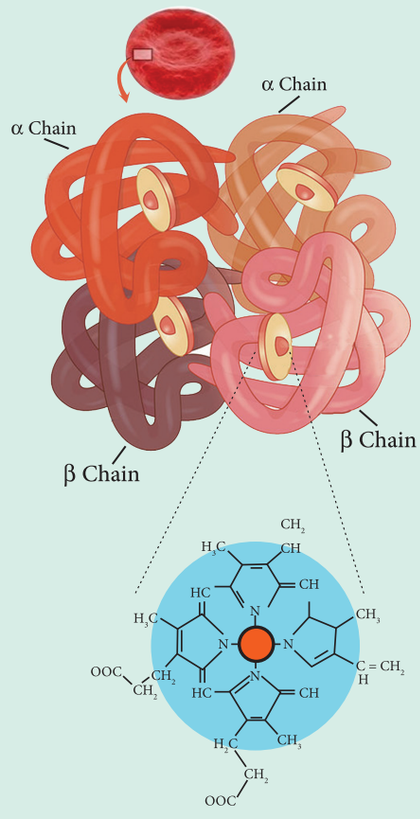
Haemoglobin and oxygen transport



Even a small amount of oxygen present in air leads to the rusting of iron, i.e. iron is oxidised to Fe^{3+}. But the Fe^{2+} present in haemoglobin which binds oxygen during transport of oxygen from lungs to tissues never gets oxidised. Do you know why?

The answer lies in the structural features of haemoglobin. Haemoglobin contains four sub units each with a porphyrin ring (heme) attached to the protein (globin) molecule. In this structure, the iron (Fe^{2+}) forms a co-ordination complex with an octahedral geometry. The four positions of the octahedron are occupied by porphyrin rings, fifth position is filled by imidazole ring of a histidine residue and the sixth position is utilized for binding the oxygen molecule. Generally the Fe^{2+} in heme is susceptible to oxidation. Since the Fe^{2+} ion in haemoglobin is surrounded by the globin protein chain that provides a hydrophobic environment, the oxidation of Fe^{2+} becomes difficult. However, 3% of haemoglobin is oxidised to methemoglobin (haemoglobin where the iron is present in Fe^{3+} state and oxygen does not bind to this) daily. The enzyme methemoglobin reductase reduces it back to haemoglobin.

Cyanide poisoning: While oxygen binds reversibly to haemoglobin, cyanide binds irreversibly to haemoglobin and blocks oxygen binding. As a result the transport of oxygen from the lungs to tissues is stopped. It leads to the quick death of the person.



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Consider the following two reactions.

Reaction 1 : $4\ Fe + 3O_2 \rightarrow 2\ Fe_2O_3$

Reaction 2 : $H_2S + Cl_2 \rightarrow 2\ HCl + S$

Both these reactions are oxidation reactions as per the classical concept.

In the first reaction which is responsible for the rusting of iron, the oxygen adds on to the metal, iron. In the second reaction, hydrogen is removed from Hydrogen sulphide (H_2S). Identity which species gets reduced.

Consider the following two reactions in which the removal of oxygen and addition of hydrogen take place respectively. These reactions are called reduction reactions as per the classical concept.

$CuO + C \rightarrow Cu + CO$ (Removal of oxygen from cupric oxide)

$S + H_2 \rightarrow H_2S$ (Addition of hydrogen to sulphur).

Oxidation-reduction reactions i.e. redox reactions are not always associated with oxygen or hydrogen. In such cases, the process can be explained on the basis of electrons. The reaction involving loss of electron is termed oxidation and gain of electron is termed reduction.

For example,

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (loss of electron-oxidation).

$Cu^{2+} + 2e^- \rightarrow Cu$ (gain of electron-reduction)

Redox reactions can be better explained using oxidation numbers.

1.8.1 Oxidation Number:

It is defined as the imaginary charge left on the atom when all other atoms of the compound have been removed in their usual oxidation states that are assigned according to set of rules. A term that is often used interchangeably with oxidation number is oxidation state

1) The oxidation state of a free element (i.e. in its uncombined state) is zero.

Example : each atom in H_2, Cl_2, Na, S_8 have the oxidation number of zero.

2) For a monatomic ion, the oxidation state is equal to the net charge on the ion.

Example : The oxidation number of sodium in Na^+ is +1.

The oxidation number of chlorine in Cl^- is –1.

3) The algebric sum of oxidation states of all atoms in a molecule is equal to zero, while in ions, it is equal to the net charge on the ion.

Example:

In H_2SO_4; 2 × (oxidation number of hydrogen) + (oxidation number of S) + 4 (oxidation number of oxygen) = 0.

In SO_4^{2-}; (oxidation number of S) + 4 (oxidation number of oxygen) = –2.

4) Hydrogen has an oxidation number of +1 in all its compounds except in metal hydrides where it has –1 value.

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Example:

Oxidation number of hydrogen in hydrogen chloride (HCl) is + 1.

Oxidation number of hydrogen in sodium hydride (NaH) is –1.

5) Fluorine has an oxidation state of – 1 in all its compounds.

6) The oxidation state of oxygen in most compounds is –2. Exceptions are peroxides, super oxides and compounds with fluorine.

Example : Oxidation number of oxygen,

i) in water (H_2O) is –2.

ii) in hydrogen peroxide (H_2O_2) is –1.

$2 (+ 1) + 2x = 0; \quad \Rightarrow 2x = -2 ; \quad \Rightarrow x = -1$

iii) in super oxides such as KO_2 is $-\frac{1}{2}$

$+1 + 2x = 0 ; \quad 2x = -1 ; \quad x = -\frac{1}{2}$

iv) in oxygen difluoride (OF_2) is + 2.

$x + 2 (-1) = 0; \quad x = +2$

7) Alkali metals have an oxidation state of + 1 and alkaline earth metals have an oxidation state of + 2 in all their compounds.

Calculation of oxidation number using the above rules.

Sl.No	Oxidation number of the element	In the compound	Calculation
1	C	CO_2	$x + 2 (-2) = 0$ $x = +4$
2	S	H_2SO_4	$2 (+1) + x + 4 (-2) = 0$ $2 + x - 8 = 0$ $x = +6$
3	Cr	$Cr_2O_7^{2-}$	$2x + 7(-2) = -2$ $2x - 14 = -2$ $x = +6$
4	C	CH_2F_2	$x + 2(+1) + 2(-1) = 0$ $x = 0$
5	S	SO_2	$x + 2(-2) = 0$ $x = +4$

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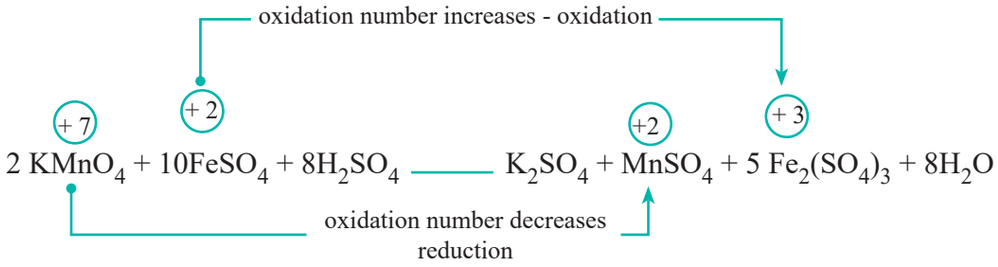
Redox reactions in terms of oxidation numbers

During redox reactions, the oxidation number of elements changes. A reaction in which oxidation number of the element increases is called oxidation. A reaction in which it decreases is called reduction.

Consider the following reaction



In this reaction, manganese in potassium permanganate ($KMnO_4$) favours the oxidation of ferrous sulphate ($FeSO_4$) into ferric sulphate ($Fe_2(SO_4)_3$ by gaining electrons and thereby gets reduced. Such reagents are called oxidising agents or oxidants. Similarly , the reagents which facilitate reduction by releasing electrons and get oxidised are called reducing agents.

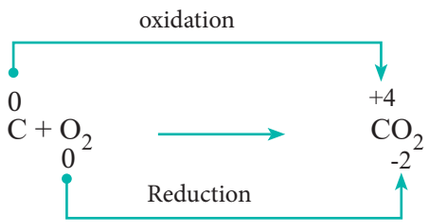
1.8.2 Types of Redox Reactions

Redox reactions are classified into the following types.

1. Combination reactions:

Redox reactions in which two substances combine to form a single compound are called combination reaction.

Example:



2. Decomposition reactions:

Redox reactions in which a compound breaks down into two or more components are called decomposition reactions. These reactions are opposite to combination reactions. In these reactions, the oxidation number of the different elements in the same substance is changed.

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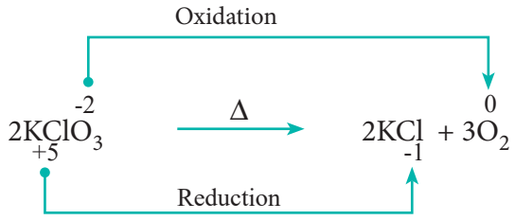
Example:



3. Displacement reactions:

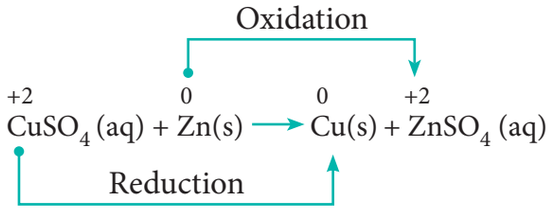
Redox reactions in which an ion (or an atom) in a compound is replaced by an ion (or atom) of another element are called displacement reactions. They are further classified into (i) metal displacement reactions (ii) non-metal displacement reactions.

(i) Metal displacement reactions:

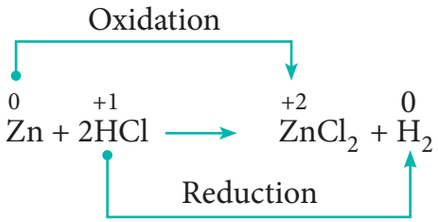
Place a zinc metal strip in an aqueous copper sulphate solution taken in a beaker. Observe the solution, the intensity of blue colour of the solution slowly reduced and finally disappeared.

The zinc metal strip became coated with brownish metallic copper. This is due to the following metal displacement reaction.





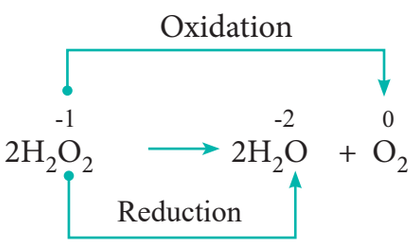
ii) Non-metal displacement

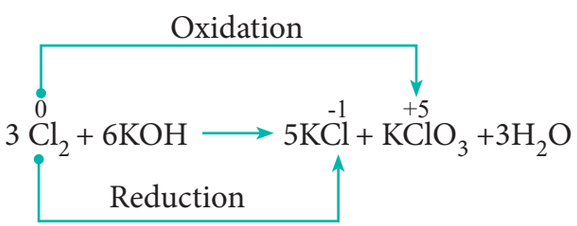


4. Disproportionation reaction (Auto redox reactions)

In some redox reactions, the same compound can undergo both oxidation and reduction. In such reactions, the oxidation state of one and the same element is both increased and decreased. These reactions are called disproportionation reactions.

Examples:





5. Competitive electron transfer reaction

In metal displacement reactions, we learnt that zinc replaces copper from copper sulphate solution. Let us examine whether the reverse reaction takes place or not. As discussed earlier, place a metallic copper strip in zinc sulphate solution. If copper replaces zinc from zinc sulphate solution, Cu^{2+} ions would be released into the solution and the colour of the solution

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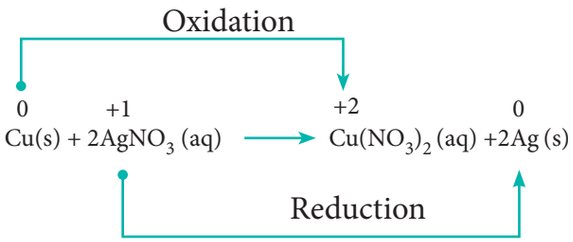
would change to blue. But no such change is observed. Therefore, we conclude that among zinc and copper, zinc has more tendency to release electrons and copper to accept the electrons.

Let us extend the reaction to copper metal and silver nitrate solution. Place a strip of metallic copper in sliver nitrate solution taken in a beaker. After some time, the solution slowly turns blue. This is due to the formation of Cu^{2+} ions, i.e. copper replaces silver from silver nitrate. The reaction is,





It indicates that between copper and silver, copper has the tendency to release electrons and silver to accept electrons.

From the above experimental observations, we can conclude that among the three metals, namely, zinc, copper and silver, the electron releasing tendency is in the following order.

Zinc > Copper > Silver

This kind of competition for electrons among various metals helps us to design (galvanic) cells. In XII standard we will study the galvanic cell in detail.

1.8.3. Balancing (the Equation) of Redox Reactions

The two methods for balancing the equation of redox reactions are as follows.

i) The oxidation number method

ii) Ion-electron method / half reaction method.

Both are based on the same principle: In oxidation - reduction reactions the total number of electrons donated by the reducing agent is equal to the total number of electrons gained by the oxidising agent.

Oxidation number method

In this method, the number of electrons lost or gained in the reaction is calculated from the oxidation numbers of elements before and after the reaction. Let us consider the oxidation of ferrous sulphate by potassium permanganate in acid medium. The unbalanced chemical equation is,

$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$

Step 1

Using oxidation number concept, identify the reactants (atom) which undergo oxidation and reduction.

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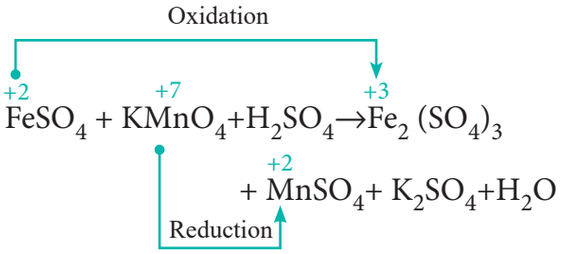
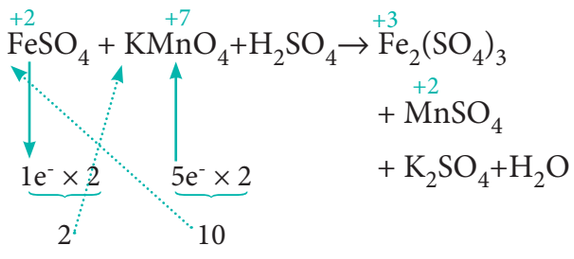


a) The oxidation number of Mn in $KMnO_4$ changes from +7 to +2 by gaining five electrons.

b) The oxidation number of Fe in $FeSO_4$ changes from +2 to +3 by loosing one electron.

Step 2

Since, the total number of electrons lost is equal to the total number of electrons gained, equate, the number of electrons, by cross multiplication of the respective formula with suitable integers on reactant side as below. Here, the product $Fe_2(SO_4)_3$ contains 2 moles of iron, So, the Coefficients $1e^-$ & $5e^-$ are multiplied by the number '2'



$10\ FeSO_4 + 2\ KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 +$

$MnSO_4 + K_2SO_4 + H_2O$

Step 3 Balance the reactant / Product - Oxidised / reduced

Now, based on the reactant side, balance the products (ie oxidised and reduced).The above equation becomes

$10FeSO_4 + 2KMnO_4 + H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + H_2O$

Step 4 Balance the other elements except H and O atoms. In this case, we have to balance K and S atoms but K is balanced automatically.

Reactant Side : 10 'S' atoms (10 $FeSO_4$)

Product Side : 18 'S' atoms

$5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4$

$15S + 2S + 1S = 18S$

Therefore the difference 8-S atoms in reactant side, has to be balanced by multiplying H_2SO_4 by '8' The equation now becomes,

$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + H_2O$

Step 5

Balancing 'H' and 'O' atoms

Reactant side '16'-H atoms ($8H_2SO_4$ i.e. 8 x 2H = 16 'H')

Product side '2' - H atoms (H_2O i.e. 1 x 2H = 2 'H')

Therefore, multiply H_2O molecules in the product side by '8'

$10\ FeSO_4 + 2\ KMnO_4 + 8\ H_2SO_4 \rightarrow$

$5\ Fe_2(SO_4)_3 + 2\ MnSO_4 + K_2SO_4 + 8H_2O$

The oxygen atom is automatically balanced. This is the balanced equation.

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Ion - Electron method

This method is used for ionic redox reactions.

Step 1

Using oxidation number concept, find out the reactants which undergo oxidation and reduction.

Step 2

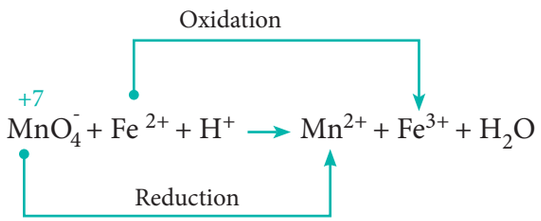
Write two separate half equations for oxidation and reduction reaction,

Let us consider the same example which we have already discussed in oxidation number method.

$KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow$

$MnSO_4 + Fe_2(SO_4)_3 + K_2SO_4 + H_2O$

The ionic form of this reaction is,



The two half reactions are,

$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$ ---------- (1)

and

$MnO_4^- + 5e^- \rightarrow Mn^{2+}$ ---------- (2)

Balance the atoms and charges on both sides of the half reactions.

Equation (1)$\Rightarrow$ No changes i.e.,

$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$ ---------- (1)

Equation (2)$\Rightarrow$ 4'O' on the reactant side, therefore add $4H_2O$ on the product side, to balance 'H' - add, $8H^+$ in the reactant side

$MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$---- (3)

Step 3

Equate both half reactions such that the number of electrons lost is equal to number of electrons gained.

Addition of two half reactions gives the balanced equation represented by equation (6).

(1) x 5 $\Rightarrow$ $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$ ---------- (4)

(3) x 1 $\Rightarrow$ $MnO_4^- + 5e^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ ----------(5)

(4) + (5) $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$----------(6)

Evaluate Yourself

8) Balance the following equation using oxidation number method

$As_2S_3 + HNO_3 + H_2O \rightarrow H_3AsO_4 + H_2SO_4 + NO$

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SUMMARY

Chemistry plays a major role in providing needs of human life in our day-to-day life. All things that we come across in life are made of matter. Anything that has mass and occupies space is called matter. Matter is classified based on the physical state and by chemical composition. An element consists of only one type of atom. Compounds contain two or more atoms of same or different elements and their properties are different from those of its constituent elements.

Atoms are too small to measure their masses directly. The IUPAC introduced relative scale of mass based on a standard atom C-12. One twelfth of the mass of a Carbon-12 atom in its ground state is called as Unified atomic mass. 1 amu (or) $1u \approx 1.6605 \times 10^{-27}$ kg. Relative atomic mass is defined as the ratio of the average atomic mass to the unified atomic mass unit. Average atomic mass of an element is the average of the atomic masses of all its naturally occurring isotopes. Molecular mass is the ratio of the mass of a molecule to the unified atomic mass unit. Relative molecular mass is obtained by adding the relative atomic masses of its constituent atoms.

Amounts of substances are usually expressed in moles. A mole is the amount of substance which contains as many elementary entities as there are in 12 gram of Carbon- 12 isotope. Avogadro number is the total number of entities present in one mole of any substance and is equal to 6.022×10^{23}. Molar mass is the mass of one mole of that substance expressed in $g\ mol^{-1}$. One mole of an ideal gas occupies a volume of 22.4 litre at 273 K and 1 atm pressure. Similar to the mole concept, the concept of equivalent mass is also used in analytical chemistry. Gram equivalent mass is the mass of an element (compound/ion) that combines or displaces 1.008 g hydrogen, 8 g oxygen or 35.5 g chlorine. Elemental analysis of a compound gives the mass percentage of atoms from which empirical and molecular formula are calculated. Empirical formula is the simplest ratio of the number of different atoms present in one molecule of the compound. Molecular formula is the formula written with the actual number of different atoms present in one molecule. A quantitative relationship between reactants and products can be understood from stoichiometry. Stoichiometry gives the numerical relationship between chemical quantities in a balanced equation. When a reaction is carried out using non-stoichiometric quantities of the reactants, the product yield will be determined by the reactant that is completely consumed and is called the limiting reagent. It limits the further reaction to take place. The other reagent which is in excess is called the excess reagent.

The reaction involving loss of electron is oxidation and gain of electron is reduction. Usually both these reactions take place simultaneously and are called as redox reactions. These redox reactions can be explained using oxidation number concept. Oxidation number is the imaginary charge left on the atom when all other atoms of the compound have

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been removed in their usual oxidation states. A reaction in which oxidation number of the element increases is called oxidation and decreases is called reduction.

Redox reactions in which

- two substances combine to form compound are called combination reaction.
- a compound breaks down into two (or) more components is called decomposition reaction
- an ion (or atom) in a compound is replaced by an atom (or ion) of another element are called displacement reactions
- the same compound can undergo both oxidation and reduction and the oxidation state of one and the same element is both increased and decreased called disproportionate reactions.
- competition for electrons occurs between various metals is called competitive electron transfer reactions.

The equation of redox reaction is balanced either by oxidation number method or by ion-electron method.

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EVALUATION

I. Choose the best answer.

1. 40 ml of methane is completely burnt using 80 ml of oxygen at room temperature The volume of gas left after cooling to room temperature is

   (a) 40 ml CO_2 gas

   (b) 40 ml CO_2 gas and 80 ml H_2O gas

   (c) 60 ml CO_2 gas and 60 ml H_2O gas

   (d) 120 ml CO_2 gas

2. An element X has the following isotopic composition ^{200}X = 90 %, ^{199}X = 8 % and ^{202}X = 2 %. The weighted average atomic mass of the element X is closest to

   (a) 201 u

   (b) 202 u

   (c) 199 u

   (d) 200 u

3. Assertion : Two mole of glucose contains 12.044×10^{23} molecules of glucose

   Reason : Total number of entities present in one mole of any substance is equal to 6.02×10^{22}

   (a) both assertion and reason are true and the reason is the correct explanation of assertion

   (b) both assertion and reason are true but reason is not the correct explanation of assertion

   (c) assertion is true but reason is false

   (d) both assertion and reason are false

4. Carbon forms two oxides, namely carbon monoxide and carbon dioxide. The equivalent mass of which element remains constant?

   (a) Carbon

   (b) oxygen

   (c) both carbon and oxygen

   (d) neither carbon nor oxygen

5. The equivalent mass of a trivalent metal element is 9 g eq^{-1} the molar mass of its anhydrous oxide is

   (a) 102 g (b) 27 g (c) 270 g (d) 78 g

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6. The number of water molecules in a drop of water weighing 0.018 g is

(a) 6.022×10^{26} (b) 6.022×10^{23}

(c) 6.022×10^{20} (d) 9.9×10^{22}

7. 1 g of an impure sample of magnesium carbonate (containing no thermally decomposable impurities) on complete thermal decomposition gave 0.44 g of carbon dioxide gas. The percentage of impurity in the sample is

(a) 0 % (b) 4.4 % (c) 16 % (d) 8.4 %

8. When 6.3 g of sodium bicarbonate is added to 30 g of acetic acid solution, the residual solution is found to weigh 33 g. The number of moles of carbon dioxide released in the reaction is

(a) 3 (b) 0.75 (c) 0.075 (d) 0.3

9. When 22.4 litres of H_2 (g) is mixed with 11.2 litres of Cl_2 (g), each at 273 K at 1 atm the moles of HCl (g), formed is equal to

(a) 2 moles of HCl (g) (b) 0.5 moles of HCl (g)

(c) 1.5 moles of HCl (g) (d) 1 moles of HCl (g)

10. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?

(a) $Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$

(b) $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

(c) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

(d) none of the above

11. Choose the disproportionation reaction among the following redox reactions.

(a) $3Mg\,(s) + N_2\,(g) \rightarrow Mg_3N_2\,(s)$

(b) $P_4\,(s) + 3\,NaOH + 3H_2O \rightarrow PH_3(g) + 3NaH_2PO_2\,(aq)$

(c) $Cl_2\,(g) + 2KI(aq) \rightarrow 2KCl(aq) + I_2$

(d) $Cr_2O_3\,(s) + 2Al\,(s) \rightarrow Al_2O_3(s) + 2Cr(s)$

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12. The equivalent mass of potassium permanganate in alkaline medium is

$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

(a) 31.6 (b) 52.7 (c) 79 (d) None of these

13. Which one of the following represents 180g of water?

(a) 5 Moles of water

(b) 90 moles of water

(c) $\frac{6.022 \times 10^{23}}{180}$ molecules of water

(d) 6.022×10^{24} molecules of water

14. 7.5 g of a gas occupies a volume of 5.6 litres at 0° C and 1 atm pressure. The gas is

(a) NO (b) N_2O (c) CO (d) CO_2

15. Total number of electrons present in 1.7 g of ammonia is

(a) 6.022×10^{23}

(b) $\frac{6.022 \times 10^{22}}{1.7}$

(c) $\frac{6.022 \times 10^{24}}{1.7}$

(d) $\frac{6.022 \times 10^{23}}{1.7}$

16. The correct increasing order of the oxidation state of sulphur in the anions

SO_4^{2-}, SO_3^{2-}, $S_2O_4^{2-}$, $S_2O_6^{2-}$ is

(a) $SO_3^{2-} < SO_4^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$

(b) $SO_4^{2-} < S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$

(c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-} < SO_4^{2-}$

(d) $S_2O_6^{2-} < S_2O_4^{2-} < SO_4^{2-} < SO_3^{2-}$

17. The equivalent mass of ferrous oxalate is

(a) $\frac{\text{molar mass of ferrous oxalate}}{1}$

(b) $\frac{\text{molar mass of ferrous oxalate}}{2}$

(c) $\frac{\text{molar mass of ferrous oxalate}}{3}$

(d) none of these

18. If Avogadro number were changed from 6.022×10^{23} to 6.022×10^{20}, this would change

(a) the ratio of chemical species to each other in a balanced equation

(b) the ratio of elements to each other in a compound

(c) the definition of mass in units of grams

(d) the mass of one mole of carbon

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19. Two 22.4 litre containers A and B contains 8 g of O_2 and 8 g of SO_2 respectively at 273 K and 1 atm pressure, then

(a) Number of molecules in A and B are same

(b) Number of molecules in B is more than that in A.

(c) The ratio between the number of molecules in A to number of molecules in B is 2:1

(d) Number of molecules in B is three times greater than the number of molecules in A.

20. What is the mass of precipitate formed when 50 ml of 8.5 % solution of $AgNO_3$ is mixed with 100 ml of 1.865 % potassium chloride solution?

(a) 3.59 g (b) 7 g (c) 14 g (d) 28 g

21. The mass of a gas that occupies a volume of 612.5 ml at room temperature and pressure (25^0 C and 1 atm pressure) is 1.1g. The molar mass of the gas is

(a) 66.25 g mol^{-1} (b) 44 g mol^{-1}

(c) 24.5 g mol^{-1} d) 662.5 g mol^{-1}

22. Which of the following contain same number of carbon atoms as in 6 g of carbon-12.

(a) 7.5 g ethane (b) 8 g methane

(c) both (a) and (b) (d) none of these

23. Which of the following compound(s) has /have percentage of carbon same as that in ethylene (C_2H_4)

(a) propene (b) ethyne

(c) benzene (d) ethane

24. Which of the following is/are true with respect to carbon -12.

(a) relative atomic mass is 12 u

(b) oxidation number of carbon is +4 in all its compounds.

(c) 1 mole of carbon-12 contain 6.022×10^{22} carbon atoms.

(d) all of these

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25. Which one of the following is used as a standard for atomic mass.

(a) $_6C^{12}$ (b) $_7C^{12}$ (c) $_6C^{13}$ (d) $_6C^{14}$

II. Write brief answer to the following questions.

26) Define relative atomic mass.

27) What do you understand by the term mole.

28) Define equivalent mass.

29) What do you understand by the term oxidation number.

30) Distinguish between oxidation and reduction.

31) Calculate the molar mass of the following compounds.

i) Urea $[CO(NH_2)_2]$

ii) Acetone $[CH_3COCH_3]$

iii) Boric acid $[H_3BO_3]$

iv) Sulphuric acid $[H_2SO_4]$

32) The density of carbon dioxide is equal to 1.965 kgm^{-3} at 273 K and 1 atm pressure. Calculate the molar mass of CO_2.

33) Which contains the greatest number of moles of oxygen atoms

i) 1 mol of ethanol

ii) 1 mol of formic acid

iii) 1 mol of H_2O

34) Calculate the average atomic mass of naturally occurring magnesium using the following data

Isotope	Isotopic atomic mass	Abundance (%)
Mg^{24}	23.99	78.99
Mg^{25}	24.99	10.00
Mg^{26}	25.98	11.01

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35) In a reaction $x + y + z_2 \rightarrow xyz_2$ identify the Limiting reagent if any, in the following reaction mixtures.

(a) 200 atoms of x + 200 atoms of y + 50 molecules of z_2

(b) 1mol of x + 1 mol of y+3 mol of z_2

(c) 50 atoms of x + 25 atoms of y+50 molecules of z_2

d) 2.5 mol of x +5 mol of y+5 mol of z_2

36) Mass of one atom of an element is 6.645×10^{-23} g. How many moles of element are there in 0.320 kg.

37) What is the difference between molecular mass and molar mass? Calculate the molecular mass and molar mass for carbon monoxide.

38) What is the empirical formula of the following ?

i) Fructose ($C_6H_{12}O_6$) found in honey

ii) Caffeine ($C_8H_{10}N_4O_2$) a substance found in tea and coffee.

39) The reaction between aluminium and ferric oxide can generate temperatures up to 3273 K and is used in welding metals. (Atomic mass of Al = 27 u Atomic mass of O = 16 u)

$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$; If, in this process, 324 g of aluminium is allowed to react with 1.12 kg of ferric oxide.

i) Calculate the mass of Al_2O_3 formed.

ii) How much of the excess reagent is left at the end of the reaction?

40) How many moles of ethane is required to produce 44 g of $CO_{2\,(g)}$ after combustion.

41) Hydrogen peroxide is an oxidising agent. It oxidises ferrous ion to ferric ion and reduced itself to water. Write a balanced equation.

42) Calculate the empirical and molecular formula of a compound containing 76.6% carbon, 6.38 % hydrogen and rest oxygen its vapour density is 47.

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43) A Compound on analysis gave Na = 14.31% S = 9.97% H= 6.22% and O= 69.5% calculate the molecular formula of the compound, if all the hydrogen in the compound is present in combination with oxygen as water of crystallization. (molecular mass of the compound is 322).

44) Balance the following equations by oxidation number method

i) $K_2Cr_2O_7 + KI + H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + I_2 + H_2O$

ii) $KMnO_4 + Na_2SO_3 \rightarrow MnO_2 + Na_2SO_4 + KOH$

iii) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO_2 + H_2O$

iv) $KMnO_4 + H_2C_2O_4 + H_2SO_4 \rightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

45) Balance the following equations by ion electron method.

i) $KMnO_4 + SnCl_2 + HCl \rightarrow MnCl_2 + SnCl_4 + H_2O + KCl$

ii) $C_2O_4^{2-} + Cr_2O_7^{2-} \rightarrow Cr^{3+} + CO_2$ (in acid medium)

iii) $Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + NaI$

iv) $Zn + NO_3^- \rightarrow Zn^{2+} + NO$ (in acid medium)

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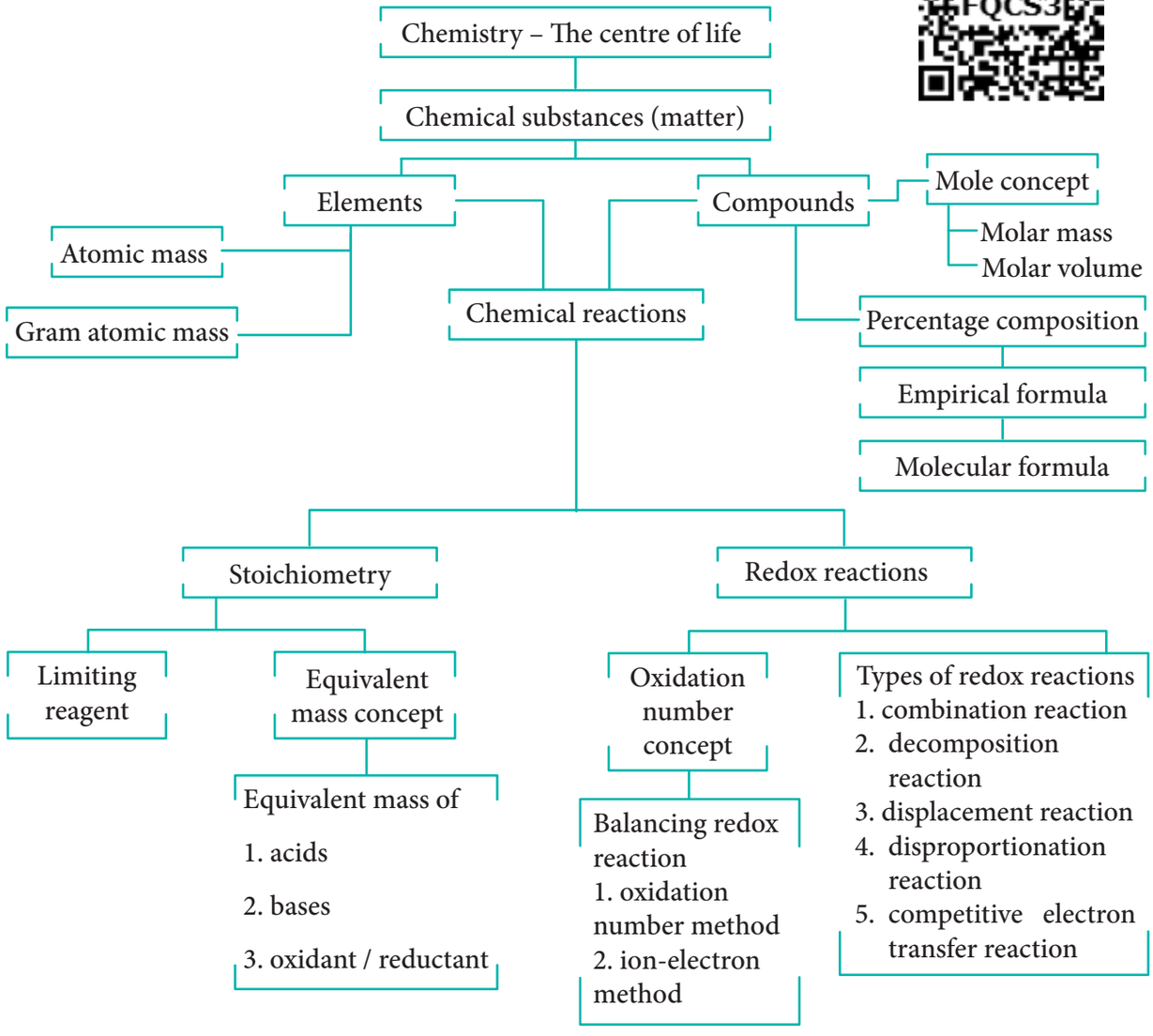
CONCEPT MAP

FQCS3



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ICT Corner

Calculation of Empirical and Molecular Formula

By using this tool you will be able to calculate the empirical and **molecular formula from the percentage composition of elements**

Please go to the URL
https://ggbm.at/FbUwkmUw
(or)
Scan the QR code on the right side

Step – 1

Open the Browser and type the URL given (or) Scan the QR Code. You can see a GeoGebra Work book named "11th Standard Chemistry". Open the worksheet named "Empirical Formula". You will see a webpage as shown in the figure.

Step – 2

Find the serial number of the elements of the compound under examination from the table present on the right side of the page and enter it in the space provided (1). And enter their percentage of composition in the corresponding space (2)

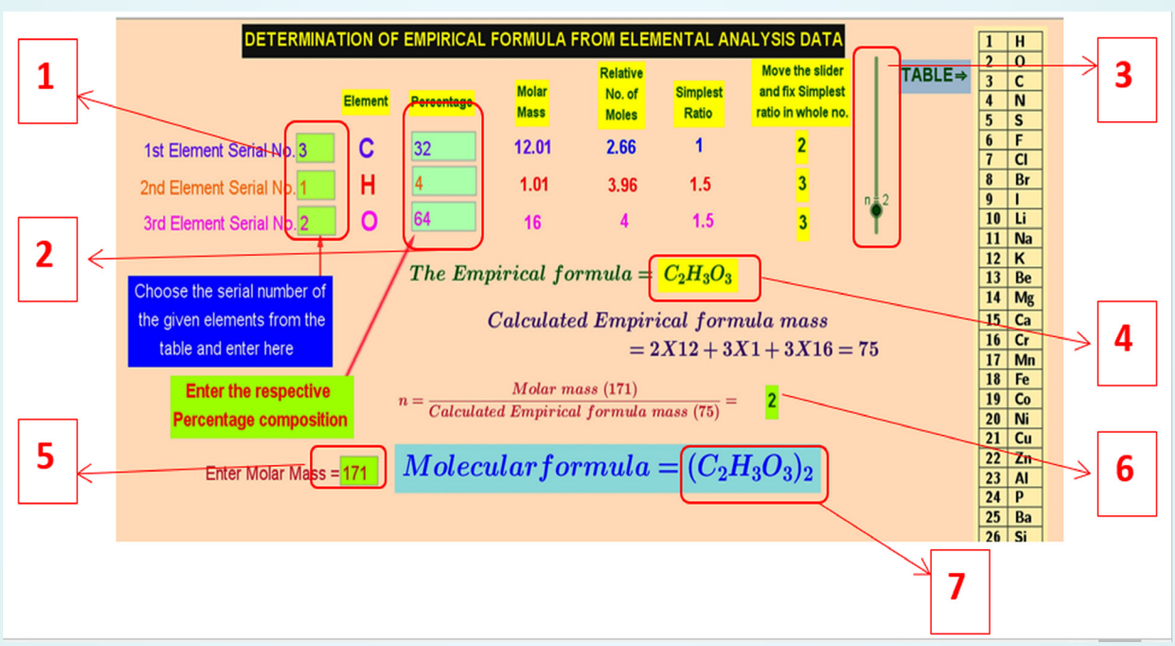
Step – 3

Now you can see the molar mass, relative no. of moles and the simplest ratio all automatically calculated and filled in the corresponding boxes. If the simplest ratio contains fractions then use the slider (3) to choose a smallest number to bring the simplest ratio to whole number.

You can now see the calculated empirical formula (4)

Step – 4

In order to calculate the Molecular formula, enter the molar mass in the corresponding box (5). Now the 'n' will be displayed (6) and Molecular formula is displayed at the bottom (7)



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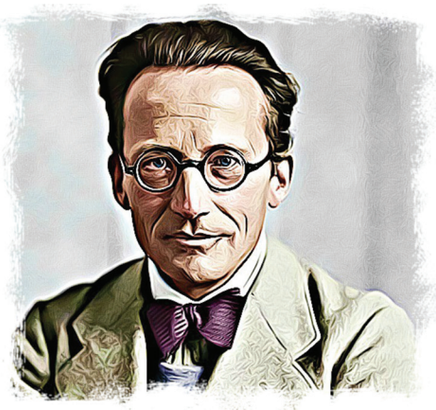
Unit 2

Quantum Mechanical Model of Atom



Erwin Schrödinger
(1887 - 1961)

Erwin Schrödinger was awarded the Nobel Prize in physics in 1933 for "the discovery of new productive forms of atomic theory". Schrödinger had wide interests starting from chemistry, physics, maths and botany. He was not satisfied with the quantum condition in Bohr's orbit theory and believed that atomic spectra should really be determined by some kind of eigenvalue problem and proposed the wave equation, now named after him.

Learning Objectives:

After studying this unit, students will be able to

- Recognise various atomic models
- Explain the dual behaviour of matter
- Derive de Broglie equation and solve numerical problems
- Explain Heisenberg's uncertainty principle and solve related problems
- Appreciate the significance of quantum numbers
- Summarise important features of quantum mechanical model of atom
- Draw the shapes of various atomic orbitals
- Explain the Aufbau principle
- Describe Hund's rule and Pauli's exclusion principle
- Apply the relevant rules for filling electrons in atoms and write the electronic configuration of various atoms

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2.1 Introduction to atom models:

Let us recall the history of the development of atomic models from the previous classes. We know that all things are made of matter. The basic unit that makes up all matter is atom. The word 'atom' has been derived from the Greek word '*a-tomio*' meaning non-divisible. Atom was considered as non-divisible until the discovery of sub-atomic particles such as electron, proton and neutron. J. J. Thomson's cathode ray experiment revealed that atoms consist of negatively charged particles called electrons. He proposed that atom is a positively charged sphere in which the electrons are embedded like the seeds in the watermelon. Later, Rutherford's α-ray scattering experiment results proved that Thomson's model was wrong. Rutherford bombarded a thin gold foil with a stream of fast moving α–particles. It was observed that

(i) most of the α–particles passed through the foil

(ii) some of them were deflected through a small angle and

(iii) very few α–particles were reflected back by 180°

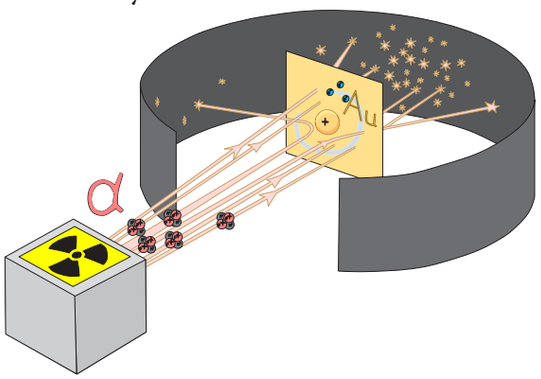

Figure. 2.1 Rutherford's α-ray scattering experiment

Based on these observations, he proposed that in an atom there is a tiny positively charged nucleus and the electrons are moving around the nucleus with high speed. The theory of electromagnetic radiation states that a moving charged particle should continuously loose its energy in the form of radiation. Therefore, the moving electron in an atom should continuously loose its energy and finally collide with nucleus resulting in the collapse of the atom. However, this doesn't happen and the atoms are stable. Moreover, this model does not explain the distribution of electrons around the nucleus and their energies.

2.1.1 Bohr atom model:

The work of Planck and Einstein showed that the energy of electromagnetic radiation is quantised in units of hν (where ν is the frequency of radiation and h is Planck's constant 6.626×10^{-34} Js). Extending Planck's quantum hypothesis to the energies of atoms, Niels Bohr proposed a new atomic model for the hydrogen atom. This model is based on the following assumptions:

1. The energies of electrons in an atom are quantised.
2. The electron is revolving around the nucleus in a certain circular path of fixed energy called stationary orbit.
3. Electron can revolve only in those orbits in which the angular momentum (mvr) of the electron must be equal to an integral multiple of h/2π.

i.e. $mvr = nh/2\pi$ -------- (2.1)

where n = 1,2,3,...etc.,

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4. As long as an electron revolves in the fixed stationary orbit, it doesn't lose its energy. However, when an electron jumps from higher energy state (E_2) to a lower energy state (E_1), the excess energy is emitted as radiation. The frequency of the emitted radiation is

$$E_2 - E_1 = h\nu$$

and

$$\nu = \frac{(E_2 - E_1)}{h} \text{ -------- (2.2)}$$

Conversely, when suitable energy is supplied to an electron, it will jump from lower energy orbit to a higher energy orbit.

Applying Bohr's postulates to a hydrogen like atom (one electron species such as H, He^+ and Li^{2+} etc..) the radius of the nth orbit and the energy of the electron revolving in the nth orbit were derived. The results are as follows:

$$r_n = \frac{(0.529)n^2}{Z} \text{ Å} \text{ ---------- (2.3)}$$

$$E_n = \frac{(-13.6)\,Z^2}{n^2} \text{ eV atom}^{-1} \text{ --------(2.4)}$$

(or)

$$E_n = \frac{(-1312.8)\,Z^2}{n^2} \text{ kJ mol}^{-1} \text{ --------(2.5)}$$

The detailed derivation of r_n and E_n will be discussed in 12th standard atomic physics unit.

2.1.2 Limitation of Bohr's atom model:

The Bohr's atom model is applicable only to species having one electron such as hydrogen, Li^{2+} etc... and not applicable to multi electron atoms. It was unable to explain the splitting of spectral lines in the presence of magnetic field (Zeeman effect) or an electric field (Stark effect). Bohr's theory was unable to explain why the electron is restricted to revolve around the nucleus in a fixed orbit in which the angular momentum of the electron is equal to $nh/2\pi$ and a logical answer for this, was provided by Louis de Broglie.

2.2 Wave particle duality of matter

Albert Einstein proposed that light has dual nature. i.e. light photons behave both like a particle and as a wave. Louis de Broglie extended this concept and proposed that all forms of matter showed dual character. To quantify this relation, he derived an equation for the wavelength of a matter wave. He combined the following two equations of energy of which one represents wave character ($h\upsilon$) and the other represents the particle nature (mc^2).

(i) Planck's quantum hypothesis:

$$E = h\nu \text{ -------- (2.6)}$$

(ii) Einstein's mass-energy relationship

$$E = mc^2 \text{ ---------(2.7)}$$

From (2.6) and (2.7)

$$h\nu = mc^2$$

$$hc/\lambda = mc^2$$

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$$\lambda = h / mc \text{ ----------(2.8)}$$

The equation 2.8 represents the wavelength of photons whose momentum is given by mc (Photons have zero rest mass)

For a particle of matter with mass m and moving with a velocity v, the equation 2.8 can be written as

$$\lambda = h / mv \text{ ---------- (2.9)}$$

This is valid only when the particle travels at speeds much less than the speed of Light.

This equation implies that a moving particle can be considered as a wave and a wave can exhibit the properties (i.e momentum) of a particle. For a particle with high linear momentum (mv) the wavelength will be so small and cannot be observed. For a microscopic particle such as an electron, the mass is of the order of 10^{-31} kg, hence the wavelength is much larger than the size of atom and it becomes significant.

Let us understand this by calculating de Broglie wavelength in the following two cases:

(i) A 6.626 kg iron ball moving at10 ms^{-1}

(ii) An electron moving at 72.73 ms^{-1}

$\lambda_{iron\ ball} = h/mv$

$$= \frac{6.626 \times 10^{-34}\,kgm^2s^{-1}}{6.626\,kg \times 10\,ms^{-1}} = 1 \times 10^{-35}\ m$$

$\lambda_{electron} = h/mv$

$$= \frac{6.626 \times 10^{-34}\,kgm^2s^{-1}}{9.11 \times 10^{-31}\,kg \times 72.73\,ms^{-1}}$$

$$= \frac{6.626}{662.6} \times 10^{-3}\ m = 1 \times 10^{-5} m$$

For the electron, the de Broglie wavelength is significant and measurable while for the iron ball it is too small to measure, hence it becomes insignificant.

Evaluate Yourself

1. Calculate the de-Broglie wavelength of an electron that has been accelerated from rest through a potential difference of 1 keV.

2.2.1 Quantisation of angular momentum and de Broglie concept:

According to the de Broglie concept, the electron that revolves around the nucleus exhibits both particle and wave character. In order for the electron wave to exist in phase, the circumference of the orbit should be an integral multiple of the wavelength of the electron wave. Otherwise, the electron wave is out of phase.

Circumference of the orbit $= n\lambda$

$$2\pi r = n\lambda \text{ ----------(2.10)}$$

$$2\pi r = nh/mv$$

Rearranging,

$$mvr = nh/2\pi \text{ ----------(2.11)}$$

Angular momentum $= nh/2\pi$

The above equation was already predicted by Bohr. Hence, De Broglie and Bohr's concepts are in agreement with each other.

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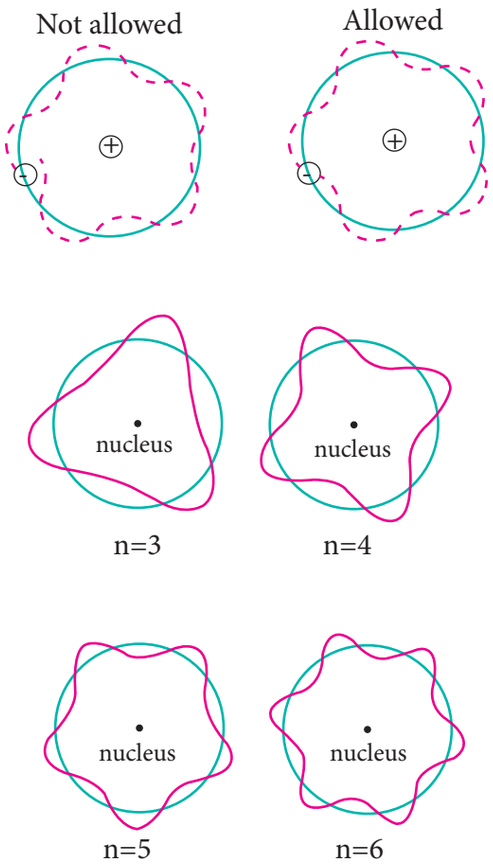

Figure. 2.2 Wave nature of electrons in allowed Bohr orbits

Davison and Germer experiment :

The wave nature of electron was experimentally confirmed by Davisson and Germer. They allowed the accelerated beam of electrons to fall on a nickel crystal and recorded the diffraction pattern. The resultant diffraction pattern is similar to the x-ray diffraction pattern. The finding of wave nature of electron leads to the development of various experimental techniques such as electron microscope, low energy electron diffraction etc…

2.3 Heisenberg's uncertainty principle

The dual nature of matter imposes a limitation on the simultaneous determination of position and momentum of a microscopic particle. Based on this, Heisenberg arrived at his uncertainty principle, which states that 'It is impossible to **accurately** determine both the position and the momentum of a microscopic particle **simultaneously**'. The product of uncertainty (error) in the measurement is expressed as follows.

$$\Delta x.\Delta p \geq h/4\pi \text{ -------- (2.11)}$$

where, Δx and Δp are uncertainties in determining the position and momentum, respectively.

The uncertainty principle has negligible effect for macroscopic objects and becomes significant only for microscopic particles such as electrons. Let us understand this by calculating the uncertainty in the velocity of the electron in hydrogen atom. (Bohr radius of 1st orbit is 0.529 Å) Assuming that the position of the electron in this orbit is determined with the accuracy of 0.5 % of the radius.

Uncertainity in position = Δx

$$= \frac{0.5\,\%}{100\,\%} \text{ x } 0.529 \text{ Å}$$

$$= \frac{0.5}{100} \text{ x } 0.529 \text{ x } 10^{-10} \text{ m}$$

$$\Delta x = 2.645 \text{ x } 10^{-13} \text{ m}$$

From the Heisenberg's uncertainity principle,

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

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$$\Delta x.(m.\Delta v) \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi.\, m\, .\, \Delta x}$$

$$\Delta v \geq \frac{6.626 \times 10^{-34}\ kg\ m^2 s^{-1}}{4 \times 3.14 \times 9.11 \times 10^{-31}\ kg \times 2.645 \times 10^{-13}\ m}$$

$$\Delta v \geq 2.189 \times 10^{8}\ ms^{-1}$$

Therefore, the uncertainty in the velocity of the electron is comparable with the velocity of light. At this high level of uncertainty it is very difficult to find out the exact velocity.

Evaluate Yourself

2. Calculate the uncertainty in the position of an electron, if the uncertainty in its velocity is $5.7 \times 10^5\ ms^{-1}$.

2.4 Quantum mechanical model of atom – Schrödinger Equation:

The motion of objects that we come across in our daily life can be well described using classical mechanics which is based on the Newton's laws of motion. In classical mechanics the physical state of the particle is defined by its position and momentum. If we know both these properties, we can predict the future state of the system based on the force acting on it using classical mechanics. However, according to Heisenberg's uncertainty principle both these properties cannot be measured simultaneously with absolute accuracy for a microscopic particle such as an electron. The classical mechanics does not consider the dual nature of the matter which is significant for microscopic particles. As a consequence, it fails to explain the motion of microscopic particles. Based on the Heisenberg's principle and the dual nature of the microscopic particles, a new mechanics called quantum mechanics was developed.

Erwin Schrödinger expressed the wave nature of electron in terms of a differential equation. This equation determines the change of wave function in space depending on the field of force in which the electron moves. The time independent Schrödinger equation can be expressed as,

$$\hat{H}\Psi = E\Psi \text{ -------(2.12)}$$

Where $\hat{H}$ is called Hamiltonian operator, Ψ is the wave function and is a funciton of position co-ordinates of the particle and is denoted as $\Psi(x,y,z)$ E is the energy of the system

$$\hat{H} = \left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right]$$

(2.12) can be written as,

$$\left[\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}\right)+V\psi\right] = E\psi$$

Multiply by $-\frac{8\pi^2 m}{h^2}$ and rearranging

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi = 0$$

------(2.13)

The above schrödinger wave equation does not contain time as a variable and is referred to as time independent Schrödinger wave equation. This equation can be solved only for certain values of E, the total energy. i.e. the energy of the system is quantised. The permitted total energy values are called eigen values and corresponding wave functions represent the atomic orbitals.

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2.4.1 Main features of the quantum mechanical model of atom

1. The energy of electrons in atoms is quantised
2. The existence of quantized electronic energy levels is a direct result of the wave like properties of electrons. The solutions of Schrödinger wave equation gives the allowed energy levels (orbits).
3. According to Heisenberg uncertainty principle, the exact position and momentum of an electron can not be determined with absolute accuracy. As a consequence, quantum mechanics introduced the concept of orbital. Orbital is a three dimensional space in which the probability of finding the electron is maximum.
4. The solution of Schrödinger wave equation for the allowed energies of an atom gives the wave function ψ, which represents an atomic orbital. The wave nature of electron present in an orbital can be well defined by the wave function ψ.
5. The wave function ψ itself has no physical meaning. However, the probability of finding the electron in a small volume dxdydz around a point (x,y,z) is proportional to $|\psi(x,y,z)|^2$ dxdydz $|\psi(x,y,z)|^2$ is known as probability density and is always positive.

2.5 Quantum numbers

The electron in an atom can be characterised by a set of four quantum numbers, namely principal quantum number (n), azimuthal quantum number (l), magnetic quantum number (m) and spin quantum number (s). When Schrödinger equation is solved for a wave function Ψ, the solution contains the first three quantum numbers n, l and m. The fourth quantum number arises due to the spinning of the electron about its own axis. However, classical pictures of species spinning around themselves are incorrect.

Principal quantum number (n):

This quantum number represents the energy level in which electron revolves around the nucleus and is denoted by the symbol 'n'.

1. The 'n' can have the values 1, 2, 3,… n=1 represents K shell; n=2 represents L shell and n = 3, 4, 5 represent the M, N, O shells, respectively.
2. The maximum number of electrons that can be accommodated in a given shell is $2n^2$.
3. 'n' gives the energy of the electron, $E_n = \frac{(-1312.8)\,Z^2}{n^2}\ \text{kJ mol}^{-1}$ and the distance of the electron from the nucleus is given by $r_n = \frac{(0.529)n^2}{Z}\ \text{Å}$

Azimuthal Quantum number (*l*) or subsidiary quantum number :

1. It is represented by the letter '*l*', and can take integral values from zero to n-1, where n is the principal quantum number
2. Each *l* value represents a subshell (orbital). *l* = 0, 1, 2, 3 and 4 represents the s, p, d, f and g orbitals respectively.
3. The maximum number of electrons that can be accommodated in a given subshell (orbital) is $2(2l+1)$.

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4. It is used to calculate the orbital angular momentum using the expression

$$Angular\ momentum = \sqrt{l(l+1)}\,\frac{h}{2\pi} ----(2.14)$$

Magnetic quantum number (m_l):

1. It is denoted by the letter 'm_l'. It takes integral values ranging from -l to +l through 0. i.e. if l=1; m = -1, 0 and +1
2. Different values of m for a given l value, represent different orientation of orbitals in space.
3. The Zeeman Effect (the splitting of spectral lines in a magnetic field) provides the experimental justification for this quantum number.
4. The magnitude of the angular momentum is determined by the quantum number l while its direction is given by magnetic quantum number.

Spin quantum number (m_s):

1. The spin quantum number represents the spin of the electron and is denoted by the letter 'm_s'
2. The electron in an atom revolves not only around the nucleus but also spins. It is usual to write this as electron spins about its own axis either in a clockwise direction or in anti-clockwise direction. The visualisation is not true. However spin is to be understood as representing a property that revealed itself in magnetic fields.
3. Corresponding to the clockwise and anti-clockwise spinning of the electron, maximum two values are possible for this quantum number.
4. The values of 'm_s' is equal to -½ and + ½

Table 2.1 Quantum numbers and its significance

Shell	Principal quantum number (n)	maximum number of electron in a shell (orbital) $2n^2$	Azimuthal quantum number (l) = 0,1.... (n-1)	Maximum no. of electron in a orbital 2 (2l+1)	Magnetic quantum number (m) different possible orientation of orbital	Designation of orbitals in a given shell
K	1	$2(1)^2 = 2$	0	2[2(0)+1] = 2	0	1s
L	2	$2(2)^2 = 8$	0	2	0	2s
			1	2[2(1)+1] =6	-1, 0, +1	$2p_y$, $2p_z$, $2p_x$

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Shell	Principal quantum number (n)	maximum number of electron in a shell (orbital) $2n^2$	Azimuthal quantum number (l) = 0,1.... (n-1)	Maximum no. of electron in a orbital 2 ($2l$+1)	Magnetic quantum number (m) different possible orientation of orbital	Designation of orbitals in a given shell
M	3	$2(3)^2 = 18$	0	2	0	3s
			1	6	-1, 0, +1	$3p_y$, $3p_z$, $3p_x$,
			2	2[2(2)+1] = 10	-2, -1, 0, +1, +2	$3d_{x^2-y^2}$, $3d_{yz}$, $3d_{z^2}$, $3d_{zx}$, $3d_{xy}$
N	4	$2(4)^2 = 32$	0	2	0	4s
			1	6	-1, 0, +1	$4p_y$, $4p_z$, $4p_x$
			2	10	-2, -1, 0, +1, +2	$4d_{x^2-y^2}$, $4d_{xy}$, $4d_{z^2}$, $4d_{yz}$, $4d_{zx}$
			3	2[2(3)+1] = 14	-3, -2, -1, 0, +1, +2, +3	$f_{y(3x^2-y^2)}$, $f_{z(x^2-y^2)}$, f_{yz^2}, f_{z^3}, f_{xz^2}, f_{xyz}, $f_{x(x^2-3y^2)}$,

The labels on the orbitals, such as p_x, d_{z^2}, f_{xyz} etc. are not associated with specific 'm' values

Evaluate Yourself

3. How many orbitals are possible in the 4th energy level? (n=4)

2.5.1 Shapes of atomic orbitals:

The solution to Schrödinger equation gives the permitted energy values called eigen values and the wave functions corresponding to the eigen values are called atomic orbitals. The solution (Ψ) of the Schrödinger wave equation for one electron system like hydrogen can be represented in the following form in spherical polar coordinates r, θ, φ as,

$$\Psi (r, \theta, \varphi) = R(r).f(\theta).g(\varphi) \text{ ------ } (2.15)$$

(where R(r) is called radial wave function, other two functions are called angular wave functions)

As we know, the Ψ itself has no physical meaning and the square of the wave function $|\Psi|^2$ is related to the probability of finding the electrons within a given volume of space. Let us analyse how $|\Psi|^2$ varies with the distance from nucleus (radial distribution of the probability) and the direction from the nucleus (angular distribution of the probability).

Radial distribution function:

Consider a single electron of hydrogen atom in the ground state for which the quantum numbers are n=1 and

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l=0. i.e. it occupies 1s orbital. The plot of $R(r)^2$ versus r for 1s orbital is given in Figure 2.3

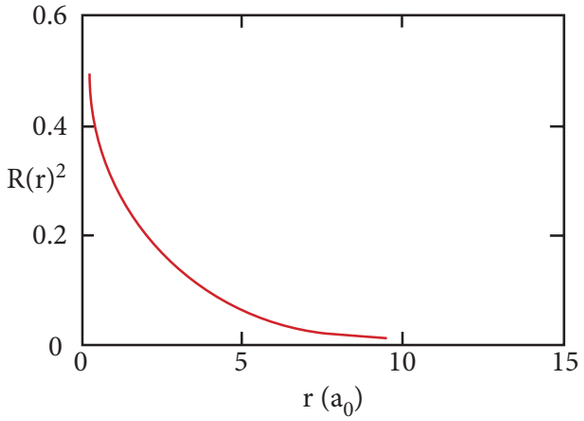

Figure. 2.3 Plot of $R(r)^2$ versus r for 1s orbital of hydrogen

The graph shows that as the distance between the electron and the nucleus decreases, the probability of finding the electron increases. At r=0, the quantity $R(r)^2$ is maximum i.e. The maximum value for $|\Psi|^2$ is at the nucleus. However, probability of finding the electron in a given spherical shell around the nucleus is important. Let us consider the volume (dV) bounded by two spheres of radii r and r+dr.

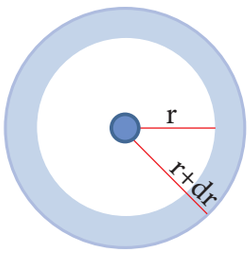

Figure 2.4

Volume of the sphere, $V = \frac{4}{3}\pi r^3$

$$\frac{dV}{dr} = \frac{4}{3}\pi(3r^2)$$

$$dV = 4\pi r^2 dr$$

$$\Psi^2 dV = 4\pi r^2 \Psi^2 dr \quad \text{---------- (2.16)}$$

The plot of $4\pi r^2 . R(r)^2$ versus r is given below.

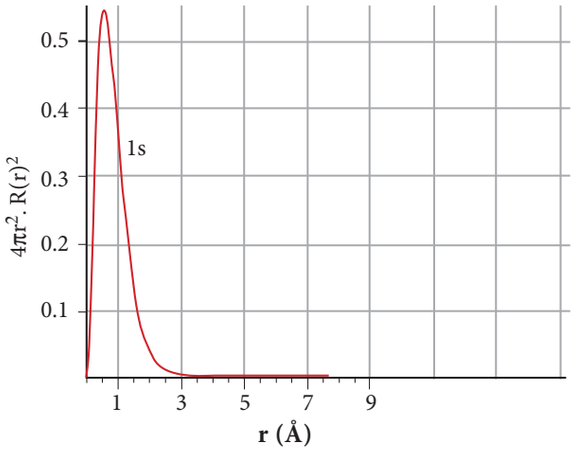

Figure 2.5 Plot of $4\pi r^2 . R(r)^2$ versus r for 1s orbital of hydrogen

The above plot shows that the maximum probability occurs at distance of 0.52 **Å** from the nucleus. This is equal to the Bohr radius. It indicates that the maximum probability of finding the electron around the nucleus is at this distance. However, there is a probability to find the electron at other distances also. The radial distribution function of 2s, 3s, 3p and 3d orbitals of the hydrogen atom are represented as follows.

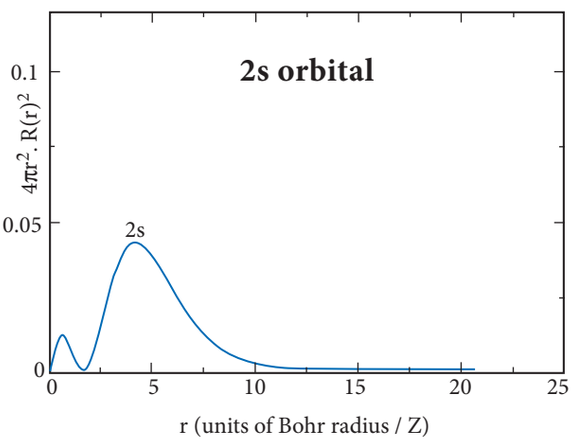

Figure 2.6 (a) - Plot of $4\pi r^2 . R(r)^2$ versus r for 2s orbitals of hydrogen

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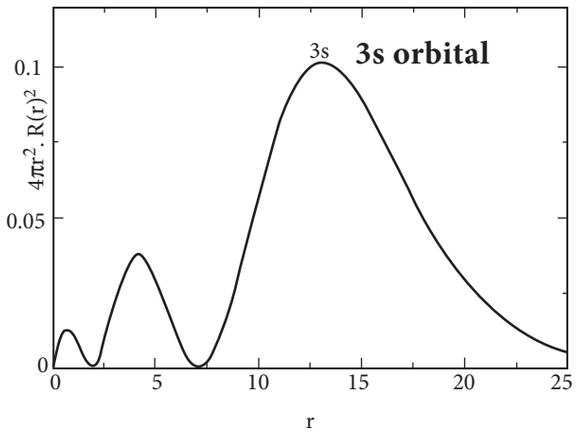

Figure 2.6 (b) - Plot of $4\pi r^2. R(r)^2$ versus r for 3s orbitals of hydrogen

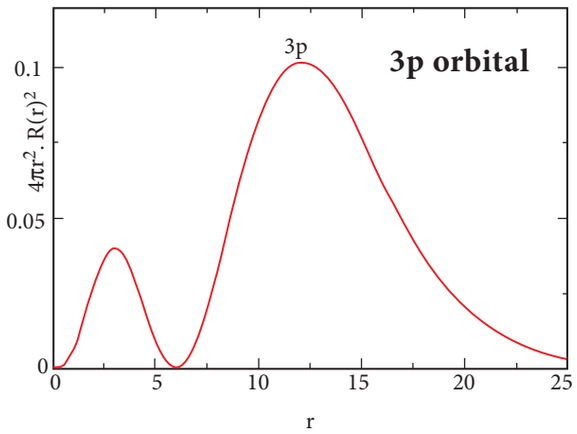

Figure 2.6 (c) - Plot of $4\pi r^2. R(r)^2$ versus r for 3p orbitals of hydrogen

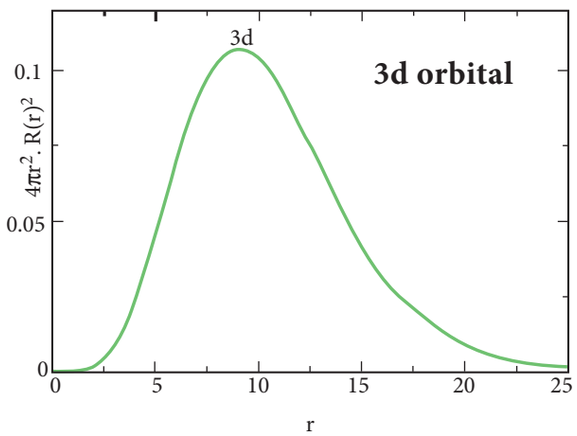

Figure 2.6 (d) - Plot of $4\pi r^2. R(r)^2$ versus r for 3d orbitals of hydrogen

For 2s orbital, as the distance from nucleus r increases, the probability density first increases, reaches a small maximum followed by a sharp decrease to zero and then increases to another maximum, after that decreases to zero. The region where this probability density function reduces to zero is called nodal surface or a radial node. In general, it has been found that ns-orbital has (n–1) nodes. In other words, number of radial nodes for 2s orbital is one, for 3s orbital it is two and so on. The plot of $4\pi r^2. R(r)^2$ versus r for 3p and 3d orbitals shows similar pattern but the number of radial nodes are equal to(n-*l*-1) (where n is principal quantum number and l is azimuthal quantum number of the orbital).

Angular distribution function:

The variation of the probability of locating the electron on a sphere with nucleus at its centre depends on the azimuthal quantum number of the orbital in which the electron is present. For 1s orbital, l=0 and m=0. $f(\theta) = 1/\sqrt{2}$ and $g(\varphi) = 1/\sqrt{2}\pi$. Therefore, the angular distribution function is equal to $1/2\sqrt{\pi}$. i.e. it is independent of the angle θ and φ. Hence, the probability of finding the electron is independent of the direction from the nucleus. The shape of the s orbital is spherical as shown in the figure 2.7

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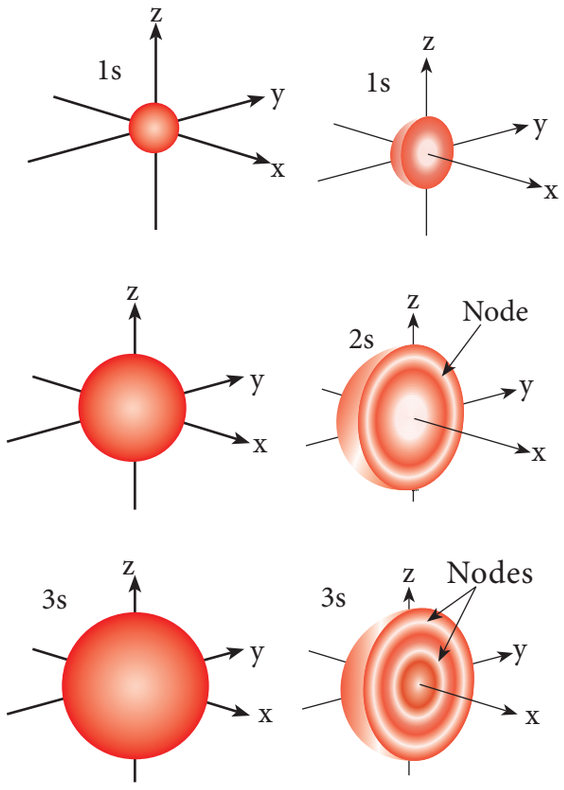
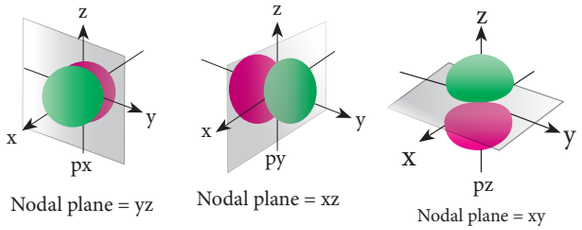


Figure 2.7 Shapes of 1s, 2s and 3s orbitals

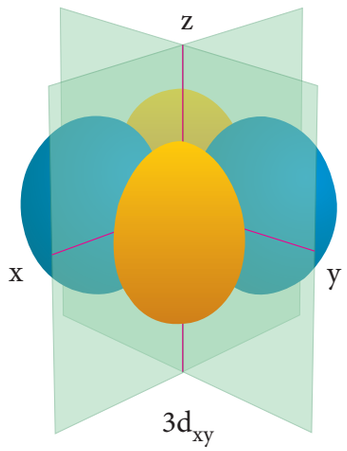
For p orbitals l=1 and the corresponding m values are -1, 0 and +1. The angular distribution functions are quite complex and are not discussed here. The shape of the p orbital is shown in Figure 2.8. The three different m values indicates that there are three different orientations possible for p orbitals. These orbitals are designated as p_x, p_y and p_z and the angular distribution for these orbitals shows that the lobes are along the x, y and z axis respectively. As seen in the Figure 2.8 the 2p orbitals have one nodal plane.

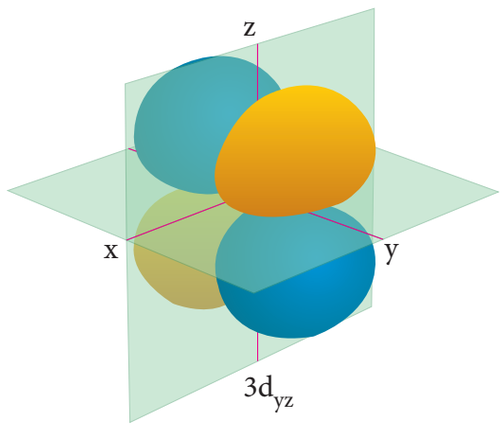


(b) Cartoon representations of 2p orbitals

Figure 2.8 Shapes of 2p orbitals

For 'd' orbital l = 2 and the corresponding m values are -2, -1, 0 +1,+2. The shape of the d orbital looks like a 'clover leaf'. The five m values give rise to five d orbitals namely d_{xy} , d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. The 3d orbitals contain two nodal planes as shown in Figure 2.9.





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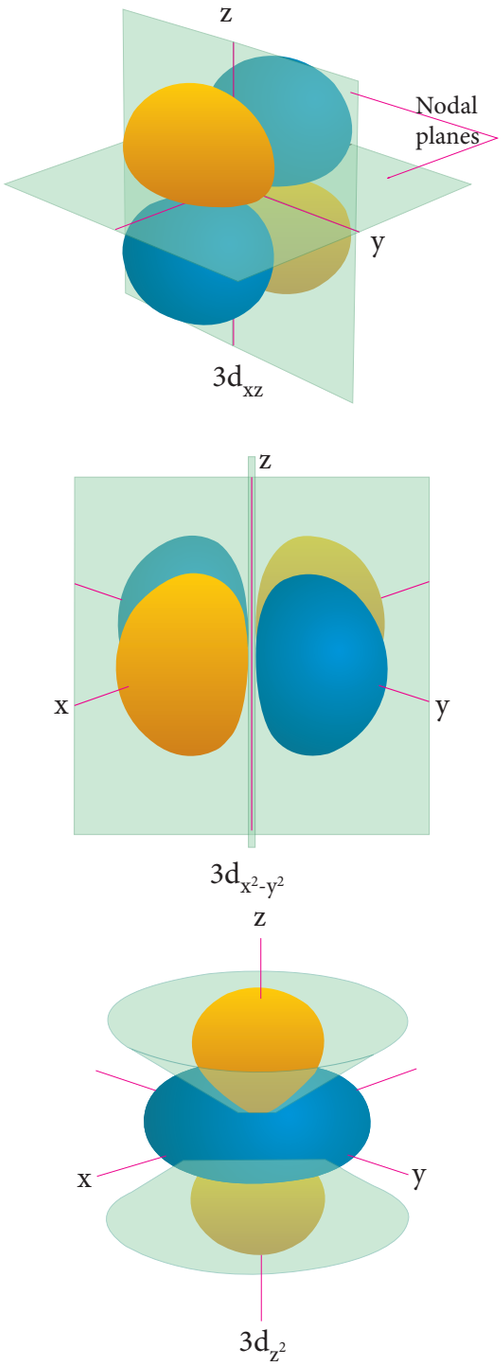

Figure 2.9 shapes of d orbitals

For 'f' orbital, $l = 3$ and the m values are -3, -2,-1, 0, +1, +2, +3 corresponding to seven f orbitals f_{z3}, f_{xz2}, f_{yz2}, f_{xyz}, $f_{z(x^2-y^2)}$, $f_{x(x^2-3y^2)}$, $f_{y(3x^2-y^2)}$, which are shown in Figure 2.10. There are 3 nodal planes in the f-orbitals.

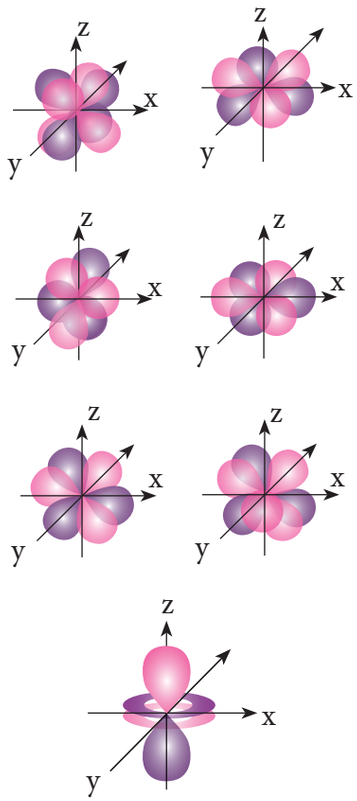

Figure 2.10 shapes of f-orbitals

Evaluate Yourself

4. Calculate the total number of angular nodes and radial nodes present in 3d and 4f orbitals.

2.5.2 Energies of orbitals

In hydrogen atom, only one electron is present. For such one electron system, the energy of the electron in the nth orbit is given by the expression

$$E_n = \frac{(-1312.8)\,Z^2}{n^2}\ \text{kJ mol}^{-1}$$

From this equation, we know that the energy depends only on the value of principal quantum number. As the n value increases the energy of the orbital also increases. The energies of various orbitals

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will be in the following order:

1s < 2s = 2p < 3s = 3p = 3d <4s = 4p = 4d = 4f < 5s = 5p = 5d = 5f < 6s = 6p = 6d = 6f < 7s

The electron in the hydrogen atom occupies the 1s orbital that has the lowest energy. This state is called ground state. When this electron gains some energy, it moves to the higher energy orbitals such as 2s, 2p etc… These states are called excited states.

However, the above order is not true for atoms other than hydrogen (multi-electron systems). For such systems the Schrödinger equation is quite complex. For these systems the relative order of energies of various orbitals is given approximately by the (n+l) rule. It states that, the lower the value of (n + l) for an orbital, the lower is its energy. If two orbitals have the same value of (n + l), the orbital with lower value of n will have the lower energy. Using this rule the order of energies of various orbitals can be expressed as follows.

Table 2.2 n+*l* values of different orbitals

Orbital	n	*l*	n+*l*
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
3d	3	2	5
4s	4	0	4
4p	4	1	5
4d	4	2	6
4f	4	3	7
5s	5	0	5
5p	5	1	6
5d	5	2	7
5f	5	3	8
6s	6	0	6
6p	6	1	7
6d	6	2	8
7s	7	0	7

Based on the (n+*l*) rule, the increasing order of energies of orbitals is as follows:

1s < 2s < 2p < 3s < 3p < 4s <3d <4p <5s<4d < 5p < 6s<4f< 5d < 6p < 7s < 5f < 6d

As we know there are three different orientations in space that are possible for a p orbital. All the three p orbitals, namely, p_x, p_y and p_z have same energies and are called degenerate orbitals. However, in the presence of magnetic or electric field the degeneracy is lost.

In a multi-electron atom, in addition to the electrostatic attractive force between the electron and nucleus, there exists a repulsive force among the electrons. These two forces are operating in the opposite direction. This results in the decrease in the nuclear force of attraction on electron. The net charge experienced by the electron is called effective nuclear charge. The effective nuclear charge depends on the shape of the orbitals and it decreases with increase in azimuthal quantum number *l*. The order of the effective nuclear charge felt by a electron in an orbital within the given shell is s > p > d > f. Greater the effective nuclear charge, greater is the stability of the orbital. Hence, within a given energy level, the energy of the orbitals are in the following order. s < p < d < f.

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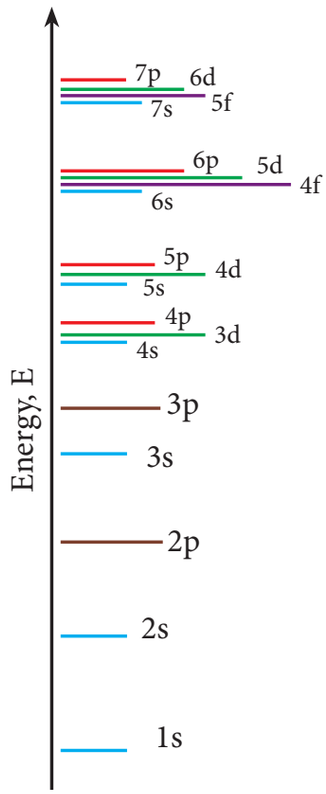

Figure. 2.11 Energy levels of atomic orbitals

The energies of same orbital decrease with an increase in the atomic number. For example, the energy of the 2s orbital of hydrogen atom is greater than that of 2s orbital of lithium and that of lithium is greater than that of sodium and so on, that is, $E_{2s}(H) > E_{2s}(Li) > E_{2s}(Na) > E_{2s}(K)$.

Evaluate Yourself

5. Energy of an electron in hydrogen atom in ground state is -13.6 eV. What is the energy of the electron in the second excited state?

2.6 Filling of orbitals:

In an atom, the electrons are filled in various orbitals according to aufbau principle, Pauli exclusion principle and Hund's rule. These rules are described below.

2.6.1 Aufbau principle:

The word Aufbau in German means 'building up'. In the ground state of the atoms, the orbitals are filled in the order of their increasing energies. That is the electrons first occupy the lowest energy orbital available to them.

Once the lower energy orbitals are completely filled, then the electrons enter the next higher energy orbitals. The order of filling of various orbitals as per the Aufbau principle is given in the figure 2.12 which is in accordance with (n+*l*) rule.

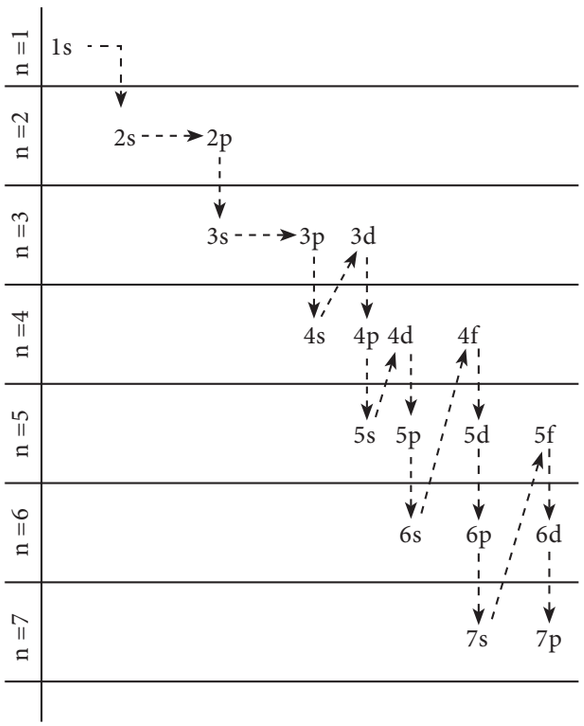

Figure. 2.12 Aufbau principle

2.6.2 Pauli Exclusion Principle :

Pauli formulated the exclusion principle which states that "No two electrons in an atom can have the same set

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of values of all four quantum numbers." It means that, each electron must have unique values for the four quantum numbers (n, *l*, m and s).

For the lone electron present in hydrogen atom, the four quantum numbers are: n = 1; l = 0; m = 0 and s = +½. For the two electrons present in helium, one electron has the quantum numbers same as the electron of hydrogen atom, n = 1, *l* = 0, m = 0 and s = +½. For other electron, the fourth quantum number is different i.e., n = 1, *l* = 0, m = 0 and s = –½.

As we know that the spin quantum number can have only two values +½ and –½, only two electrons can be accommodated in a given orbital in accordance with Pauli exclusion principle. Let us understand this by writing all the four quantum numbers for the eight electron in L shell.

Table 2.3 Quantum numbers of electrons in L shell

Electron	n	*l*	m	s
1st	2	0	0	+½
2nd	2	0	0	-½
3rd	2	1	-1	+½
4th	2	1	0	+½
5th	2	1	+1	+½
6th	2	1	-1	-½
7th	2	1	0	- ½
8th	2	1	+1	-½

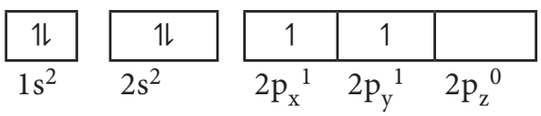
2.6.3 Hund's rule of maximum multiplicity

The Aufbau principle describes how the electrons are filled in various orbitals. But the rule does not deal with the filling of electrons in the degenerate orbitals (i.e. orbitals having same energy) such as p_x, p_y and p_z. In what order these orbitals to be filled? The answer is provided by the Hund's rule of maximum multiplicity. It states that electron pairing in the degenerate orbitals does not take place until all the available orbitals contains one electron each.

We know that there are three p orbitals, five d orbitals and seven f orbitals. According to this rule, pairing of electrons in these orbitals starts only when the 4th, 6th and 8th electron enters the p, d and f orbitals respectively.

For example, consider the carbon atom which has six electrons. According to Aufbau principle, the electronic configuration is $1s^2$, $2s^2$, $2p^2$

It can be represented as below,



In this case, in order to minimise the electron-electron repulsion, the sixth electron enters the unoccupied $2p_y$ orbital as per Hunds rule. i.e. it does not get paired with the fifth electron already present in the $2p_x$ orbital.

Evaluate Yourself

6. How many unpaired electrons are present in the ground state of Fe^{3+} (z=26), Mn^{2+} (z=25) and argon (z=18)?

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2.6.4 Electronic configuration of atoms

The distribution of electrons into various orbitals of an atom is called its electronic configuration. It can be written by applying the aufbau principle, Pauli exclusion principle and Hund's rule. The electronic configuration is written as nl^x , where n represents the principle of quantum number, '*l*' represents the letter designation of the orbital [s(*l*=0), p (*l*=1), d(*l*=2) and f(*l*=3)] and 'x' represents the number of electron present in that orbital.

Let us consider the hydrogen atom which has only one electron and it occupies the lowest energy orbital i.e. 1s according to aufbau principle. In this case n=1; *l*=s; x=1.

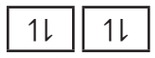
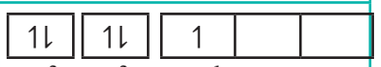
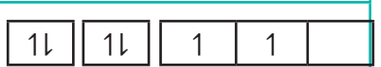
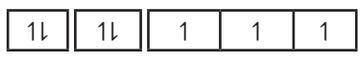
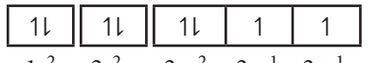
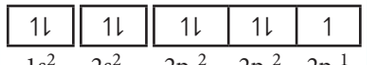
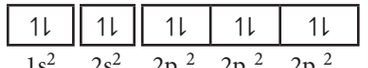
Hence the electronic configuration is $1s^1$. (read as one-ess-one).

The orbital diagram for this configuration is,



The electronic configuration and orbital diagram for the elements upto atomic number 10 are given below :

Table 2. 4 Electronic configuration and orbital diagrams for first 10 elements

Element	Electronic Configuration	Orbital diagram
H^1	$1s^1$	
He^2	$1s^2$	
Li^3	$1s^2\ 2s^1$	
Be^4	$1s^2\ 2s^2$	
B^5	$1s^2\ 2s^2\ 2p^1$	
C^6	$1s^2\ 2s^2\ 2p^2$	
N^7	$1s^2\ 2s^2\ 2p^3$	
O^8	$1s^2\ 2s^2\ 2p^4$	
F^9	$1s^2\ 2s^2\ 2p^5$	
Ne^{10}	$1s^2\ 2s^2\ 2p^6$	

The actual electronic configuration of some elements such as chromium and copper slightly differ from the expected electronic configuration in accordance with the Aufbau principle.

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For chromium - 24

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

For copper - 29

Expected configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^9\ 4s^2$

Actual configuration :

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

The reason for above observed configuration is that fully filled orbitals and half filled orbitals have been found to have extra stability. In other words, p^3, p^6, d^5, d^{10}, f^7 and f^{14} configurations are more stable than p^2, p^5, d^4, d^9, f^6 and f^{13}. Due to this stability, one of the 4s electrons occupies the 3d orbital in chromium and copper to attain the half filled and the completely filled configurations respectively.

Evaluate Yourself

7. Explain the meaning of the symbol $4f^2$. Write all the four quantum numbers for these electrons.

2.6.5 Stability of half filled and completely filled orbitals:

The exactly half filled and completely filled orbitals have greater stability than other partially filled configurations in degenerate orbitals. This can be explained on the basis of symmetry and exchange energy. For example chromium has the electronic configuration of $[Ar]3d^5\ 4s^1$ and not $[Ar]3d^4\ 4s^2$ due to the symmetrical distribution and exchange energies of d electrons.

Symmetrical distribution of electron:

Symmetry leads to stability. The half filled and fully filled configurations have symmetrical distribution of electrons (Figure 2.13) and hence they are more stable than the unsymmetrical configurations.

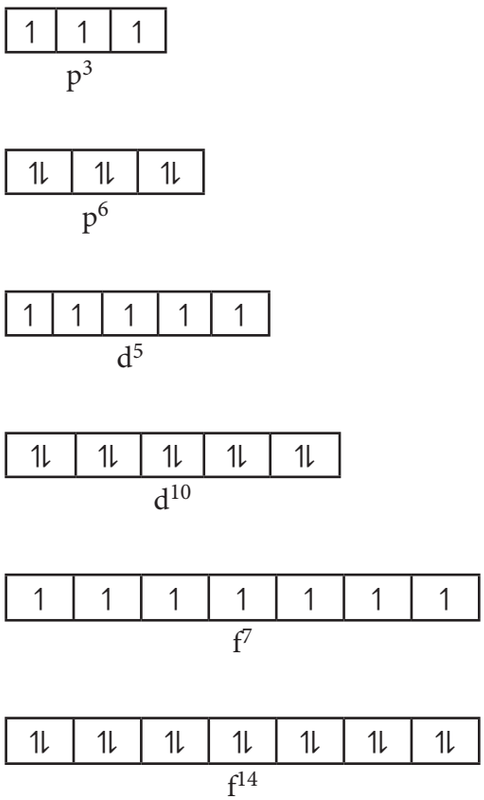

Figure 2.13 Half filled and fully filled p, d and f orbitals

The degenerate orbitals such as p_x, p_y and p_z have equal energies and their orientation in space are different as shown

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in Figure 2.14. Due to this symmetrical distribution, the shielding of one electron on the other is relatively small and hence the electrons are attracted more strongly by the nucleus and it increases the stability.

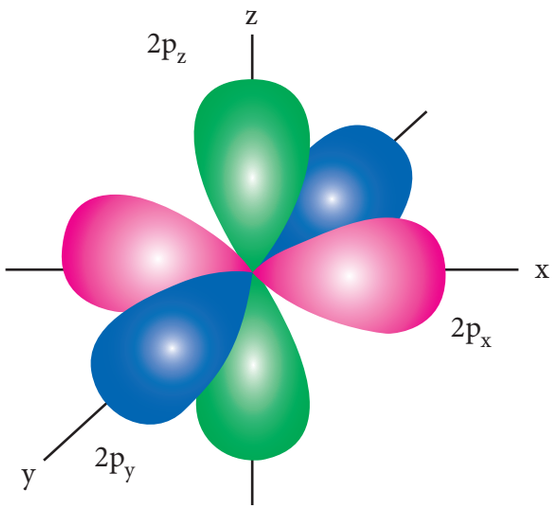
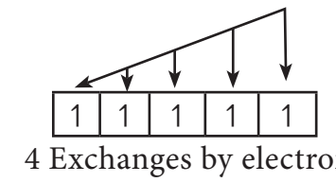


Figure 2.14 Shape of the degenerate p orbitals.

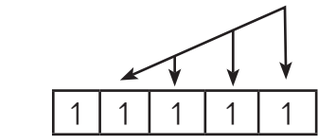
Exchange energy:

If two or more electrons with the same spin are present in degenerate orbitals, there is a possibility for exchanging their positions. During exchange process the energy is released and the released energy is called exchange energy. If more number of exchanges are possible, more exchange energy is released. More number of exchanges are possible only in case of half filled and fully filled configurations.

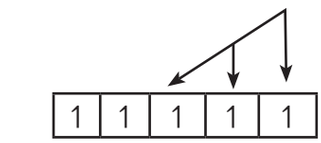
For example, in chromium the electronic configuration is $[Ar]3d^5\ 4s^1$. The 3d orbital is half filled and there are ten possible exchanges as shown in Figure 2.15. On the other hand only six exchanges are possible for $[Ar]3d^4\ 4s^2$ configuration. Hence, exchange energy for the half filled configuration is more. This increases the stability of half filled 3d orbitals.



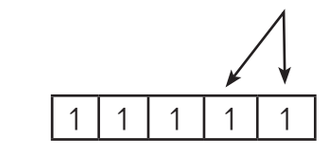
4 Exchanges by electrons



3 Exchanges by electrons



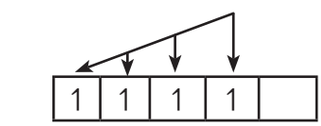
2 Exchanges by electrons



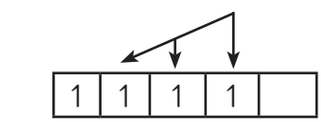
1 Exchange by electrons

Overall electron exchanges (4+3+2+1 = 10)

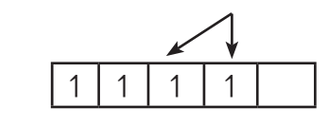
Figure 2.15 (a)



3 Exchanges by electrons



2 Exchanges by electrons



1 Exchange by electrons

Overall electron exchanges (3+2+1 = 6)

Figure 2.15 (b)

Figure 2.15 Possible exchanges in chromium d orbitals: a) for d^5 configuration b) for d^4 configuration

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The exchange energy is the basis for Hund's rule, which allows maximum multiplicity, that is electron pairing is possible only when all the degenerate orbitals contain one electron each.

Evaluate Yourself



8. Which ion has the stable electronic configuration? Ni^{2+} or Fe^{3+}.

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SUMMARY

The atoms were believed to be non -divisible until the discovery of subatomic particles. J. J. Thomson proposed that the atom is a positively charged sphere in which the electrons are embedded. However, it fails to explain the stability of atoms. Rutherford, based on his α-rays scattering experiment, introduced the term nucleus which is a positively charged one and the negatively charged electrons are revolving around it, at high speeds. Bohr modified the Rutherford theory and introduced stationary orbits by taking into account the quantisation of energy. Louis de Broglie proposed that all matter possess dual nature. i.e. they behave both as a wave and a particle. De Broglie wavelength $\lambda = h / mv = h / \sqrt{2mev}$ is significant for a microscopic particle such as an electron. The wave nature of electron is also proved by Davisson and Germer through electron diffraction. For a microscopic particle such as an electron, the simultaneous measurement of the conjugate variables such as position and momentum involves uncertainty which is known as Heisenberg's uncertainty principle and it is expressed as
$\Delta x.\Delta p \geq h/4\pi$.

De Broglie's concept and Heisenberg's uncertainty principle lead to the development of quantum mechanical model of atom. Erwin Schrodinger, developed an equation for an electron wave which is expressed as $\hat{H}\psi = E\psi$. This second order differential equation is exactly solvable for one electron system such as H, He^+ etc... but it is quite complex for multi-electron systems. The Schrödinger wave equation is solvable for certain energy values called eigen values. The wave functions corresponding to these eigen values are called atomic orbitals. The wave function ψ itself has no physical meaning. However, $|\psi|^2$ is related to the probability of finding electron around the nucleus. Thus the quantum mechanical model introduced us the term orbital which is the three dimensional space in which the probability of finding the electron is maximum. The electron in an orbital can be described by a set of four quantum numbers namely, principal quantum number (n) representing the principal energy level, azimuthal quantum number (*l*) representing the sub shell (orbital), magnetic quantum number (m) representing the different orientation of orbitals in space and spin quantum number (s) representing the spinning of electron about its own axis.

The general solution of Schrodinger for a one electron system can be expressed in spherical polar coordinates (r, θ, φ)

$$\Psi (r, \theta, \varphi) = R(r).f(\theta).g(\varphi)$$

(where R(r) is called radial wave function, other two functions are called angular wave functions).

The plot of $4\pi r^2. R(r)^2$ versus r gives the radial distribution curves. The number of radial nodes is given by(n-*l*-1) whereas the angular nodes is equal to *l*. The angular distribution curve gives the boundary space diagram of orbital.

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s orbital is spherical in nature and the d orbital has clover leaf shape.

Electrons are filled in various orbitals in the increasing order of their energies which is known as Aufbau principle. The relative energies of various orbitals are given by (n+l) rule which states that, the lower the value of (n + l) for an orbital, the lower is its energy. If two orbitals have the same value of (n + l), the orbital with lower value of n will have the lower energy. As per Pauli's exclusion principle, the maximum number of electrons that can be accommodated in an orbital is two. In the case of degenerate orbitals electron pairing does not take place until all the available degenerate orbitals contain one electron each. This is known as Hund's rule. Based on these principles, electronic configurations of atoms can be written. In degenerate orbitals, the completely filled and half filled configurations are more stable than the partially filled configurations. This is due to the symmetry and exchange energies.

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EVALUATION :

Choose the best answer

1. Electronic configuration of species M^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ and its atomic weight is 56. The number of neutrons in the nucleus of species M is

   a) 26 b) 22 c) 30 d) 24

2. The energy of light of wavelength 45 nm is

   a) 6.67×10^{15}J b) 6.67×10^{11}J

   c) 4.42×10^{-18}J d) 4.42×10^{-15}J

3. The energies E_1 and E_2 of two radiations are 25 eV and 50 eV respectively. The relation between their wavelengths ie λ_1 and λ_2 will be

   a) $\frac{\lambda_1}{\lambda_2} = 1$ b) $\lambda_1 = 2\lambda_2$ c) $\lambda_1 = \sqrt{25 \times 50}\ \lambda_2$ d) $2\lambda_1 = \lambda_2$

4. Splitting of spectral lines in an electric field is called

   a) Zeeman effect b) Shielding effect

   c) Compton effect d) Stark effect

5. Based on equation $E = -2.178 \times 10^{-18}\ J \left(\frac{z^2}{n^2}\right)$, certain conclusions are written. Which of them is not correct ? (NEET)

   a) Equation can be used to calculate the change in energy when the electron changes orbit

   b) For n = 1, the electron has a more negative energy than it does for n = 6 which means that the electron is more loosely bound in the smallest allowed orbit

   c) The negative sign in equation simply means that the energy of electron bound to the nucleus is lower than it would be if the electrons were at the infinite distance from the nucleus.

   d) Larger the value of n, the larger is the orbit radius.

6. According to the Bohr Theory, which of the following transitions in the hydrogen atom will give rise to the least energetic photon ?

   a) n = 6 to n = 1 b) n = 5 to n = 4

   c) n = 5 to n = 3 d) n = 6 to n = 5

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7. Assertion : The spectrum of He^+ is expected to be similar to that of hydrogen

Reason : He^+ is also one electron system.

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false

(d) If both assertion and reason are false

8. Which of the following pairs of d-orbitals will have electron density along the axes ? (NEET Phase - II)

a) d_{z^2}, d_{xz} b) d_{xz}, d_{yz} c) d_{z^2}, $d_{x^2-y^2}$ d) d_{xy}, $d_{x^2-y^2}$

9. Two electrons occupying the same orbital are distinguished by

a) azimuthal quantum number b) spin quantum number

c) magnetic quantum number d) orbital quantum number

10. The electronic configuration of Eu (Atomic no. 63) Gd (Atomic no. 64) and Tb (Atomic no. 65) are (NEET - Phase II)

a) [Xe] $4f^6\ 5d^1\ 6s^2$, [Xe] $4f^7\ 5d^1\ 6s^2$ and [Xe] $4f^8\ 5d^1\ 6s^2$

b) [Xe] $4f^7$, $6s^2$, [Xe] $4f^7\ 5d^1\ 6s^2$ and [Xe] $4f^9\ 6s^2$

c) [Xe] $4f^7$, $6s^2$, [Xe] $4f^8\ 6s^2$ and [Xe] $4f^8\ 5d^1\ 6s^2$

d) [Xe] $4f^6\ 5d^1\ 6s^2$, [Xe] $4f^7\ 5d^1\ 6s^2$ and [Xe] $4f^9\ 6s^2$

11. The maximum number of electrons in a sub shell is given by the expression

a) $2n^2$ b) $2l + 1$ c) $4l + 2$ d) none of these

12. For d-electron, the orbital angular momentum is

a) $\frac{\sqrt{2}h}{2\pi}$ b) $\frac{\sqrt{2h}}{2\pi}$ c) $\frac{\sqrt{2\times4}\ h}{2\pi}$ d) $\frac{\sqrt{6}\ h}{2\pi}$

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13. What is the maximum numbers of electrons that can be associated with the following set of quantum numbers ? n = 3, l = 1 and m = –1

a) 4 b) 6 c) 2 d) = 10

14. Assertion : Number of radial and angular nodes for 3p orbital are 1, 1 respectively.

Reason : Number of radial and angular nodes depends only on principal quantum number.

(a) both assertion and reason are true and reason is the correct explanation of assertion.

(b) both assertion and reason are true but reason is not the correct explanation of assertion.

(c) assertion is true but reason is false

(d) both assertion and reason are false

15. The total number of orbitals associated with the principal quantum number n = 3 is

a) 9 b) 8 c) 5 d) 7

16. If n = 6, the correct sequence for filling of electrons will be,

a) ns → (n – 2) f → (n – 1)d → np b) ns → (n – 1) d → (n – 2) f → np

c) ns → (n – 2) f → np → (n – 1) d d) none of these are correct

17. Consider the following sets of quantum numbers :

	n	*l*	m	s
(i)	3	0	0	$+\frac{1}{2}$
(ii)	2	2	1	$-\frac{1}{2}$
(iii)	4	3	–2	$+\frac{1}{2}$
(iv)	1	0	–1	$+\frac{1}{2}$
(v)	3	4	3	$-\frac{1}{2}$

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Which of the following sets of quantum number is not possible ?

a) (i), (ii), (iii) and (iv)
b) (ii), (iv) and (v)
c) (i) and (iii)
d) (ii), (iii) and (iv)

18. How many electrons in an atom with atomic number 105 can have (n + l) = 8 ?

a) 30 b) 17 c) 15 d) unpredictable

19. Electron density in the yz plane of $3d_{xy}$ orbital is

a) zero b) 0.50 c) 0.75 d) 0.90

20. If uncertainty in position and momentum are equal, then minimum uncertainty in velocity is

a) $\frac{1}{m}\sqrt{\frac{h}{\pi}}$ d) $\sqrt{\frac{h}{\pi}}$ c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ d) $\frac{h}{4\pi}$

21. A macroscopic particle of mass 100 g and moving at a velocity of 100 cm s^{-1} will have a de Broglie wavelength of

a) 6.6×10^{-29} cm b) 6.6×10^{-30} cm c) 6.6×10^{-31} cm d) 6.6×10^{-32} cm

22. The ratio of de Broglie wavelengths of a deuterium atom to that of an α - particle, when the velocity of the former is five times greater than that of later, is

a) 4 b) 0.2 c) 2.5 d) 0.4

23. The energy of an electron in the 3rd orbit of hydrogen atom is –E. The energy of an electron in the first orbit will be

a) –3E b) $-E/3$ c) $-E/9$ d) –9E

24. Time independent Schnodinger wave equation is

a) $\hat{H}\psi = E\psi$
b) $\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E+V)\psi = 0$
c) $\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{h^2}(E-V)\psi = 0$
d) all of these

25. Which of the following does not represent the mathematical expression for the Heisenberg uncertainty principle ?

a) $\Delta x \,.\, \Delta p \geq h/4\pi$
b) $\Delta x \,.\, \Delta v \geq h/4\pi m$
c) $\Delta E \,.\, \Delta t \geq h/4\pi$
d) $\Delta E \,.\, \Delta x \geq h/4\pi$

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Write brief answer to the following questions

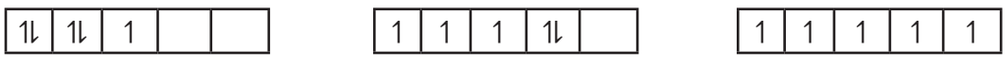
26. Which quantum number reveal information about the shape, energy, orientation and size of orbitals?

27. How many orbitals are possible for n =4?

28. How many radial nodes for 2s, 4p, 5d and 4f orbitals exhibit? How many angular nodes?

29. The stabilisation of a half filled d - orbital is more pronounced than that of the p-orbital why?

30. Consider the following electronic arrangements for the d^5 configuration.



(a) (b) (c)

(i) which of these represents the ground state

(ii) which configuration has the maximum exchange energy.

31. State and explain pauli exclusion principle.

32. Define orbital? what are the n and l values for $3p_x$ and $4d_{x^2-y^2}$ electron?

33. Explain briefly the time independent schrodinger wave equation?

34. Calculate the uncertainty in position of an electron, if $\Delta v = 0.1\%$ and $\upsilon = 2.2 \times 10^6$ ms^{-1}

35. Determine the values of all the four quantum numbers of the 8th electron in O- atom and 15th electron in Cl atom.

36. The quantum mechanical treatment of the hydrogen atom gives the energy value:

$$E_n = \frac{-13.6}{n^2} \text{ ev atom}^{-1}$$

i) use this expression to find ΔE between n = 3 and n=4

ii) Calculate the wavelength corresponding to the above transition.

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37. How fast must a 54g tennis ball travel in order to have a de Broglie wavelength that is equal to that of a photon of green light 5400Å?

38. For each of the following, give the sub level designation, the allowable m values and the number of orbitals

i) n = 4, l =2, ii) n =5, l = 3 iii) n=7, l=0

39. Give the electronic configuration of Mn^{2+} and Cr^{3+}

40. Describe the Aufbau principle

41. An atom of an element contains 35 electrons and 45 neutrons. Deduce

i) the number of protons

ii) the electronic configuration for the element

iii) All the four quantum numbers for the last electron

42. Show that the circumference of the Bohr orbit for the hydrogen atom is an integral multiple of the de Broglie wave length associated with the electron revolving arround the nucleus.

43. Calculate the energy required for the process.

$$He^{+}_{(g)} \rightarrow He^{2+}_{(g)} + e^{-}$$

The ionisation energy for the H atom in its ground state is - 13.6 ev $atom^{-1}$.

44. An ion with mass number 37 possesses unit negative charge. If the ion contains 11.1% more neutrons than electrons. Find the symbol of the ion.

45. The Li^{2+} ion is a hydrogen like ion that can be described by the Bohr model. Calculate the Bohr radius of the third orbit and calculate the energy of an electron in 4th orbit.

46. Protons can be accelerated in particle accelerators. Calculate the wavelength (in Å) of such accelerated proton moving at 2.85×10^{8} ms^{-1} (the mass of proton is 1.673×10^{-27} Kg).

47. What is the de Broglie wavelength (in cm) of a 160g cricket ball travelling at 140 Km hr^{-1}.

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48. Suppose that the uncertainty in determining the position of an electron in an orbit is 0.6 Å. What is the uncertainty in its momentum?

49. Show that if the measurement of the uncertainty in the location of the particle is equal to its de Broglie wavelength, the minimum uncertainty in its velocity (ΔV)is equal to 1/ 4π of its velocity(V)

50. What is the de Broglie wave length of an electron, which is accelerated from the rest, through a potential difference of 100V?

51. Identify the missing quantum numbers and the sub energy level

n	l	m	Sub energy level
?	?	0	4d
3	1	0	?
?	?	?	5p
?	?	-2	3d

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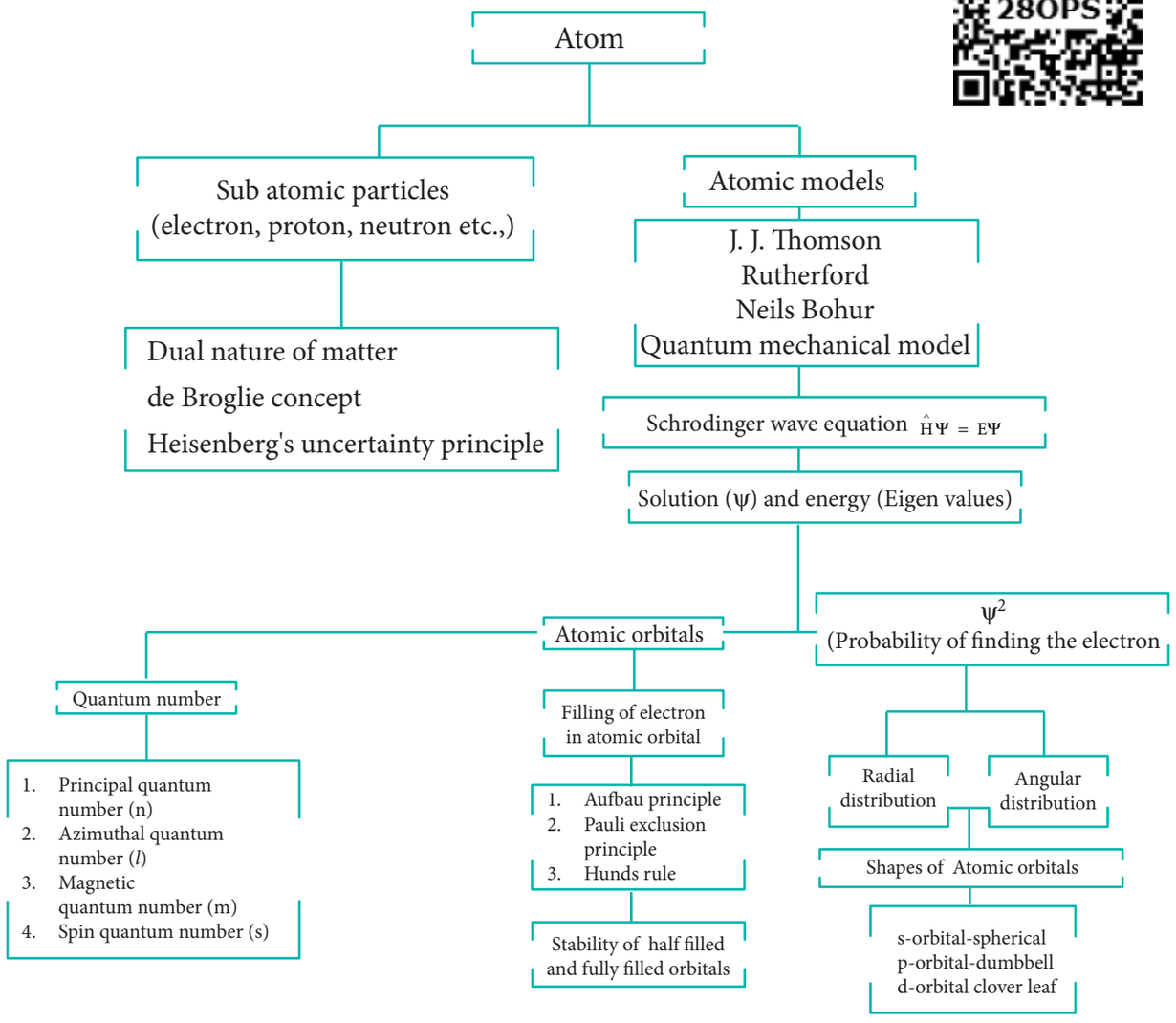
CONCEPT MAP



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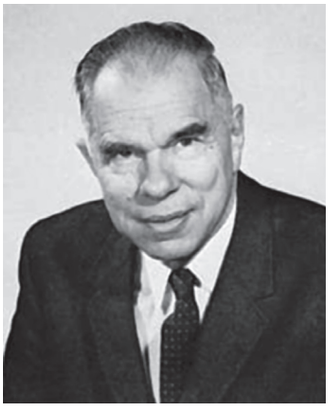
Unit 3

PERIODIC CLASSIFICATION OF ELEMENTS

"An awareness of the periodic table is essential to anyone who wishes to disentangle the world and see how it is built up from the fundamental building blocks of the chemistry, the chemical elements "

- Glenn T. Seaborg



Glenn T. Seaborg

Glenn Theodore Seaborg received Nobel Prize in 1951 in chemistry for the discoveries of trans-uranium elements. He was the co-discoverer of plutonium and other trans-uranium elements. He along with his colleagues has discovered over a hundred isotopes of other elements. He demonstrated that actinide elements are analogues to rare earth series of lanthanide elements.

Learning Objectives

After studying this unit, students will be able to

L4OQU

- recognise the development of the periodic table
- explain the work of Mosley's and modern periodic law
- outline the concept of grouping elements
- name the elements with atomic number greater than 100 using IUPAC nomenclature
- classify the elements into s, p, d and f blocks
- recognise the periodic trends and describe qualitatively the variation in periodic properties such as atomic radius, ionisation energy etc.
- explain the anomalies in the expected trend in the periodic properties
- calculate the effective nuclear charge using Slater's rule
- calculate the ionic radius using Pauling's method
- predict the probable position for a given element in the periodic table
- explain the anomalous properties of second period elements and the diagonal relationship

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Introduction

There are millions of chemical compounds existing in nature with different compositions and properties, formed from less than 100 naturally occurring elements.

The discovery of elements is linked with human civilization. In stone age, man has used some metals to suit his needs without knowing that they are elements. Soon he learnt to extract elements from ores and fashion them into his daily life. Over the years, more and more elements were discovered. In 1789, Lavoisier from France, published the first list of chemical elements containing 23 elements after several experimental investigations.

Antoine Lavoisier classified the substances into four groups of elements namely acid-making elements, gas-like elements, metallic elements and earthy elements

Table 3.1 Lavoisier table

acid-making elements	gas-like elements	metallic elements	earthy elements
sulphur	light	cobalt, mercury, tin	lime (calcium oxide)
phosphorus	caloric (heat)	copper, nickel, iron	magnesia (magnesium oxide)
charcoal (carbon)	oxygen	gold, lead, silver, zinc	barytes (barium sulphate)
	azote (nitrogen)	manganese, tungten	argilla (aluminium oxide)
	hydrogen	platina (platinum)	silex (silicon dioxide)

3.1 Classification of Elements

During the 19th century, scientists have isolated several elements and the list of known elements increased. Currently, we have 118 known elements. Out of 118 elements, 92 elements with atomic numbers 1 to 92 are found in nature. Scientists have found out there are some similarities in properties among certain elements. This observation has led to the idea of classification of elements based on their properties. In fact, classification will be beneficial for the effective utilization of these elements. Several attempts were made to classify the elements. However, classification based on the atomic weights led to the construction of a proper form of periodic table.

In 1817, J. W. Döbereiner classified some elements such as chlorine, bromine and iodine with similar chemical properties into the group of three elements called as triads. In triads, the atomic weight of the middle element nearly equal to the arithmetic mean of the atomic weights of the remaining two elements. However, only a limited number of elements can be grouped as triads.

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Table 3.2 Döbereiner Triads

S. No.	Elements in the Triad	Atomic weight of middle element	Average atomic weight of the remaining elements
1	Li, Na, K	23	$\frac{7+39}{2} = 23$
2	Cl, Br, I	80	$\frac{35.5+127}{2} = 81.25$
3	Ca, Sr, Ba	88	$\frac{40+137}{2} = 88.5$

This concept can not be extended to some triads which have nearly same atomic masses such as [Fe, Co, Ni], [Ru, Rh, Pd] and [Os, Ir, Pt].

In 1862, A. E. B. de Chancourtois reported a correlation between the properties of the elements and their atomic weights. He said 'the properties of bodies are the properties of numbers'. He intended the term numbers to mean the value of atomic weights. He designed a helix by tracing at an angle 45° to the vertical axis of a cylinder with circumference of 16 units. He arranged the elements in the increasing atomic weights along the helix on the surface of this cylinder. One complete turn of a helix corresponds to an atomic weight increase of 16. Elements which lie on the 16 equidistant vertical lines drawn on the surface of cylinder shows similar properties. This was the first reasonable attempt towards the creation of periodic table. However, it did not attract much attention.

In 1864, J. Newland made an attempt to classify the elements and proposed the law of octaves. On arranging the elements in the increasing order of atomic weights, he observed that the properties of every eighth element are similar to the properties of the first element. This law holds good for lighter elements up to calcium.

Table 3.3 Newlands' Octaves

^{7}Li	^{9}Be	^{11}B	^{12}C	^{14}N	^{16}O	^{19}F
^{23}Na	^{24}Mg	^{27}Al	^{29}Si	^{31}P	^{32}S	$^{35.5}Cl$
^{39}K	^{40}Ca					

3.1.1 Mendeleev's Classification

In 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. He plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and observed a periodical pattern.

During same period Dmitri Mendeleev independently proposed that "the properties of the elements are the periodic functions of their atomic weights" and this is called periodic law. Mendeleev listed 70 elements, which were known till histime in several vertical columns in order of increasing atomic weights. Thus, Mendeleev constructed the first periodic table based on the periodic law.

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Table 3.4 Mendeleev's periodic table

Series	Group of Elements											
	0	1	II	III	IV	V	VI	VII	VIII			
1		Hydrogen										
	-	**H**	-	-	-							
		1.0008										
2	Helium	Lithium	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine				
	He	**Li**	**Be**	**B**	**C**	**N**	**O**	**F**				
	4.0	7.03	9.1	11.0	12.0	14.04	16.00	19.0				
3	Neon	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine				
	Ne	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**				
	19.9	23.5	24.3	27.0	28.04	31.0	32.06	35.45				
4	Argon	Potassium	Calcium	Scandium	Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt		Nickel
	Ar	**K**	**Ca**	**Sc**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**(Ni**	**(Cu**
	38	39.1	40.1	44.1	48.1	51.4	52.1	55.0	55.9	59		59
5		Copper	Zinc	Gallium	Germanium	Arsenic	Selenium	Bromine				
		Cu	**Zn**	**Ga**	**Ge**	**As**	**Se**	**Br**				
		63.6	65.4	70.0	72.3	75	79	79.95				
6	Krypton	Rubidium	Strontium	Yttrium	Zirconium	Niobium	Molybdenum	-	Ruthenium	Rhodium		Palladium
	Kr	**Rb**	**Sr**	**Y**	**Zr**	**Nb**	**Mo**		**Ru**	**Rh**	**(Pd**	**(Ag**
	81.8	85.4	87.6	89.0	90.6	94.0	96.0		101.7	**103**		106.5
7		Silver	Cadmium	Indium	Tin	Antimony	Tellurium	Iodine				
		Ag	**Cd**	**In**	**Sn**	**Sb**	**Te**	**I**				
		107.9	112.4	114.0	119.0	120.0	127.6	126.9				
8	Xenon	Caesium	Barium	Lanthanum	Cerium	-	-	-	-			
	Xe	**Cs**	**Ba**	**La**	**Ce**							
	128	132.9	137.4	139	140							
9	-	-	-	-	-	-	-	-	-			
10				Ytterbium		Tantalum	Tungsten		Osmium	Iridium		Platinum
	-	-	-	**Yb**	-	**Ta**	**W**	-	**Os**	**Ir**	**(Pt**	**(Au**
				173		183	184		191	193		194.9
11		Gold	Mercury	Thallium	Lead	Bismuth		-	-			
		Au	**Hg**	**Tl**	**Pb**	**Bi**						
		197.2	200.0	204.1	206.9	208						
12			Radium		Thorium		Uranium					
	-	-	**Ra**	-	**Th**	-	**U**					
			224		232		239					

As shown in the periodic table, he left some blank spaces since there were no known elements with the appropriate properties at that time. He and others predicted the physical and chemical properties of the missing elements. Eventually these missing elements were discovered and found to have the predicted properties. For example, Gallium (Ga) of group III and germanium (Ge) of group IV were unknown at that time. But Mendeleev predicted their existence and properties. He referred the predicted elements as eka-aluminium and eka-silicon. After discovery of the actual elements, their properties were found to match closely to those predicted by Mendeleev (Table 3.4).

Table 3.5 Properties predicted for Eka-aluminium and Eka-silicon

S.No.	Property	Eka-aluminium (Predicted)	Gallium (Observed)	Eka-silicon (Predicted)	Germanium (Observed)
1.	Atomic weight	68	70	72	72.59
2.	Density (g/cm^3)	5.9	5.94	5.5	5.36
3.	Melting point	low	29.78°C	High	947°C
4.	Formula of oxide	E_2O_3	Ga_2O_3	EO_2	GeO_2
5.	Formula of chloride	ECl_3	$GaCl_3$	ECl_4	$GeCl_4$

3.1.2 Anomalies of Mendeleev's Periodic Table

Some elements with similar properties were placed in different groups and those with dissimilar properties were placed in same group. Similarly elements with higher atomic weights were placed before lower atomic weights based on their properties in contradiction to his periodic law. Example $^{59}Co_{27}$ was placed before $^{58.7}Ni_{28}$; Tellurium (127.6) was placed in VI group but Iodine (127.0) was placed in VII group.

3.2 Moseley's Work and Modern Periodic Law

In 1913, Henry Moseley studied the characteristic X-rays spectra of several elements by bombarding them with high energy electrons and observed a linear correlation between atomic number and the frequency of X-rays emitted which is given by the following expression.

$$\sqrt{\upsilon} = a(Z - b)$$

Where, υ is the frequency of the X-rays emitted by the element with atomic number 'Z'; a and b are constants and have same values for all the elements.

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The plot of $\sqrt{\upsilon}$ against Z gives a straight line. Using this relationship, we can determine the atomic number of an unknown (new) element from the frequency of X-ray emitted.

Based on his work, the modern periodic law was developed which states that, "the physical and chemical properties of the elements are periodic functions of their atomic numbers." Based on this law, the elements were arranged in order of their increasing atomic numbers. This mode of arrangement reveals an important truth that the elements with similar properties recur after regular intervals. The repetition of physical and chemical properties at regular intervals is called periodicity.

3.2.1 Modern Periodic Table

The physical and chemical properties of the elements are correlated to the arrangement of electrons in their outermost shell (valence shell). Different elements having similar outer shell electronic configuration possess similar properties. For example, elements having one electron in their valence shell s-orbital possess similar physical and chemical properties. These elements are grouped together in the modern periodic table as first group elements.

Table 3.6 Electronic configuration of alkali metals (ns^1)

Elements in Group 1	Atomic number	Number of electrons in various shells in the order K, L, M, N, P	Valence shell configuration
Li	3	2, 1	$2s^1$
Na	11	2, 8, 1	$3s^1$
K	19	2, 8, 8, 1	$4s^1$
Rb	37	2,8,18,8,1	$5s^1$
Cs	55	2, 8, 18, 18, 8, 1	$6s^1$
Fr	87	2, 8, 18, 32, 18, 8, 1	$7s^1$

Similarly, all the elements are arranged in the modern periodic table which contains 18 vertical columns and 7 horizontal rows. The vertical columns are called groups and the horizontal rows are called periods. Groups are numbered 1 to 18 in accordance with the IUPAC recommendation which replaces the old numbering scheme IA to VIIA, IB to VIIB and VIII.

Each period starts with the element having general outer electronic configuration ns^1 and ends with $ns^2\ np^6$. Here 'n' corresponds to the period number (principal quantum number). The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the modern periodic table.

Evaluate Yourself

1. What is the basic difference in approach between Mendeleev's periodic table and modern periodic table ?

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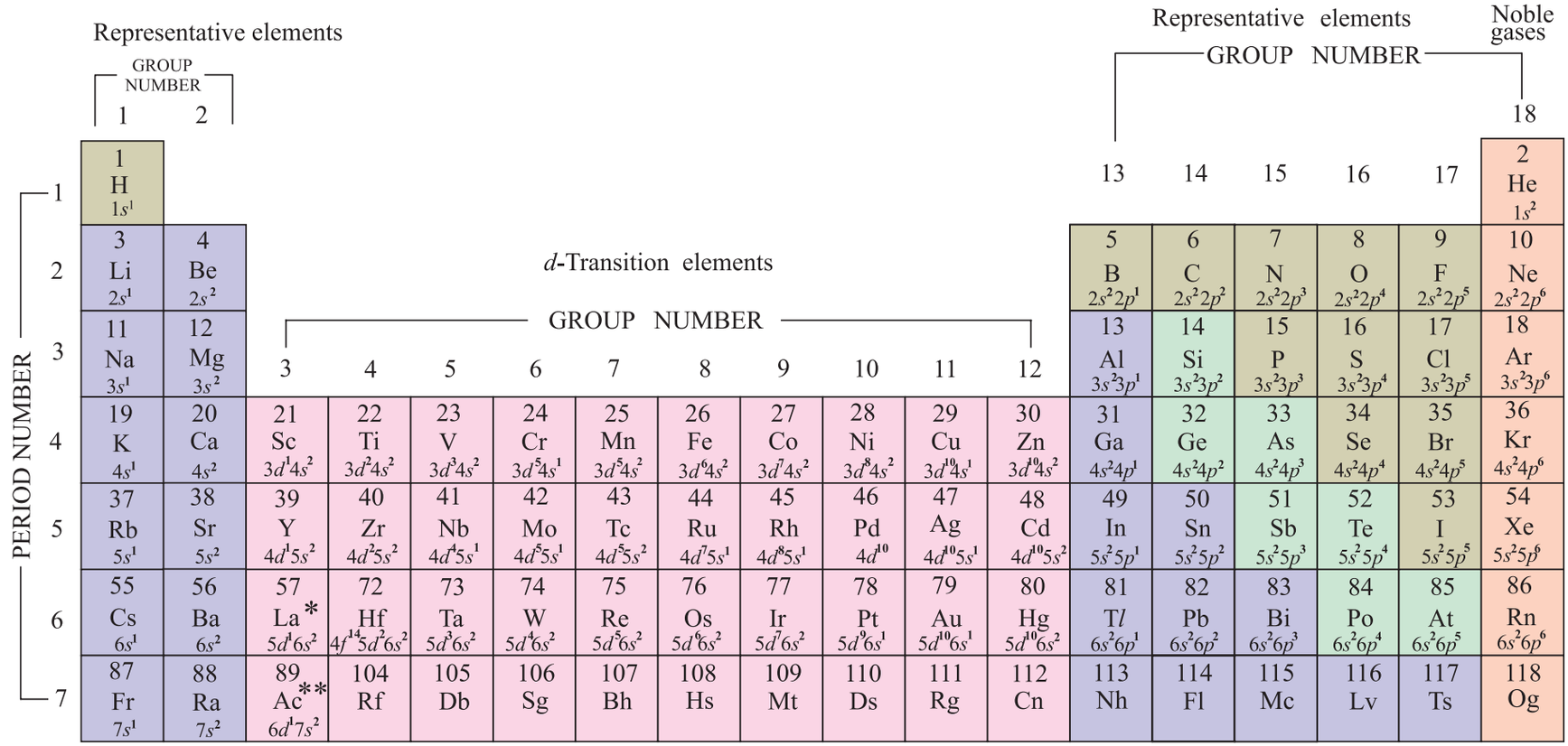

f - Inner transition elements

*Lanthanoids $4f^{n}5d^{0\text{-}1}6s^{2}$	58 Ce $4f^{1}5d^{1}6s^{2}$	59 Pr $4f^{3}5d^{0}6s^{2}$	60 Nd $4f^{4}5d^{0}6s^{2}$	61 Pm $4f^{5}5d^{0}6s^{2}$	62 Sm $4f^{6}5d^{0}6s^{2}$	63 Eu $4f^{7}5d^{0}6s^{2}$	64 Gd $4f^{7}5d^{1}6s^{2}$	65 Tb $4f^{9}5d^{0}6s^{2}$	66 Dy $4f^{10}5d^{0}6s^{2}$	67 Ho $4f^{11}5d^{0}6s^{2}$	68 Er $4f^{12}5d^{0}6s^{2}$	69 Tm $4f^{13}5d^{0}6s^{2}$	70 Yb $4f^{14}5d^{0}6s^{2}$	71 Lu $4f^{14}5d^{1}6s^{2}$
**Actinoids $5f^{n}6d^{0\text{-}2}7s^{2}$	90 Th $5f^{0}6d^{2}7s^{2}$	91 Pa $5f^{2}6d^{1}7s^{2}$	92 U $5f^{3}6d^{1}7s^{2}$	93 Np $5f^{4}6d^{1}7s^{2}$	94 Pu $5f^{6}6d^{0}7s^{2}$	95 Am $5f^{7}6d^{0}7s^{2}$	96 Cm $5f^{7}6d^{1}7s^{2}$	97 Bk $5f^{9}6d^{0}7s^{2}$	98 Cf $5f^{10}6d^{0}7s^{2}$	99 Es $5f^{11}6d^{0}7s^{2}$	100 Fm $5f^{12}6d^{0}7s^{2}$	101 Md $5f^{13}6d^{0}7s^{2}$	102 No $5f^{14}6d^{0}7s^{2}$	103 Lr $5f^{14}6d^{1}7s^{2}$

Table 3.7 Modern periodic table

3.3 Nomenclature of Elements with Atomic Number Greater than 100

Usually, when a new element is discovered, the discoverer suggests a name following IUPAC guidelines which will be approved after a public opinion. In the meantime, the new element will be called by a temporary name coined using the following IUPAC rules, until the IUPAC recognises the new name.

1. The name was derived directly from the atomic number of the new element using the following numerical roots.

Table 3.8 Notation for IUPAC Nomenclature of elements

Digit	0	1	2	3	4	5	6	7	8	9
Root	nil	un	bi	tri	quad	pent	hex	sept	oct	enn
Abbreviation	n	u	b	t	q	p	h	s	o	e

2. The numerical roots corresponding to the atomic number are put together and 'ium' is added as suffix

3. The final 'n' of 'enn' is omitted when it is written before 'nil' (enn + nil = enil) similarly the final 'i' of 'bi' and 'tri' is omitted when it written before 'ium' (bi + ium = bium; tri + ium = trium)

4. The symbol of the new element is derived from the first letter of the numerical roots.

The following table illustrates these facts.

Table 3.9 Name of elements with atomic number above 100

Atomic number	Temporary Name	Temporary Symbol	Name of the element	Symbol
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordiium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs

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Atomic number	Temp. Name	Temp. Symbol	Name of the element	Symbol
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Uun	Darmstadtium	Ds
111	Unununium	Uuu	Roentgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uuq	Flerovium	Fl
115	Ununpentium	Uup	Moscovium	Mc
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uuo	Oganesson	Og

Evaluate Yourself

2. The element with atomic number 120 has not been discovered so far. What would be the IUPAC name and the symbol for this element? Predict the possible electronic configuration of this element.

3.4 Grouping of Elements based on Electronic Configurations

In the modern periodic table, the elements are organised in 7 periods and 18 groups based on the modern periodic law. The placement of element in the periodic table is closely related to its outer shell electronic configuration. Let us analyse the change in the electronic configuration of elements along the periods and down the groups.

3.4.1 Variation of Electronic Configuration along the periods

We have already learnt that each period starts with the element having general outer electronic configuration ns^1 and ends with ns^2, np^6 where n is the period number. The first period starts with the filling of valence electrons in 1s orbital, which can accommodate only two electrons. Hence, the first period has two elements, namely hydrogen and helium. The second period starts with the filling of valence electrons in 2s orbital followed by three 2p orbitals with eight elements from lithium to neon. The third period starts with filling of valence electrons in the 3s orbital followed by 3p orbitals. The fourth period starts with filling of valence electrons from 4s orbital followed by 3d and 4p orbitals in accordance with Aufbau principle. Similarly, we can explain the electronic configuration of elements in the subsequent periods (Table 3.10).

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Table 3.10 Electronic configuration of elements in a period

Period number (n)	Filling of electrons in orbitals		Number of elements	Outer shell Electronic configuration	
	Starts from	Ends with		First element	Last element
1	1s	1s	2	H – $1s^1$	He – $1s^2$
2	2s	2p	8	Li – $2s^1$	Ne– $2s^2 2p^6$
3	3s	3p	8	Na – $3s^1$	Ar – $3s^2 3p^6$
4	4s	4p	18	K – $4s^1$	Kr– $4s^2 4p^6$
5	5s	5p	18	Rb – $5s^1$	Xe – $5s^2 5p^6$
6	6s	6p	32	Cs – $6s^1$	Rn – $6s^2 6p^6$
7	7s	7p	32	Fr – $7s^1$	Og – $7s^2 7p^6$

In the fourth period the filling of 3d orbitals starts with scandium and ends with zinc. These 10 elements are called first transition series. Similarly 4d, 5d and 6d orbitals are filled in successive periods and the corresponding series of elements are called second, third and fourth transition series respectively.

In the sixth period the filling of valence electrons starts with 6s orbital followed by 4f, 5d and 6p orbitals. The filling up of 4f orbitals begins with Cerium (Z=58) and ends at Lutetium (Z=71). These 14 elements constitute the first inner-transition series called Lanthanides. Similarly, in the seventh period 5f orbitals are filled, and it's -14 elements constitute the second inner-transition series called Actinides. These two series are placed separately at the bottom of the modern periodic table.

3.4.2 Variation of Electronic Configuration in the Groups:

Elements of a group have similar electronic configuration in the outer shell. The general outer electronic configurations for the 18 groups are listed in the Table 3.11. The groups can be combined as s, p, d and f block elements on the basis of the orbital in which the last valence electron enters.

The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. The group 1 elements are called alkali metals while the group 2 elements are called alkaline earth metals. These are soft metals and possess low melting and boiling points with low ionisation enthalpies. They are highly reactive and form ionic compounds. They are highly electropositive in nature and most of the elements imparts colour to the flame. We will study the properties of these group elements in detail in subsequent chapters.

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The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns^2, np^{1-6}. The elements of the group 16 and 17 are called chalcogens and halogens respectively. The elements of 18th group contain completely filled valence shell electronic configuration (ns^2, np^6) and are called inert gases or nobles gases. The elements of p-block have high negative electron gain enthalpies. The ionisation energies are higher than that of s-block elements. They form mostly covalent compounds and shows more than one oxidation states in their compounds.

The elements of the groups 3 to 12 are called d-block elements or transition elements with general valence shell electronic configuration ns^{1-2}, $(n-1)d^{1-10}$. These elements also show more than one oxidation state and form ionic, covalent and co-ordination compounds. They can form interstitial compounds and alloys which can also act as catalysts. These elements have high melting points and are good conductors of heat and electricity.

The lanthanides ($4f^{1-14}$, $5d^{0-1}$, $6s^2$) and the actinides ($5f^{0-14}$, $6d^{0-2}$, $7s^2$) are called f-block elements. These elements are metallic in nature and have high melting points. Their compounds are mostly coloured. These elements also show variable oxidation states.

Table 3.11 General outer electronic configuration of elements in groups:

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ns^1	ns^2	$ns^2(n-1)d^1$	$ns^2(n-1)d^2$	$ns^2(n-1)d^3$	$ns^1(n-1)d^5$	$ns^2(n-1)d^5$	$ns^2(n-1)d^6$	$ns^2(n-1)d^7$	$ns^2(n-1)d^8$	$ns^1(n-1)d^{10}$	$ns^2(n-1)d^{10}$	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
s-block elements		d-block elements										p-block elements					
f-block elements		Lanthanides $4f^{1-14}\,5d^{0-1}\,6s^2$															
		Actinides $5f^{0-14}\,6d^{0-2}\,7s^2$															

Evaluate Yourself

3. Predict the position of the element in periodic table satisfying the electronic configuration $(n-1)d^2$, ns^2 where n=5

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3.5 Periodic Trends in Properties

As discussed earlier, the electronic configuration of the elements shows a periodic variation with increase in atomic numbers. Similarly a periodic trend is observed in physical and chemical behaviour of elements. In this section, we will study the periodic trends in the following properties of elements.

1. Atomic radius
2. Ionic radius
3. Ionisation enthalpy (energy)
4. Electron gain enthalpy (electron affinity)
5. Electronegativity

3.5.1 Atomic radius

Atomic radius of an atom is defined as the distance between the centre of its nucleus and the outermost shell containing the valence electron.

It is not possible to measure the radius of an isolated atom directly. Except for noble gases, usually atomic radius is referred to as covalent radius or metallic radius depending upon the nature of bonding between the concerned atoms.

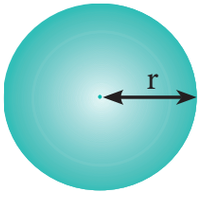

Figure 3.1 (a) Atomic radius

Covalent radius

It is one-half of the internuclear distance between two identical atoms linked together by a single covalent bond. Inter nuclear distance can be determined using x-ray diffraction studies.

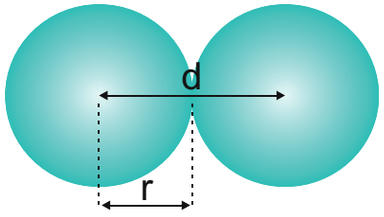

Figure 3.1 (b) Atomic and covalent radius

Example:

The experimental internuclear distance in Cl_2 molecule is 1.98 Å. The covalent radius of chlorine is calculated as below.

$$d_{Cl\text{-}Cl} = r_{Cl} + r_{Cl}$$

$$\Rightarrow d_{Cl\text{-}Cl} = 2r_{Cl}$$

$$\Rightarrow r_{Cl} = \frac{d_{Cl\text{-}Cl}}{2}$$

$$\Rightarrow r_{Cl} = \frac{1.98}{2} = 0.99\text{Å}$$

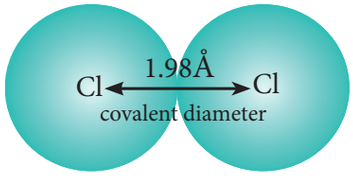

Figure 3.1 (c) Covalent radius of Cl

The formation of covalent bond involves the overlapping of atomic orbitals and it reduces the expected internuclear distance. Therefore covalent radius is always shorter than the actual atomic radius.

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In case of hetero nuclear diatomic molecules, the covalent radius of individual atom can also be calculated using the internuclear distance (d_{A-B}) between two different atoms A and B. The simplest method proposed by Schomaker and Stevenson is as follows.

$$d_{A-B} = r_A + r_B - 0.09\ (\chi_A - \chi_B)$$

where χ_A and χ_B are the electronegativities of A and B respectively in Pauling units. Here $\chi_A > \chi_B$ and radius is in Å.

Let us calculate the covalent radius of hydrogen using the experimental d_{H-Cl} value is 1.28 Å and the covalent radius of chlorine is 0.99 Å. In pauling scale the electronegativity of chlorine and hydrogen are 3 and 2.1 respectively.

$$d_{H-Cl} = r_H + r_{Cl} - 0.09\ (\chi_{Cl} - \chi_H)$$

$$1.28 = r_H + 0.99 - 0.09\ (3 - 2.1)$$

$$1.28 = r_H + 0.99 - 0.09\ (0.9)$$

$$1.28 = r_H + 0.99 - 0.081$$

$$1.28 = r_H + 0.909$$

$$\therefore r_H = 1.28 - 0.909 = 0.371\ Å$$

Metallic radius

It is defined as one-half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

For example, the distance between the adjacent copper atoms in solid copper is 2.56 Å and therefore the metallic radius of copper is

$$\frac{2.56}{2} = 1.28\ Å$$

The metallic radius can be calculated using the unit cell length of the metallic crystal. You will study the detailed calculation procedure in XII standard solid state unit.

Periodic Trends in Atomic Radius

Variation in Periods

Atomic radius tends to decrease in a period. As we move from left to right along a period, the valence electrons are added to the same shell. The simultaneous addition of protons to the nucleus, increases the nuclear charge, as well as the electrostatic attractive force between the valence electrons and the nucleus. Therefore atomic radius decreases along a period.

Effective nuclear charge

In addition to the electrostatic forces of attraction between the nucleus and the electrons, there exists repulsive forces among the electrons. The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect.

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge. It is approximated by the below mentioned equation.

$$Z_{eff} = Z - S$$

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Where Z is the atomic number and 'S' is the screening constant which can be calculated using Slater's rules as described below.

Step 1 :

Write the electronic configuration of the atom and rearrange it by grouping ns and np orbitals together and others separately in the following form.

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)...

Step 2 :

Identify the group in which the electron of interest is present. The electron present right to this group does not contribute to the shielding effect.

Each of the electrons within the identified group (denoted by 'n') shields to an extent of 0.35 unit of nuclear charge. However, it is 0.30 unit for 1s electron.

Step 3 :

Shielding of inner shell electrons.

If the electron of interest belongs to either s or p orbital,

i) each electron within the (n-1) group shields to an extent of 0.85 unit of nuclear charge, and

ii) each electron within the (n-2) group (or) even lesser group (n-3), (n-4) etc... completely shields i.e. to an extent of 1.00 unit of nuclear charge.

If the electron of interest belongs to d or f orbital, then each of electron left of the group of electron of interest shields to an extent of 1.00 unit of nuclear charge.

Step 4 :

Summation of the shielding effect of all the electrons gives the shielding constant 'S'

Example: Let us explain the calculation of effective nuclear charge on 4s electron and 3d electron in scandium. The electronic configuration of scandium is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^1$. we can rearrange as below.

$\underbrace{(1s)^2}_{(n-3)}\ \underbrace{(2s,2p)^8}_{(n-2)}\ \underbrace{(3s,3p)^8\,(3d)^1}_{(n-1)}\ \underbrace{(4s)^2}_{n}$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
(n)	1	0.35	0.35
(n-1)	9	0.85	7.65
(n-2) & others	10	1	10.00
S value			18.00

$Z_{eff} = Z - S$ i.e.= 21- 18 $\therefore Z_{eff} = 3$

Calculation of effective nuclear charge on 3d electron

$\underbrace{(1s)^2}_{(n-3)}\ \underbrace{(2s,2p)^8}_{(n-2)}\ \underbrace{(3s,3p)^8}_{(n-1)}\ (3d)^1\ \underbrace{(4s)^2}_{n}$

Group	number of electron in the group	contribution of each electron to 'S' value	contribution of a particular group to electrons to 'S' value
n	0	0.35	0
(n-1) & others	18	1	18
S Value			18

$\therefore Z_{eff} = Z - S$ i.e. =21 - 18 $\therefore Z_{eff} = 3$

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Table 3.12 Shielding effect from inner shell electrons (Slater's rules)

Electron Group	Electron of interest either S or P	Electron of interest either d or f
n	0.35 (0.30 for (S electron)	0.35
(n-1)	0.85	1.00
(n-2) and others	1.00	1.00

Table 3.13 Atomic radius (covalent radius) of second period elements.

Elements	Effective nuclear charge	Covalent radius (pm)
$_3$Li	1.30	152
$_4$Be	1.95	111
$_5$B	2.60	89
$_6$C	3.25	77
$_7$N	3.90	74
$_8$O	4.55	66
$_9$F	5.20	64
$_{10}$Ne	5.85	

* Van der waals radius

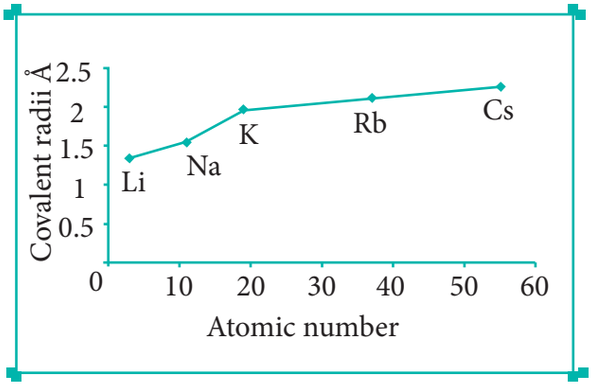
Evaluate Yourself

4. Using Slater's rule calculate the effective nuclear charge on a 3p electron in aluminium and chlorine. Explain how these results relate to the atomic radii of the two atoms.

Variation in Group

In the periodic table, the atomic radius of elements increases down the group. As we move down a group, new shells are opened to accommodate the newly added valence electrons. As a result, the distance between the centre of the nucleus and the outermost shell containing the valence electron increases. Hence, the atomic radius increases. The trend in the variation of the atomic radius of the alkali metals down the group os shown below.

Table 3.14 Variation of covalent radius of group 1 elements



Element	Outermost shell containing valence electron	Covalent radius (Å)
Li	L (n=2)	1.34
Na	M (n=3)	1.54
K	N (n=4)	1.96
Rb	O (n=5)	2.11
Cs	P (n=6)	2.25

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Activity 3.1

Covalent radii (in Å) for some elements of different groups and periods are listed below. Plot these values against atomic number. From the plot, explain the variation along a period and a group.

2nd group elements : Be (0.89), Mg (1.36), Ca (1.74), Sr (1.91) Ba(1.98)

17th group elements : F (0.72), Cl (0.99), Br (1.14), I (1.33)

3rd Period elements : Na(1.57), Mg(1.36), Al (1.25), Si(1.17), P(1.10), S(1.04), Cl(0.99)

4th period elements: K(2.03), Ca(1.74), Sc(1.44), Ti(1.32), V(1.22), Cr(1.17), Mn(1.17), Fe(1.17), Co(1.16), Ni(1.15), Cu(1.17), Zn(1.25), Ga(1.25), Ge(1.22), As(1.21), Se(1.14), Br(1.14)

3.5.2 Ionic radius

It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. Ionic radius of uni-univalent crystal can be calculated using Pauling's method from the inter ionic distance between the nuclei of the cation and anion. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other. Therefore,

$$d = r_{C^+} + r_{A^-} \quad \text{----------} \quad (1)$$

Where d is the distance between the centre of the nucleus of cation C^+ and anion A^- and r_{C^+}, r_{A^-} are the radius of the cation and anion respectively.

Pauling also assumed that the radius of the ion having noble gas electronic configuration (Na^+ and Cl^- having $1s^2$ $2s^2$, $2p^6$ configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

$$\text{i.e. } r_{C^+} \alpha \frac{1}{(Z_{eff})_{C^+}} \quad \text{----------} \quad (2)$$

and

$$r_{A^-} \alpha \frac{1}{(Z_{eff})_{A^-}} \quad \text{----------} \quad (3)$$

Where Z_{eff} is the effective nuclear charge and $Z_{eff} = Z - S$

Dividing the equation 2 by 3

$$\frac{r_{C^+}}{r_{A^-}} = \frac{(Z_{eff})_{A^-}}{(Z_{eff})_{C^+}} \text{----(4)}$$

On solving equation (1) and (4) the values of r_{C^+} and r_{A^-} can be obtained

Let us explain this method by calculating the ionic radii of Na^+ and F^- in NaF crystal whose interionic distance is equal to 231 pm .

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$d = r_{Na^+} + r_{F^-} \quad ---(5)$

i.e. $r_{Na^+} + r_{F^-} = 231\ pm \quad ---(6)$

We know that

$$\frac{r_{Na^+}}{r_{F^-}} = \frac{(Z_{eff})_{F^-}}{(Z_{eff})_{Na^+}}$$

$(Z_{eff})_{F^-} = Z - S$

$= 9 - 4.15$

$= 4.85$

$(Z_{eff})_{Na^+} = 11 - 4.15$

$= 6.85$

$$\therefore \frac{r_{Na^+}}{r_{F^-}} = \frac{4.85}{6.85}$$

$= 0.71$

$\Rightarrow r_{Na^+} = 0.71 \times r_{F^-}$

Substituting r_{Na^+} in (5)

$(5) \Rightarrow \quad 0.71\, r_{F^-} + r_{F^-} = 231\ pm$

$1.71\, r_{F^-} = 231\ pm$

$$r_{F^-} = \frac{231}{1.71} = 135.1\ pm$$

Substituting the value of r_{F^-} in equation (6)

$r_{Na^+} + 135.1 = 231$

$r_{Na^+} = 95.9\ pm$

Evaluate Yourself

5. A student reported the ionic radii of isoelectronic species X^{3+}, Y^{2+} and Z^- as 136 pm, 64 pm and 49 pm respectively. Is that order correct? Comment.

3.5.3 Ionisation energy

It is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state. It is expressed in kJ mol^{-1} or in electron volts (eV).

$$M_{(g)} + IE_1 \rightarrow M^+_{(g)} + 1\ e^-$$

Where IE_1 represents the first ionisation energy.

Successive Ionisation energies

The minimum amount of energy required to remove an electron from a unipositive cation is called second ionisation energy. It is represented by the following equation.

$$M^+_{(g)} + IE_2 \rightarrow M^{2+}_{(g)} + 1\ e^-$$

In this way we can define the successive ionisation energies such as third, fourth etc.

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order

$$IE_1 < IE_2 < IE_3 < .....$$

Periodic Trends in Ionisation Energy

The ionisation energy usually increases along a period with few exceptions. As discussed earlier, when we move from left to right along a period, the valence electrons are added to the same shell, at the same time protons are added to the nucleus. This successive increase of nuclear charge increases the electrostatic attractive force on the valence electron and more energy is required to remove the valence electron resulting in high ionisation energy.

Let us consider the variation in ionisation energy of second period

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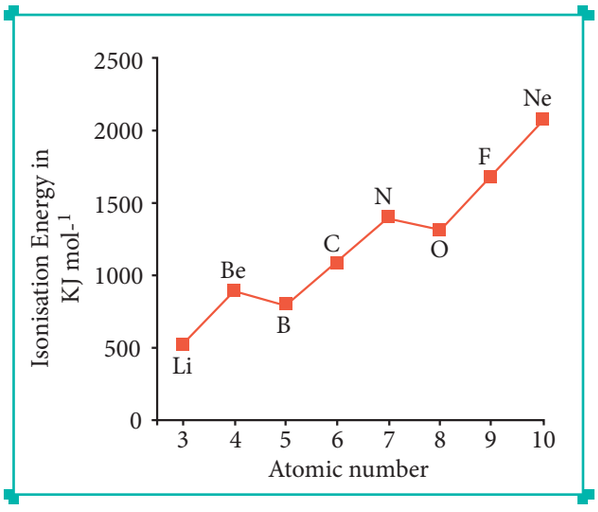
elements. The plot of atomic number vs ionisation energy is given below.

In the following graph, there are two deviation in the trends of ionisiation energy. It is expected that boron has higher ionisation energy than beryllium since it has higher nuclear charge. However, the actual ionisation energies of beryllium and boron are 899 and 800 kJ mol^{-1} respectively contrary to the expectation. It is due to the fact that beryllium with completely filled 2s orbital, is more stable than partially filled valence shell electronic configuration of boron. ($2s^2$, $2p^1$)

Figure 3.2 Variation of Ionisation energy along the II period



The electronic configuration of beryllium (Z=4) in its ground state is $1s^2$, $2s^2$ and that of boran is (Z = 5) $1s^2$ $2s^2$ $2p^1$

Similarly, nitrogen with $1s^2$, $2s^2$, $2p^3$ electronic configuration has higher ionisation energy (1402 kJ mol^{-1}) than oxygen (1314 kJ mol^{-1}). Since the half filled electronic configuration is more stable, it requires higher energy to remove an electron from 2p orbital of nitrogen. Whereas the removal one 2p electron from oxygen leads to a stable half filled configuration. This makes comparatively easier to remove 2p electron from oxygen.

Periodic variation in group

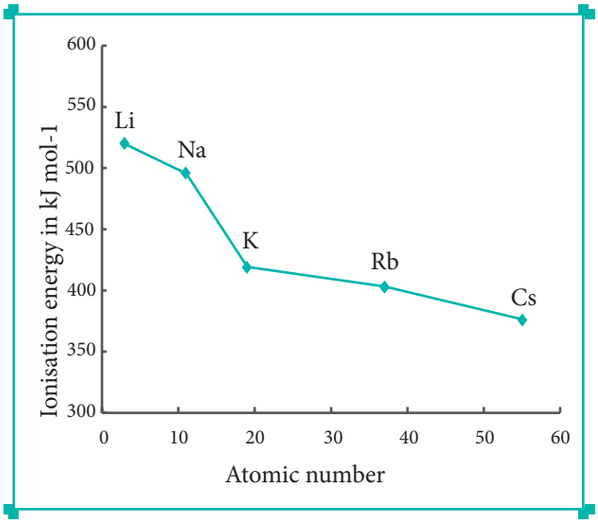
The ionisation energy decreases down a group. As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases. So, the nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

Ionisation energy and shielding effect

As we move down a group, the number of inner shell electron increases which in turn increases the repulsive force exerted by them on the valence electrons, i.e. the increased shielding effect caused by the inner electrons decreases the attractive force acting on the valence electron by the nucleus. Therefore the ionisation energy decreases.

Let us understand this trend by considering the ionisation energy of alkali metals.

Figure 3.3 Variation of Ionisation energy down the I Group.



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Evaluate Yourself

6. The first ionisation energy (IE_1) and second ionisation energy (IE_2) of elements X, Y and Z are given below.

Element	IE_1 (kJ mol^{-1})	IE_2 (kJ mol^{-1})
X	2370	5250
Y	522	7298
Z	1680	3381

Which one of the above elements is the most reactive metal, the least reactive metal and a noble gas?

3.5.4 Electron Affinity

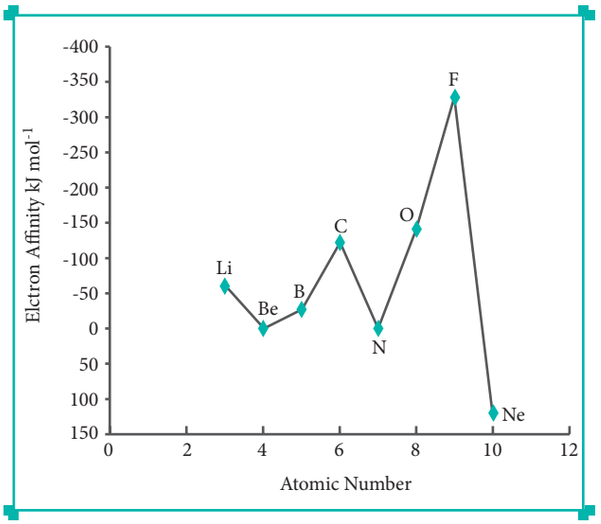
It is defined as the amount of energy released (required in the case noble gases) when an electron is added to the valence shell of an isolated neutral gaseous atom in its ground state to form its anion. It is expressed in kJ mol^{-1}

$$A + e^- \rightarrow A^- + EA$$

Variation of Electron Affinity in a period:

The variation of electron affinity is not as systematic as in the case of ionisation energy. As we move from alkali metals to halogens in a period, generally electron affinity increases, i.e. the amount of energy released will be more. This is due to an increase in the nuclear charge and decrease in size of the atoms. However, in case of elements such as beryllium ($1s^2$, $2s^2$), nitrogen ($1s^2$, $2s^2$, $2p^3$) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

Figure 3.4 Variation of electron affinity (electron gain energy) along II period



Noble gases have stable ns^2, np^6 configuration, and the addition of further electron is unfavourable and requires energy. Halogens having the general electronic configuration of ns^2, np^5 readily accept an electron to get the stable noble gas electronic configuration (ns^2, np^6), and therefore in each period the halogen has high electron affinity. (high negative values)

Variation of Electron affinity in a group:

As we move down a group, generally the electron affinity decreases. It is due to increase in atomic size and the shielding effect of inner shell electrons. However, oxygen and fluorine have lower affinity than sulphur and chlorine respectively. The sizes of oxygen and fluorine atoms are comparatively small and they have high electron density. Moreover, the extra electron added to oxygen and fluorine has to be accommodated in the 2p orbital which is relatively compact compared to the 3p orbital of sulphur

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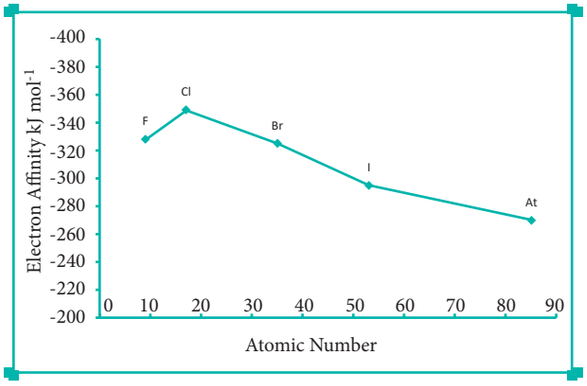
and chlorine so, oxygen and fluorine have lower electron affinity than their respective group elements sulphur and chlorine.

Figure 3.5 Variation of Electron Affinity (electron gain energy) along 17th group



Evaluate Yourself

7. The electron gain enthalpy of chlorine is 348 kJ mol^{-1}. How much energy in kJ is released when 17.5 g of chlorine is completely converted into Cl^- ions in the gaseous state?

3.5.5 Electronegativity:

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

Electronegativity is not a measurable quantity. However, a number of scales are available to calculate its value. One such method was developed by Pauling, he assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.1 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression

$$(\chi_A - \chi_B) = 0.182\sqrt{E_{AB} - (E_{AA} x E_{BB})^{½}}$$

Where E_{AB}, E_{AA} and E_{BB} are the bond dissociation energies (K cal) of AB, A_2 and B_2 molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound. The electronegativity values play an important role in predicting the nature of the bond.

Variation of Electronegativity in a period:

The electronegativity generally increases across a period from left to right. As discussed earlier, the atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electronegativity also increases in a period

Figure 3.6 Variation of Electronegativity along II period

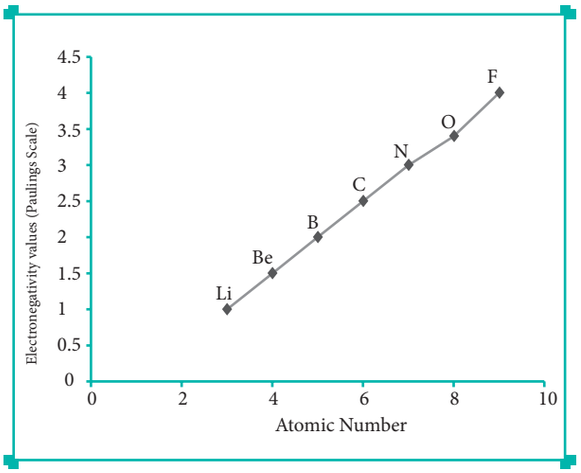


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Table 3.15 Electronegativities of various elements (Paulings scale)

H 2.1																
Li 1.0	Be 1.6											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.9	Ni 1.9	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.0	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.9	Bi 1.9	Po 2.0	At 2.1

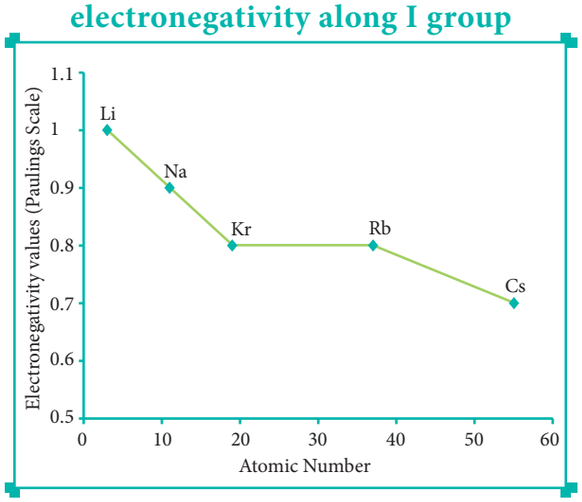
low → medium → high

Variation of Electronegativity in a group:

The electronegativity generally decreases down a group. As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence, the electronegativity decreases.

Noble gases are assigned zero electronegativity. The electronegativity values of the elements of s-block show the expected decreasing order in a group. Except 13th and 14th group all other p-block elements follow the expected decreasing trend in electronegativity.

Figure 3.7 Variation of electronegativity along I group



3.6 Periodic Trends in Chemical Properties:

So far, we have studied the periodicity of the physical properties such as atomic radius, ionisation enthalpy, electron gain enthalpy and electronegativity. In addition, the chemical properties such as reactivity, valence, oxidation state etc… also show periodicity to certain extent.

In this section, we will discuss briefly about the periodicity in valence (oxidation state) and anomalous behaviour of second period elements (diagonal relationship).

Valence or Oxidation States

The valence of an atom is the combining capacity relative to hydrogen atom. It is usually equal to the total number of electrons in the valence shell or equal to eight minus the number of valence electrons. It is more convenient to use oxidation state in the place of valence.

Periodicity of Valence or Oxidation States

The valence of an atom primarily depends on the number of electrons in the

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valence shell. As the number of valence electrons remains same for the elements in same group, the maximum valence also remains the same. However, in a period the number of valence electrons increases, hence the valence also increases.

Table 3.16 Variation of valence in groups

Alkali Metals (Group 1)			Group 15		
Element	No. of electrons in valence shell	Valence	Element	No. of electrons in valence shell	Valence
Li	1	1	N	5	3, 5
Na	1	1	P	5	3, 5
K	1	1	As	5	3, 5
Rb	1	1	Sb	5	3, 5
Cs	1	1	Bi	5	3, 5
Fr	1	1			

Table 3.17 Variation of valence in period (1st period)

Element	Li	Be	B	C	N	O	F	Ne
No. of electrons in valence shell	1	2	3	4	5	6	7	8
Valence (Combining capacity)	1	2	3	4	5, 3	6, 2	7, 1	8, 0

In addition to that some elements have variable valence. For example, most of the elements of group 15 which have 5 valence electrons show two valences 3 and 5. Similarly transition metals and inner transition metals also show variable oxidation states.

3.6.1 Anomalous properties of second period elements:

As we know, the elements of the same group show similar physical and chemical properties. However, the first element of each group differs from other members of the group in certain properties. For example, lithium and beryllium form more covalent compounds, unlike the alkali and alkaline earth metals which predominantly form ionic compounds. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences. For example, boron forms BF_4^- and aluminium forms AlF_6^{3-}

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Diagonal Relationship

On moving diagonally across the periodic table, the second and third period elements show certain similarities. Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.



The similarity in properties existing between the diagonally placed elements is called 'diagonal relationship'.

3.6.2 Periodic Trends and Chemical Reactivity:

The physical and chemical properties of elements depend on the valence shell electronic configuration as discussed earlier. The elements on the left side of the periodic table have less ionisation energy and readily lose their valence electrons. On the other hand, the elements on right side of the periodic table have high electron affinity and readily accept electrons. As a consequence of this, elements of these extreme ends show high reactivity when compared to the elements present in the middle. The noble gases having completely filled electronic configuration neither accept nor lose their electron readily and hence they are chemically inert in nature.

The ionisation energy is directly related to the metallic character and the elements located in the lower left portion of the periodic table have less ionisation energy and therefore show metallic character. On the other hand the elements located in the top right portion have very high ionisation energy and are non-metallic in nature.

Let us analyse the nature of the compounds formed by elements from both sides of the periodic table. Consider the reaction of alkali metals and halogens with oxygen to give the corresponding oxides.

$4\ Na + O_2 \rightarrow 2\ Na_2O$

$2\ Cl_2 + 7\ O_2 \rightarrow 2\ Cl_2O_7$

Since sodium oxide reacts with water to give strong base sodium hydroxide, it is a basic oxide. Conversely Cl_2O_7 gives strong acid called perchloric acid upon reaction with water So, it is an acidic oxide.

$Na_2O + H_2O \rightarrow 2NaOH$

$Cl_2O_7 + H_2O \rightarrow 2\ HClO_4$

Thus, the elements from the two extreme ends of the periodic table behave differently as expected.

As we move down the group, the ionisation energy decreases and the electropositive character of elements increases. Hence, the hydroxides of these elements become more basic. For example,let us consider the nature of the second group hydroxides:

$Be(OH)_2$ amphoteric; $Mg(OH)_2$ weakly basic; $Ba(OH)_2$ strongly basic

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Beryllium hydroxide reacts with both acid and base as it is amphoteric in nature.

$Be(OH)_2 + 2HCl \rightarrow BeCl_2 + 2H_2O$

$Be(OH)_2 + 2\ NaOH \rightarrow Na_2BeO_2 + 2H_2O$

Activity 3.2

The electronegativity for some elements on pauling scale of different groups and periods are listed below. Plot these values against atomic number. From the pattern, explain the variation along a period and a group.

2nd group elements : Be (1.6), Mg (1.2), Ca (1.0), Sr (1.0) Ba(0.9)

17th group elements : F (4.0), Cl (3.0), Br (2.8), I (2.5)

3rd Period elements : Na(0.9), Mg(1.2), Al (1.5), Si(1.8), P(2.1), S(2.5), Cl(3.0)

4th period elements: K(0.8), Ca(1.0), Sc(1.3), Ti(1.5), V(1.6), Cr(1.6), Mn(1.5), Fe(1.8), Co(1.9), Ni(1.9), Cu(1.9), Zn(1.6), Ga(1.6), Ge(1.8), As(2.0), Se(2.4), Br(2.8)

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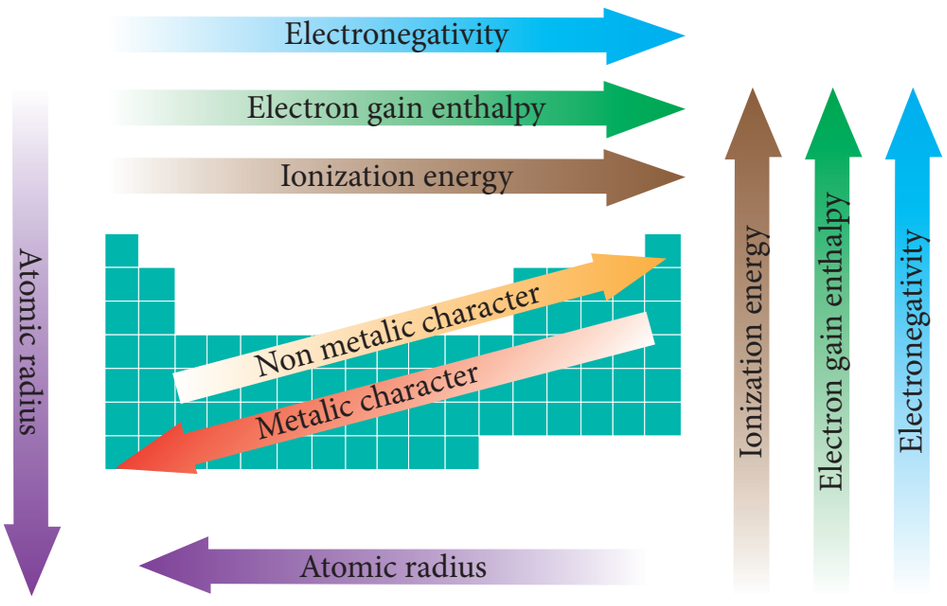
SUMMARY

The periodic table was developed to systematically arrange the different elements. Lavoisier made the first attempt to arrange the known elements in a particular order based on properties. This followed by Johann Dobereiner, A. E. B. de Chancourtois and Newlands. First meaningful periodic table was constructed by Mendeleeve based on atomic mass. This was later modified based on the modern periodic law which states that the properties of elements are the periodic functions of their atomic numbers. The modern periodic table is made up of 18 groups and 7 periods.

The elements in the same groups have similar properties because their valence shell electronic configurations are similar. The properties of the elements of the same period differ because they have different valence shell electronic configurations. On the basis of electronic configuration the elements are also classified as s-block, p-block, d-block and f-block elements. The elements belonging to "s, p, d and f" blocks have unique characteristic properties. In this table, more than 78% of all known elements are metals. They appear on the left side of the periodic table. Non-metals are located at the top right hand side of the periodic table. Some elements show properties that are characteristic of both metals and non-metals and are called semi-metals or metalloids.

The periodic properties such as atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy, electronegativity are possessing periodic trends. The variations of these properties are described in the following scheme.

The elements at the extreme left exhibit strong reducing property whereas the elements at extreme right strong oxidizing property. The reactivity of elements at the centre of the periodic table is low compared to elements at the extreme right and left. The similarity in chemical properties observed between the elements of second and third period which are diagonally related.



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EVALUATION :

I. Choose the best Answer:

1. What would be the IUPAC name for an element with atomic number 222?

   a) bibibiium b) bididium c) didibium d)bibibium

2. The electronic configuration of the elements A and B are $1s^2$, $2s^2$, $2p^6$,$3s^2$ and $1s^2$, $2s^2$, $2p^5$ respectively. The formula of the ionic compound that can be formed between these elements is

   a) AB b) AB_2 c) A_2B d) none of the above.

3. The group of elements in which the differentiating electron enters the anti penultimate shell of atoms are called

   a) p-block elements b) d-block elements

   c) s-block elements d) f-block elements

4. In which of the following options the order of arrangement does not agree with the variation of property indicated against it? (NEET 2016 Phase 1)

   a) I < Br < Cl < F (increasing electron gain enthalpy)

   b) Li < Na < K < Rb (increasing metallic radius)

   c) $Al^{3+} < Mg^{2+} < Na^{+} < F^{-}$ (increasing ionic size)

   d) B < C < O < N (increasing first ionisation enthalpy)

5. Which of the following elements will have the highest electronegativity?

   a) Chlorine b) Nitrogen c) Cesium d) Fluorine

6. Various successive ionisation enthalpies (in kJ mol^{-1}) of an element are given below.

IE_1	IE_2	IE_3	IE_4	IE_5
577.5	1,810	2,750	11,580	14,820

   The element is

   a) phosphorus b) Sodium c) Aluminium d) Silicon

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7. In the third period the first ionization potential is of the order.

a) Na > Al > Mg > Si > P

b) Na < Al < Mg < Si < P

c) Mg > Na > Si > P > Al

d) Na< Al < Mg < P < Si

8. Identify the wrong statement.

a) Amongst the isoelectronic species, smaller the positive charge on cation, smaller is the ionic radius

b) Amongst isoelectric species greater the negative charge on the anion, larger is the ionic radius

c) Atomic radius of the elements increases as one moves down the first group of the periodic table

d) Atomic radius of the elements decreases as one moves across from left to right in the 2nd period of the periodic table.

9. Which one of the following arrangements represent the correct order of least negative to most negative electron gain enthalpy

a) Al < O < C < Ca < F

b) Al < Ca < O < C < F

c) C < F < O < Al < Ca

d) Ca < Al < C < O < F

10. The correct order of electron gain enthalpy with negative sign of F, Cl, Br and I having atomic number 9, 17, 35 and 53 respectively is

a) I > Br > Cl > F

b) F > Cl > Br > I

c) Cl > F > Br > I

d) Br > I > Cl > F

11. Which one of the following is the least electronegative element?

a) Bromine b) Chlorine c) Iodine d) Hydrogen

12. The element with positive electron gain enthalpy is

a) Hydrogen b) Sodium c) Argon d) Fluorine

13. The correct order of decreasing electronegativity values among the elements X, Y, Z and A with atomic numbers 4, 8 , 7 and 12 respectively

a) Y > Z > X > A

b) Z > A > Y > X

c) X > Y > Z > A

d) X > Y > A > Z

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14. Assertion: Helium has the highest value of ionisation energy among all the elements known

Reason: Helium has the highest value of electron affinity among all the elements known

a) Both assertion and reason are true and reason is correct explanation for the assertion

b) Both assertion and reason are true but the reason is not the correct explanation for the assertion

c) Assertion is true and the reason is false

d) Both assertion and the reason are false

15. The electronic configuration of the atom having maximum difference in first and second ionisation energies is

a) $1s^2, 2s^2, 2p^6, 3s^1$ b) $1s^2, 2s^2, 2p^6, 3s^2$

c) $1s^2, 2s^2, 2p^6, 3s^2, 3s^2, 3p^6, 4s^1$ d) $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

16. Which of the following is second most electronegative element?

a) Chlorine b) Fluorine c) Oxygen d) Sulphur

17. IE_1 and IE_2 of Mg are 179 and 348 kcal mol^{-1} respectively. The energy required for the reaction $Mg \rightarrow Mg^{2+} + 2\ e^-$ is

a) +169 kcal mol^{-1} b) - 169 kcal mol^{-1}

c) + 527 kcal mol^{-1} d) - 527 kcal mol^{-1}

18. In a given shell the order of screening effect is

a) s > p > d > f b) s > p > f > d c) f > d > p > s d) f > p > s > d

19. Which of the following orders of ionic radii is correct?

a) $H^- > H^+ > H$ b) $Na^+ > F^- > O^{2-}$ c) $F > O^{2-} > Na^+$ d) None of these

20. The First ionisation potential of Na, Mg and Si are 496, 737 and 786 kJ mol^{-1} respectively. The ionisation potential of Al will be closer to

a) 760 kJ mol^{-1} b) 575 kJ mol^{-1} c) 801 kJ mol^{-1} d) 419 kJ mol^{-1}

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21. Which one of the following is true about metallic character when we move from left to right in a period and top to bottom in a group?

a) Decreases in a period and increases along the group

b) Increases in a period and decreases in a group

c) Increases both in the period and the group

d) Decreases both in the period and in the group

22. How does electron affinity change when we move from left to right in a period in the periodic table?

a) Generally increases b) Generally decreases

c) Remains unchanged d) First increases and then decreases

23. Which of the following pairs of elements exhibit diagonal relationship?

a) Be and Mg b) Li and Be c) Be and B d) Be and Al

II. Write brief answer to the following questions

24. Define modern periodic law.

25. What are isoelectronic ions? Give examples.

26. What is effective nuclear charge ?

27. Is the definition given below for ionisation enthalpy is correct?

"Ionisation enthalpy is defined as the energy required to remove the most loosely bound electron from the valence shell of an atom"

28. Magnesium loses electrons successively to form Mg^{+}, Mg^{2+} and Mg^{3+} ions. Which step will have the highest ionisation energy and why?

29. Define electronegativity.

30. How would you explain the fact that the second ionisation potential is always higher than first ionisation potential?

31. Energy of an electron in the ground state of the hydrogen atom is -2.18×10^{-18} J. Calculate the ionisation enthalpy of atomic hydrogen in terms of kJ mol^{-1}.

32. The electronic configuration of atom is one of the important factor which affects the value of ionisation potential and electron gain enthalpy. Explain

33. In what period and group will an element with Z = 118 will be present?

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34. Justify that the fifth period of the periodic table should have 18 elements on the basis of quantum numbers.

35. Elements a, b, c and d have the following electronic configurations:

a: $1s^2, 2s^2, 2p^6$ b: $1s^2, 2s^2, 2p^6, 3s^2, 3p^1$

c: $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$ d: $1s^2, 2s^2, 2p^1$

Which elements among these will belong to the same group of periodic table

36. Give the general electronic configuration of lanthanides and actinides?

37. Why halogens act as oxidising agents?

38. Mention any two anomalous properties of second period elements.

39. Explain the pauling method for the determination of ionic radius.

40. Explain the periodic trend of ionisation potential.

41. Explain the diagonal relationship.

42. Why the first ionisation enthalpy of sodium is lower than that of magnesium while its second ionisation enthalpy is higher than that of magnesium?

43. By using paulings method calculate the ionic radii of K^+ and Cl^- ions in the potassium chloride crystal. Given that $d_{K^+-Cl^-} = 3.14$ Å

44. Explain the following, give appropriate reasons.

(i) Ionisation potential of N is greater than that of O

(ii) First ionisation potential of C-atom is greater than that of B atom, where as the reverse is true is for second ionisation potential.

(iii) The electron affinity values of Be and Mg are almost zero and those of N (0.02 eV) and P (0.80 eV) are very low

(iv) The formation of F^- (g) from F(g) is exothermic while that of O^{2-}(g) from O (g) is endothermic.

45. What is screening effect?

46. Briefly give the basis for pauling's scale of electronegativity.

47. State the trends in the variation of electronegativity in group and periods.

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CONCEPT MAP

Classification of Elements

MODERN PERIODIC TABLE

By Mosley-(1912)
The physical and chemical properties of elements are periodic functions of their atomic number

Periods and Groups

Groups:

Vertical columns contain elements having similar outer electronic configurations.

(18 Groups)

Periods:

Horizontal rows. Period number corresponds to the highest principal quantum number (n) of the elements.

Periods 1 to 6 contains 2,8,8,18,18,32 elements respectively.

Period 6 contains 14 elements (lanthanides)

Period 7 contains 14 elements (actinides)

Blocks

s- block:
group-1 : hydrogen and alkali metals
group 2 : alkaline earth metals

P block:
Group 13
Group 14
Group 15 :Pnictogens
Group-16 :Chalcogens
Group-17 : Halogens
Group 18: Noble gases

d block:

Contains 4 series

F block:
Contains 2 series
I series : lanthanides
II Series : actinides

PERIODIC TRENDS IN PROPERTIES OF ELEMENTS

TRENDS IN PHYSICAL PROPERTIES

Atomic Radii & Ionic Radii
- Along period decreases
- Within a group increases

Ionisation Enthalpy,

Electron affinity,

Electronegativity
- Along period increases
- Within a group decreases

TRENDS IN CHEMICAL PROPERTIES

- Valence or oxidation state
- Strength of oxyacids of non-metal
- Acidity of hydrides
- Acidity of oxides

Anomalous behavior of elements of II period: diagonal relationship : some elements of II period show similarities with diagonally placed III period elements

Eg : Li & Mg , Be & Al

6EDGL

ICT Corner

Properties of Elements

By using this modern periodic table you will be able to visualise the elements belonging to a specific group, period and block and other properties of the elements.

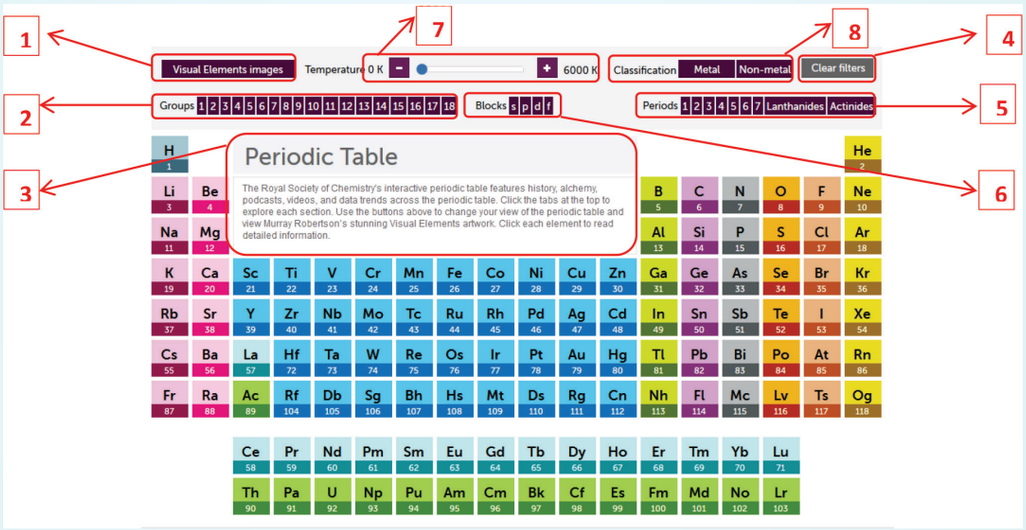
Please go to the URL
http://www.rsc.org/periodic-table/
(or)
Scan the QR code on the right side

Q6H4M

Open the Browser and type the URL given (or) Scan the QR Code. You can see an interactive modern periodic table of elements from atomic number 1 to 118.

Options:

1. You can hover over any element in the periodic table to get the basic information such as electronic configuration, ionisation energy, density etc. in the panel (3).
2. If you click on any elements it shows the complete list of properties of the elements.
3. Click the Visual Elements Image (1) to view the Images for each element. If you hover over any element additional information regarding the element will be displayed in the panel (3)
4. You can view metals and non-metals present in the periodic table by choosing the appropriate choice (8)
5. You can view the physical state of the elements at a given temperature by using the slider (7)
6. You can view s, p, d or f block elements by selecting a specific block (6)
7. You can view ze the elements of a specific group (2) or a period (5) by selecting the group or period
8. You can clear the selections you have made by clicking the clear filters (4)



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Unit 4

Hydrogen

Hydrogen, third most abundant on the surface of the Universe, is being visualised as the major feature source of energy



Antoine - Laurent de Lavoisier (1743-1794)

He recognised and named hydrogen and oxygen. He introduced a new system for chemical nomenclature in 1787

Learning Objectives

After studying this unit, the students will be able to

- Justify the position of hydrogen in the periodic table
- Recognise the different isotopes of hydrogen
- Explain the methods of preparation of hydrogen.
- Explain the properties of hydrogen
- Appraise the uses of hydrogen
- Differentiate various types of hydrides
- Translate the knowledge of structure of water for explaining its physical and chemical properties
- Differentiate hard and soft water and select the suitable method for water softening.
- Recognise heavy water and explain its properties.
- Explain the preparation and properties of hydrogen peroxide
- List the uses of hydrogen peroxide

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4.1 Introduction

Hydrogen is the simplest atom which contains one electron and one proton. In contrast to other elements (except helium) its valence electron is directly in the sphere of action of the nucleus. It is invariably present in most of the compounds we come across in our daily life such as water, carbohydrate, proteins etc. As it has an unpaired electron, it is reactive and exists as a diatomic molecule (H_2). However, the abundance of hydrogen gas in the earth's atmosphere is very small.

4.1.1 Position in Periodic Table

The hydrogen has the electronic configuration of $1s^1$ which resembles with ns^1 general valence shell configuration of alkali metals and shows similarity with them as follows:

1. It forms unipositive ion (H^+) like alkali metals (Na^+, K^+, Cs^+)
2. It forms halides (HX), oxides (H_2O), peroxides (H_2O_2) and sulphides (H_2S) like alkali metals (NaX, Na_2O, Na_2O_2, Na_2S)
3. It also acts as a reducing agent.

However, unlike alkali metals which have ionization energy ranging from 377 to 520 kJ mol^{-1}, the hydrogen has 1,314 KJ mol^{-1} which is much higher than alkali metals.

Like the formation of halides (X^-) from halogens, hydrogen also has a tendency to gain one electron to form hydride ion (H^-) whose electronic configuration is similar to the noble gas, helium. However, the electron affinity of hydrogen is much less than that of halogen atoms. Hence, the tendency of hydrogen to form hydride ion is low compared to that of halogens to form the halide ions as evident from the following reactions:

$$\frac{1}{2} H_2 + e^- \rightarrow H^- \qquad \Delta H = +36 \text{ kcal mol}^{-1}$$

$$\frac{1}{2} Br_2 + e^- \rightarrow Br^- \qquad \Delta H = -55 \text{ kcal mol}^{-1}$$

Since, hydrogen has similarities with alkali metals as well as the halogens; it is difficult to find the right position in the periodic table. However, in most of its compounds hydrogen exists in +1 oxidation state. Therefore, it is reasonable to place the hydrogen in group 1 along with alkali metals as shown in the latest periodic table published by IUPAC.

4.1.2 Isotopes of Hydrogen

Hydrogen has three naturally occurring isotopes, viz., protium ($_1H^1$ or H), deuterium ($_1H^2$ or D) and tritium ($_1H^3$ or T). Protium ($_1H^1$) is the predominant form (99.985 %) and it is the only isotope that does not contain a neutron.

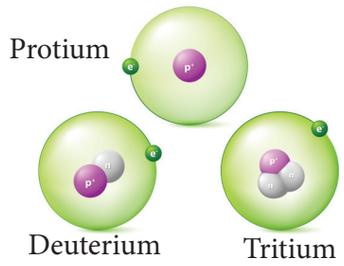

Figure 4.1 Isotopes of hydrogen

Deuterium, also known as heavy hydrogen, constitutes about 0.015 %. The third isotope, tritium is a radioactive isotope of hydrogen which occurs only in traces (~1 atom per 10^{18} hydrogen atoms). Due to the existence of these isotopes naturally occurring hydrogen exists as H_2, HD, D_2, HT, T_2, and DT. The properties of these isotopes are shown in Table 4.1.

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Table 4.1 Properties of Hydrogen, Deuterium and Tritium molecules.

Property	Protium	Deuterium	Tritium
Atomic Hydrogen			
Symbol	H	D	T
Atomic mass (*amu*)	1.008	2.014	3.016
No of electron / protons / neutrons	1 / 1 / 0	1 / 1 / 1	1 / 1 / 2
Nuclear stability	Stable	Stable	Radioactive ($t_{1/2}$=12.3 yrs)
Molecular Hydrogen	H_2	D_2	T_2
Abundance (%)	99.985	0.0156	~10^{-15}
Molecular mass (*amu*)	2.016	4.028	6.032
Melting point (*K*)	13.96	18.73	20.62
Boiling point (*K*)	20.39	23.67	25.04
Internuclear distance (*pm*)	74.14	74.14	74.14
Critical Temperature (*K*)	33.19	38.35	40.60
Enthalpy of dissociation (kJ/*mol*)†	435.9	443.4	446.9

† Bond dissociation energy

4.1.3 Ortho and Para–Hydrogen:

In the hydrogen atom, the nucleus has a spin. When molecular hydrogen is formed, the spins of two hydrogen nuclei can be in the same direction or in the opposite direction as shown in the figure. These two forms of hydrogen molecules are called *ortho* and *para* hydrogens respectively.



Ortho-hydrogen Para-hydrogen

At room temperature, normal hydrogen consists of about 75% ortho-form and 25% para-form. As the ortho-form is more stable than para-form, the conversion of one isomer into the other is a slow process. However, the equilibrium shifts in favour of para hydrogen when the temperature is lowered. The para-form can be catalytically transformed into ortho-form using platinum or iron. Alternatively, it can also be converted by passing an electric discharge, heating above 800°C and mixing with paramagnetic molecules such as O_2, NO, NO_2 or with nascent/atomic hydrogen.

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Ortho and para hydrogen are similar in chemical properties but differ in some of the physical properties. For example, the melting point of para hydrogen is 13.83 K while that of ortho hydrogen 13.95 K; boiling point of para hydrogen is 20.26 K while that of ortho hydrogen 20.39 K. Since the nuclear spins are in opposite directions the magnetic moment of para hydrogen is zero and ortho hydrogen has magnetic moment twice that of a proton.

4.2 Preparation of Hydrogen

High purity hydrogen (>99.9 %) is obtained by the electrolysis of water containing traces of acid or alkali or the electrolysis of aqueous solution of sodium hydroxide or potassium hydroxide using a nickel anode and iron cathode. However, this process is not economical for large-scale production.

At anode : $2\ OH^- \rightarrow H_2O + \frac{1}{2}\ O_2 + 2e^-$

At cathode : $2\ H_2O + 2\ e^- \rightarrow 2\ OH^- + H_2$

Overall reaction : $H_2O \rightarrow H_2 + \frac{1}{2}\ O_2$

4.2.1 Laboratory Preparation

Hydrogen is conveniently prepared in laboratory by the reaction of metals, such as zinc, iron, tin with dilute acid.

$$Zn + 2\ HCl \rightarrow ZnCl_2 + H_2\uparrow$$

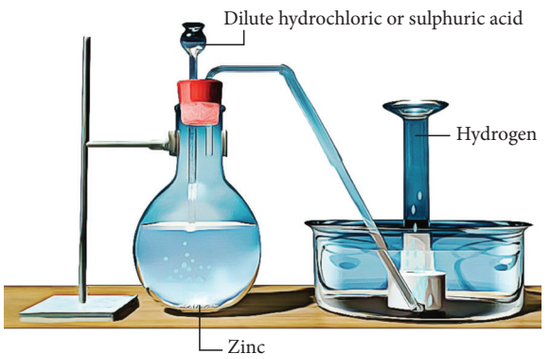

Figure 4.2 Laboratory preparation of hydrogen

4.2.2 Industrial Production

In the large-scale, hydrogen is produced by steam-reforming of hydrocarbons. In this method hydrocarbon such as methane is mixed with steam and passed over nickel catalyst in the range 800-900 °C and 35 atm pressures.

$$CH_4 + H_2O \xrightarrow{Ni} CO + 3H_2$$

In an another process, steam is passed over a red-hot coke to produce carbon monoxide and hydrogen. The mixture of gases produced in this way is known as *water gas* ($CO+H_2$). This is also called *syngas* (Synthetic gas) as it is used in the synthesis of organic compounds such as methanol and simple hydrocarbons.

$$C + H_2O \xrightarrow{1000^\circ C} \underbrace{CO + H_2}_{\text{Water gas/Syngas}}$$

Conversion of Carbon monoxide in water gas to Carbon dioxide:

The carbon monoxide of the water gas can be converted to carbon dioxide by mixing the gas mixture with more steam at 400°C and passed over a shift converter containing iron/copper catalyst. This reaction is called as *water-gas shift reaction*.

$$CO + H_2O \rightarrow CO_2 + H_2$$

The CO_2 formed in the above process is absorbed in a solution of potassium carbonate.

$$CO_2 + K_2CO_3 + H_2O \rightarrow 2\ KHCO_3$$

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4.2.3 Preparation of Deuterium:

Electrolysis of heavy water:

Normal water contains 1.6 x 10^{-4} percentage of heavy water. The dissociation of protium water (H_2O) is more than heavy water (D_2O). Therefore, when water is electrolysed, hydrogen is liberated much faster than D_2. The electrolysis is continued until the resulting solution becomes enriched in heavy water. Further electrolysis of the heavy water gives deuterium.

$$2\,D_2O \xrightarrow{\text{Electrolysis}} 2\,D_2 + O_2$$

4.2.4 Preparation of Tritium:

As explained earlier the tritium is present only in trace amounts. So it can be artificially prepared by bombarding lithium with slow neutrons in a nuclear fission reactor. The nuclear transmutation reaction for this process is as follows.

$${}^{6}_{3}Li + {}^{1}_{0}n \rightarrow {}^{4}_{2}He + {}^{3}_{1}T$$

4.3 Properties of Hydrogen

4.3.1 Physical Properties:

Hydrogen is a colorless, odorless, tasteless, lightest and highly flammable gas. It is a non-polar diatomic molecule. It can be liquefied under low temperature and high pressure. Hydrogen is a good reducing agent. Various physical constants of hydrogen molecule are listed in Table 4.1.

4.3.2 Chemical Properties:

Hydrogen reacts with oxygen to give water. This is an explosive reaction and releases lot of energy. This is used in fuel cells to generate electricity.

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

Similarly, hydrogen also reacts with halogens to give corresponding halides. Reaction with fluorine takes place even in dark with explosive violence while with chlorine at room temperature under light. It combines with bromine on heating and reaction with iodine is a photochemical reaction.

$$H_2 + X_2 \rightarrow 2\,HX \quad (X = F, Cl, Br \,\&\, I)$$

In the above reactions the hydrogen has an oxidation state of +1. It also has a tendency to react with reactive metals such as lithium, sodium and calcium to give corresponding hydrides in which the oxidation state of hydrogen is -1.

$$2\,Li + H_2 \rightarrow 2\,LiH$$

$$2\,Na + H_2 \rightarrow 2\,NaH$$

These hydrides are used as reducing agents in synthetic organic chemistry. It is used to prepare other important hydrides such as lithium aluminium hydride and sodium boro hydride.

$$4\,LiH + AlCl_3 \rightarrow Li[AlH_4] + 3\,LiCl$$

$$4\,NaH + B(OCH_3)_3 \rightarrow Na[BH_4] + 3\,CH_3ONa$$

Hydrogen itself acts as a reducing agent. In the presence of finely divided nickel, it adds to the unsaturated organic compounds to form saturated compounds.

$$HC \equiv CH \xrightarrow{Ni/H_2} H_2C = CH_2 \xrightarrow{Ni/H_2} H_3C - CH_3$$

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4.3.3 Chemical properties of Deuterium

Like hydrogen, deuterium also reacts with oxygen to form deuterium oxide called heavy water. It also reacts with halogen to give corresponding halides.

$2\ D_2 + O_2 \rightarrow 2\ D_2O$

$D_2 + X_2 \rightarrow 2\ DX$

(X = F, Cl, Br & I)

Deuterium exchange reactions:

Deuterium can replace reversibly hydrogen in compounds either partially or completely depending upon the reaction conditions. These reactions occur in the presence of deuterium or heavy water.

$CH_4 + 2\ D_2 \rightarrow CD_4 + 2\ H_2$

$2\ NH_3 + 3\ D_2 \rightarrow 2\ ND_3 + 3\ H_2$

4.3.4 Properties of Tritium

It is a β-emitter with a half-life period of 12.3 years .

$^{3}_{1}T \rightarrow {}^{3}_{2}He + {}^{0}_{-1}e$

4.4 Uses of Hydrogen

1. Over 90 % hydrogen produced in industry is used for synthetic applications. One such process is Haber process which is used to synthesis ammonia in large scales. Ammonia is used for the manufacture of chemicals such as nitric acid, fertilizers and explosives.

$$N_2 + 3H_2 \underset{200\ atm/Fe}{\overset{380\text{-}450^\circ C}{\rightleftharpoons}} 2\ NH_3$$

2. It can be used to manufacture the industrial solvent, methanol from carbon monoxide using copper as catalyst.

$$CO + 2H_2 \xrightarrow{Cu} CH_3OH$$

3. Unsaturated fatty oils can be converted into saturated fats called Vanaspati (margarine) by the reduction reaction with Pt/H_2.

4. In metallurgy, hydrogen can be used to reduce many metal oxides to metals at high temperatures.

$CuO + H_2 \rightarrow Cu + H_2O$

$WO_3 + 3\ H_2 \rightarrow W + 3\ H_2O$

5. Atomic hydrogen and oxy-hydrogen torches are used for cutting and welding.

6. Liquid hydrogen is used as a rocket fuel.

7. Hydrogen is also used in fuel cells for generating electrical energy. The reversible uptake of hydrogen in metals is also attractive for rechargeable metal hydride battery.

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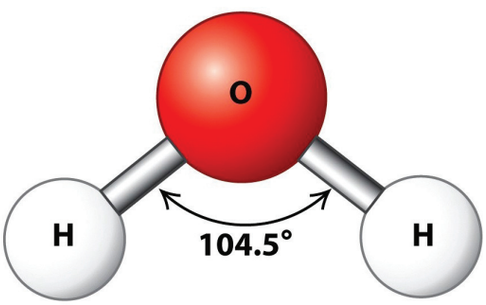
Figure 4.3: Application of rocket fuel

4.5 Compounds of Hydrogen

4.5.1 Water

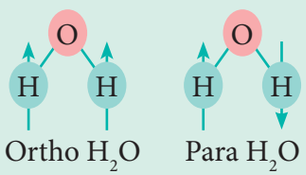
Water is one of the most abundant compounds of hydrogen and our earth's surface contains approximately 70 % of ocean which is the major source of water. However, sea water contains many dissolved salts hence it can not be used directly. Water is essential for all living things and our body contains about 65% water.





Ortho-H_2O and Para-H_2O

Water exists in the interstellar clouds and icy satellites of the solar system. In particular, the ortho-to-para ratio (OPR) of water in space has recently received attention. Like hydrogen, water can also be classified into ortho-H_2O, in which the spin directions of the nuclei of the hydrogen atoms are parallel, and para-H_2O, in which the directions are antiparallel. OPR of H_2(300K) on earth should be 3:1. OPR of H_2O(50K) in interstellar clouds and comets should be 2:5:1.



4.5.2 Physical Properties:

Water is a colourless and volatile liquid. The peculiar properties of water in the condensed phases are due to the presence of inter molecular hydrogen bonding between water molecules. Hydrogen bonding is responsible for the high melting and boiling points of water. Some of the physical parameters of water are listed in Table 4.2.

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Table 4.2 Properties of water, heavy water and super heavy water†.

Property	H_2O	D_2O	T_2O
Molecular weight	18.015	20.0276	22.031
Melting point (*K*)	273.0	276.8	277.5
Boiling point (*K*)	373.0	374.4	374.5
Temperature of maximum density (*K*)	277.0	284.2	286.4
Maximum density (g/cm^3)	1.000	1.106	1.215
Density (g/cm^3)	0.997	1.104	1.214
Vapour pressure (*mm* Hg)	23.75	20.51	19.80
Viscosity (*cP*)	0.890	1.107	---
Dielectric constant	78.39	78.06	---
Enthalpy of formation (*kJ/mol*)	– 285.9	– 294.6	---
Enthalpy of vaporization (*kJ/mol*)	40.66	41.61	---

†Unless otherwise stated, all data are at 298 *K*.

4.5.3 Chemical Properties:

Water reacts with metals, non-metals and other compounds differently. The most reactive metals are the alkali metals. They decompose water even in cold with the evolution of hydrogen leaving an alkali solution.

$$2Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$$

The group 2 metals (except beryllium) react in a similar way but less violently. The hydroxides are less soluble than those of Group 1.

$$Ba + 2H_2O \rightarrow Ba(OH)_2 + H_2$$

Some transition metals react with hot water or steam to form the corresponding oxides. For example, steam passed over red hot iron results in the formation of iron oxide with the release of hydrogen.

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$$

Lead and copper decompose water only at a white heat. Silver, gold, mercury and platinum do not have any effect on water. In the elemental form, the non-metals such as carbon, sulphur and phosphorus normally do not react with water. However, as we have seen earlier, carbon will react with steam when it is red (or white) hot to give *water gas*.

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On the other hand, the halogens react with water to give an acidic solution. For example, chlorine forms hydrochloric acid and hypo chlorous acid. It is responsible for the antibacterial action of chlorine water, and for its use as bleach.

$$Cl_2 + H_2O \rightarrow HCl + HOCl$$

Fluorine reacts differently to liberate oxygen from water.

$$2F_2 + 2\ H_2O \rightarrow 4HF + O_2$$

In a similar way, compounds of non-metals react with water to give acidic or alkaline solutions. For example, solutions of carbonates are slightly alkaline.

$$CO_3^{2-} + H_2O \rightarrow HCO_3^{-} + OH^{-}$$

Water is an amphoteric oxide. It has the ability to accept as well as donate protons and hence it can act as an acid or a base. For example, in the reaction with HCl it accepts proton where as in the reaction with weak base ammonia it donates proton.

$$NH_3 + H_2O \rightarrow NH_4^{+} + OH^{-}$$

$$HCl + H_2O \rightarrow H_3O^{+} + Cl^{-}$$

Water dissolves ionic compounds. In addition, it also hydrolyses some covalent compounds.

$$SiCl_4 + 2\ H_2O \rightarrow SiO_2 + 4\ HCl$$

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$$

Many salts crystallized from aqueous solutions form hydrated crystals. The water in the hydrated salts may form co-ordinate bond or just present in interstitial positions of crystals.

Examples: $[Cr(H_2O)_6]Cl_3$ – All six water molecules form co-ordinate bond

$BaCl_2.2H_2O$ – Both the water molecules are present in interstitial positions.

$CuSO_4.5H_2O$ – In this compound four water molecules form co-ordinate bonds while the fifth water molecule, present outside the co-ordination, can form intermolecular hydrogen bond with another molecule. $[Cu(H_2O)_4]SO_4.H_2O$

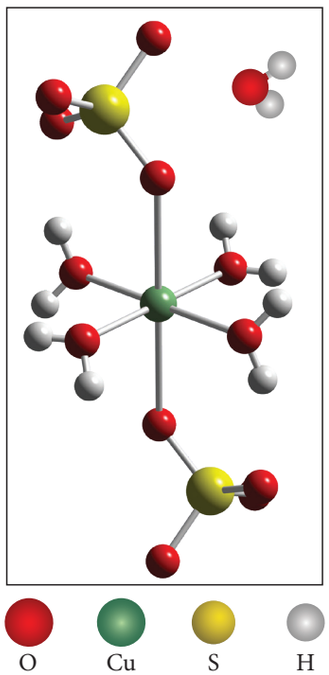

Figure 4.4 structure of copper sulphate pentahydrate

4.5.4 Hard and Soft Water:

Hard water contains high amounts of mineral ions. The most common ions found in hard water are the soluble metal cations such as magnesium & calcium, though iron, aluminium, and manganese may also be found in certain areas. Presence of these metal salts in the form of bicarbonate,

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chloride and sulphate in water makes water 'hard'. When hard water is boiled carbonates of magnesium and calcium present in it gets precipitated. On the other hand, water free from soluble salts of calcium and magnesium is called soft water. The hardness of water is of two types, viz., temporary hardness and permanent hardness.

Temporary Hardness and its removal:

Temporary hardness is primarily due to the presence of soluble bicarbonates of magnesium and calcium. This can be removed by boiling the hard water followed by filtration. Upon boiling, these salts decompose into insoluble carbonate which leads to their precipitation. The magnesium carbonate thus formed further hydrolysed to give insoluble magnesium hydroxide.

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$$

$$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2$$

$$MgCO_3 + H_2O \rightarrow Mg(OH)_2 + CO_2$$

The resulting precipitates can be removed by filtration.

Alternatively, we can use Clark's method in which, calculated amount of lime is added to hard water containing the magnesium and calcium, and the resulting carbonates and hydroxides can be filtered-off.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$$

$$Mg(HCO_3)_2 + 2\,Ca(OH)_2 \downarrow 2CaCO_3 + Mg(OH)_2 + 2H_2O$$

Permanent Hardness:

Permanent hardness of water is due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in it. It can be removed by adding washing soda, which reacts with these metal (M = Ca or Mg) chlorides and sulphates in hard water to form insoluble carbonates.

$$MCl_2 + Na_2CO_3 \rightarrow MCO_3 + 2\,NaCl$$

$$MSO_4 + Na_2CO_3 \rightarrow MCO_3 + Na_2SO_4$$

In another way to soften the hard water is by using a process called ion-exchange. That is, hardness can be removed by passing through an ion-exchange bed like zeolites or column containing ion-exchange resin. Zeolites are hydrated sodium alumino-silicates with a general formula, $Na_2O{\cdot}Al_2O_3{\cdot}xSiO_2{\cdot}yH_2O$ (x = 2 to 10, y = 2 to 6). Zeolites have porous structure in which the monovalent sodium ions are loosely held and can be exchanged with hardness producing metal ions (M = Ca^{2+} or Mg^{2+}) in water. The complex structure can conveniently be represented as Na_2-Z with sodium as exchangeable cations.

$$Na_2\text{-}Z + M^{2+} \rightarrow M\text{-}Z + 2\,Na^+$$

When exhausted, the materials can be regenerated by treating with aqueous sodium chloride. The metal ions (Ca^{2+} and Mg^{2+}) caught in the zeolite (or resin) are released and they get replenished with sodium ions.

$$M\text{-}Z + 2NaCl \rightarrow Na_2\text{-}Z + MCl_2$$

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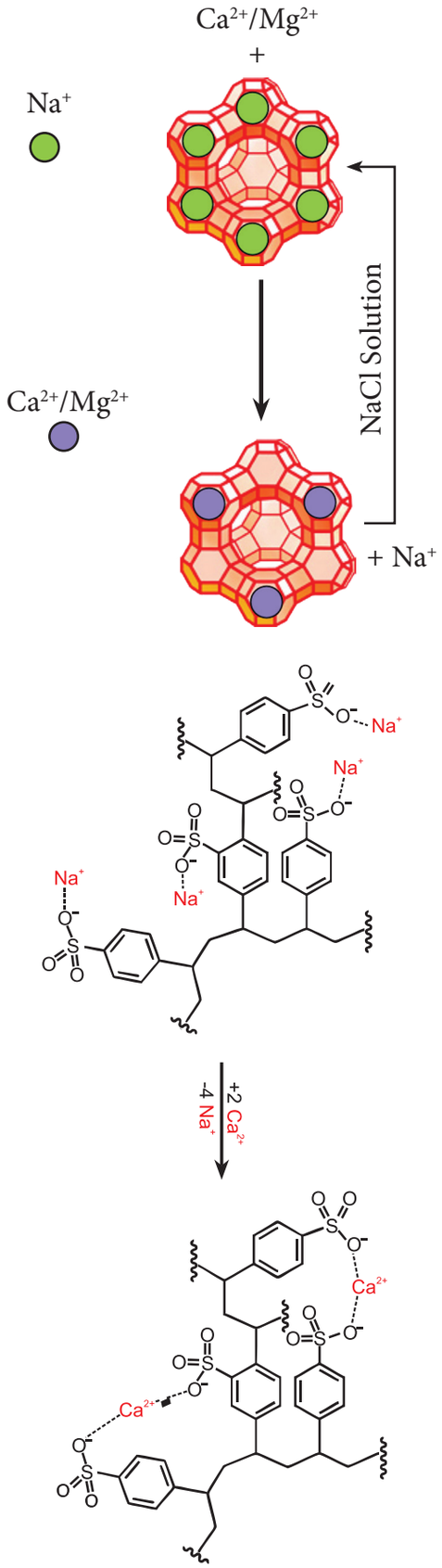

4.6 Heavy Water:

Heavy water (D_2O) is the oxide of heavy hydrogen. One part of heavy water is present in 5000 parts of ordinary water. It is mainly obtained as the product of electrolysis of water, as D_2O does not undergo electrolysis as easily as H_2O.

D_2O is a colorless, odorless and tasteless liquid. However, there is a marked difference between physical properties of water and heavy water as shown in Table 4.2.



Hard water produces less foam with detergents. Do you know why?

The cleaning capacity of soap is reduced when used in hard water. Soaps are sodium or potassium salts of long chain fatty acids (e.g., coconut oil). When soap is added to hard water, the divalent magnesium and calcium ions present in hard water react with soap. The sodium salts present in soaps are converted to their corresponding magnesium and calcium salts which are precipitated as scum/precipitate.

$$M^{2+} + 2RCOONa \rightarrow (RCOO)_2M + 2Na^+$$

M = Ca or Mg

$R = C_{17}H_{35}$

4.6.1 Chemical properties of heavy water:

When compounds containing hydrogen are treated with D_2O, hydrogen undergoes an exchange for deuterium

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$2NaOH + D_2O \rightarrow 2NaOD + HOD$

$HCl + D_2O \rightarrow DCl + HOD$

$NH_4Cl + 4D_2O \rightarrow ND_4Cl + 4HOD$

These exchange reactions are useful in determining the number of ionic hydrogens present in a given compound.

For example, when D_2O is treated with of hypo-phosphorus acid only one hydrogen atom is exchanged with deuterium. It indicates that, it is a monobasic acid.

$H_3PO_2 + D_2O \rightarrow H_2DPO_2 + HDO$

It is also used to prepare some deuterium compounds:

$Al_4C_3 + 12D_2O \rightarrow 4Al(OD)_3 + 3CD_4$

$CaC_2 + 2D_2O \rightarrow Ca(OD)_2 + C_2D_2$

$Mg_3N_2 + 6D_2O \rightarrow 3Mg(OD)_2 + 2ND_3$

$Ca_3P_2 + 6D_2O \rightarrow 3Ca(OD)_2 + 2PD_3$

4.6.2 Uses of heavy water:

1. Heavy water is widely used as moderator in nuclear reactors as it can lower the energies of fast neutrons
2. It is commonly used as a tracer to study organic reaction mechanisms and mechanism of metabolic reactions
3. It is also used as a coolant in nuclear reactors as it absorbs the heat generated.

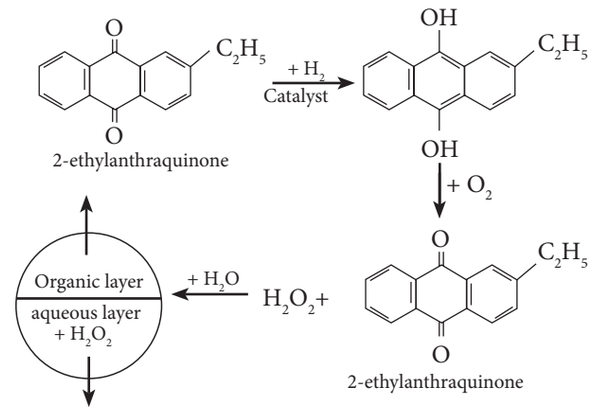
4.7 Hydrogen Peroxide:

Hydrogen peroxide (H_2O_2) is one of the most important peroxides. It can be prepared by treating metal peroxide with dilute acid.

$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2$

$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$

On an industrial scale, hydrogen peroxide is now prepared exclusively by autoxidation of 2-alkyl anthraquinol.



40% solution of H_2O_2

4.7.1 Physical properties:

Pure hydrogen peroxide is almost a colorless liquid (pale blue), less volatile and more viscous than water.

A 30 % solution of hydrogen peroxide is marketed as '100-volume' hydrogen peroxide indicating that at S.T.P., 100 ml of oxygen is liberated by 1 ml of this solution on heating.

4.7.2 Chemical properties:

Hydrogen peroxide is highly unstable and the aqueous solution spontaneously

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disproportionates to give oxygen and water. The reaction is, however, slow but is explosive when catalyzed by metal. If it is stored in glass container, it dissolves the alkali metals from the glass, which catalyzes the disproportionation reaction. For this reason, H_2O_2 solutions are stored in plastic bottles.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$

Hydrogen peroxide can act both as an oxidizing agent and a reducing agent. Oxidation is usually performed in acidic medium while the reduction reactions are performed in basic medium

In acidic conditions:

$$H_2O_2 + 2\,H^+ + 2\,e^- \rightarrow 2\,H_2O \quad (E^0 = +\,1.77\ V)$$

For example

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O$$

In basic conditions:

$$HO_2^- + OH^- \rightarrow O_2 + H_2O + 2\,e^-$$

$$(E^0 = +\,0.08\ V)$$

For Example,

$$2KMnO_4\,(aq) + 3\,H_2O_2\,(aq) \downarrow$$

$$2MnO_2 + 2\,KOH + 2\,H_2O + 3O_2\,(g)$$

4.7.3 Uses of hydrogen peroxide:

The oxidizing ability of hydrogen peroxide and the harmless nature of its products, i.e., water and oxygen, lead to its many applications. It is used in water treatment to oxidize pollutants, as a mild antiseptic, and as bleach in textile, paper and hair-care industry.

Hydrogen peroxide is used to restore the white colour of the old paintings which was lost due to the reaction of hydrogen sulphide in air with the white pigment $Pb_3(OH)_2(CO_3)_2$ to form black colored lead sulphide. Hydrogen peroxide oxidises black coloured lead sulphide to white coloured lead sulphate, there by restoring the colour.

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

4.7.4 Structure of hydrogen peroxide:

Both in gas-phase and solid-phase, the molecule adopts a skew conformation due to repulsive interaction of the OH bonds with lone-pairs of electrons on each oxygen atom. Indeed, it is the smallest molecule known to show hindered rotation about a single bond.

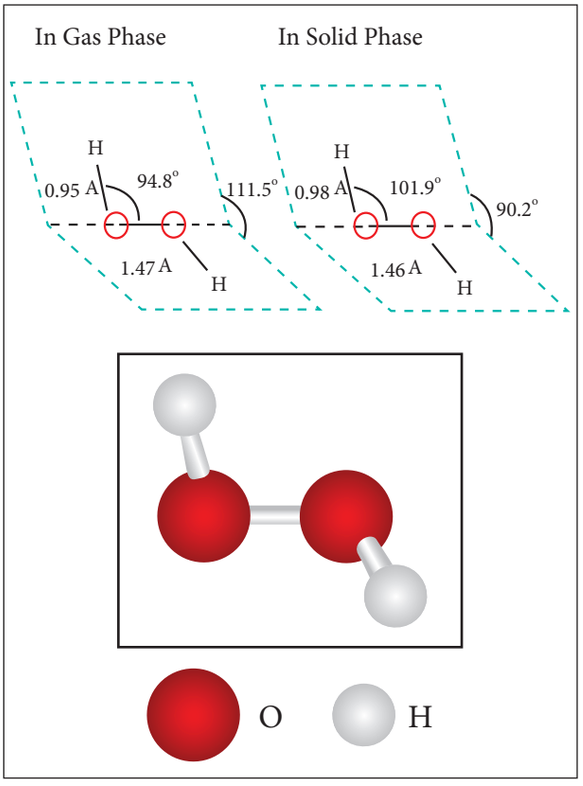

Figure 4.5 structure of H_2O_2

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H_2O_2 has a non-planar structure. The molecular dimensions in the gas phase and solid phase differ as shown in figure 4.5. Structurally, H_2O_2 is represented by the dihydroxyl formula in which the two OH^- groups do not lie in the same plane. One way of explaining the shape of hydrogen peroxide is that the hydrogen atoms would lie on the pages of a partly opened book, and the oxygen atoms along the spine. In the solid phase of molecule, the dihedral angle reduces to 90.2° due to hydrogen bonding and the O-O-H angle expands from 94.8 ° to 101.9°.

4.8 Hydrides

Hydrogen forms binary hydrides with many electropositive elements including metals and non-metals. It also forms ternary hydrides with two metals. E.g., $LiBH_4$ and $LiAlH_4$. The hydrides are classified as ionic, covalent and metallic hydrides according to the nature of bonding. Hydrides formed with elements having lower electronegativity than hydrogen are often ionic, whereas with elements having higher electronegativity than hydrogen form covalent hydrides.

Ionic (Saline) hydrides: These are hydrides composed of an electropositive metal, generally, an alkali or alkaline-earth metal, except beryllium and magnesium, formed by transfer of electrons from metal to hydrogen atoms. They can be prepared by the reaction of elements at about 400° C. These are salt-like, high-melting, white crystalline solids having hydride ions (H^-) and metal cations (M^{n+}).

$2\ Li + H_2 \rightarrow 2\ LiH$

$2\ Ca + 2H_2 \rightarrow 2\ CaH_2$

Covalent (Molecular) hydrides: They are compounds in which hydrogen is attached to another element by sharing of electrons. The most common examples of covalent hydrides of non-metals are methane, ammonia, water and hydrogen chloride. Covalent hydrides are further divided into three categories, viz., electron precise (CH_4, C_2H_6, SiH_4, GeH_4), electron-deficient (B_2H_6) and electron-rich hydrides (NH_3, H_2O). Since most of the covalent hydrides consist of discrete, small molecules that have relatively weak intermolecular forces, they are generally gases or volatile liquids.

Metallic (Interstitial) hydrides: Metallic hydrides are usually obtained by hydrogenation of metals and alloys in which hydrogen occupies the interstitial sites (voids). Hence, they are called interstitial hydrides; the hydrides show properties similar to parent metals and hence they are also known as metallic hydrides. Most of the hydrides are non-stoichiometric with variable composition ($TiH_{1.5\text{-}1.8}$ and $PdH_{0.6\text{-}0.8}$), some are relatively light, inexpensive and thermally unstable which make them useful for hydrogen storage applications. Electropositive metals and some other metals form hydrides with the stoichiometry MH or sometimes MH_2 (M = Ti, Zr, Hf, V, Zn).

4.9 Hydrogen Bonding

Hydrogen bonding is one of the most important natural phenomena occurring in chemical and biological sciences. These interactions play a major role in the

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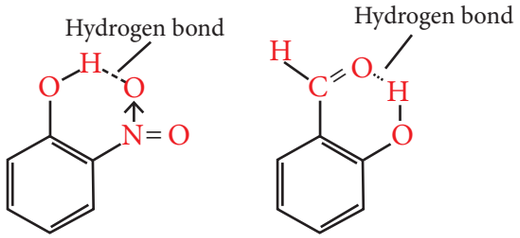
structure of proteins and DNA. When a hydrogen atom (H) is covalently bonded to a highly electronegative atom such as fluorine (F) or oxygen (O) or nitrogen (N), the bond is polarized. Due to this effect, the polarized hydrogen atom is able to form a weak electrostatic interaction with another electronegative atom present in the vicinity. This interaction is called as a hydrogen bond (20-50 $kJ\ mol^{-1}$) and is denoted by dotted lines (…).

It is weaker than covalent bond (> 100 $kJ\ mol^{-1}$) but stronger than the van der Waals interaction (< 20 $kJ\ mol^{-1}$). Hydrogen bond has profound effect on various physical properties including vapour pressure (H_2O and H_2S), boiling point, miscibility of liquids (H_2O and C_2H_5OH), surface tension, densities, viscosity, heat of vaporization and fusion, etc. Hydrogen bonds can occur within a molecule (*intramolecular hydrogen bonding*) and between two molecules of the same type or different type (*intermolecular hydrogen bonding*).

Intramolecular Hydrogen Bond

Intramolecular hydrogen bonds are those which occur within a single molecule.



Ortho-Nitrophenol Salicilaldehyde

Figure 4.6 Intramolecular hydrogen bonding

Intermolecular hydrogen bond

Intermolecular hydrogen bonds occur between two separate molecules. They can occur between any numbers of like or unlike molecules as long as hydrogen donors and acceptors are present in positions which enable the hydrogen bonding interactions. For example, intermolecular hydrogen bonds can occur between ammonia molecule themselves or between water molecules themselves or between ammonia and water.

Water molecules form strong hydrogen bonds with one another. For example, each water molecule is linked to four others through hydrogen bonds. The shorter distances (100 pm) correspond to covalent bonds (solid lines), and the longer distances (180 pm) correspond to hydrogen bonds (dotted lines).

In ice, each atom is surrounded tetrahedrally by four water molecules through hydrogen bonds. That is, the presence of two hydrogen atoms and two lone pairs of electron on oxygen atoms in each water molecule allows formation of a three-dimensional structure. This arrangement creates an open structure, which accounts for the lower density of ice compared with water at 0°C. While in liquid water, unlike ice where hydrogen bonding occurs over a long-range, the strong hydrogen bonding prevails only in a short range and therefore the denser packing.

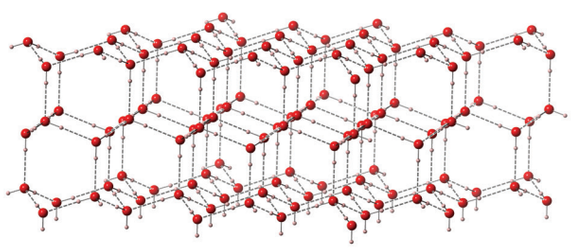


Figure 4.7 (a) Structure of Ice

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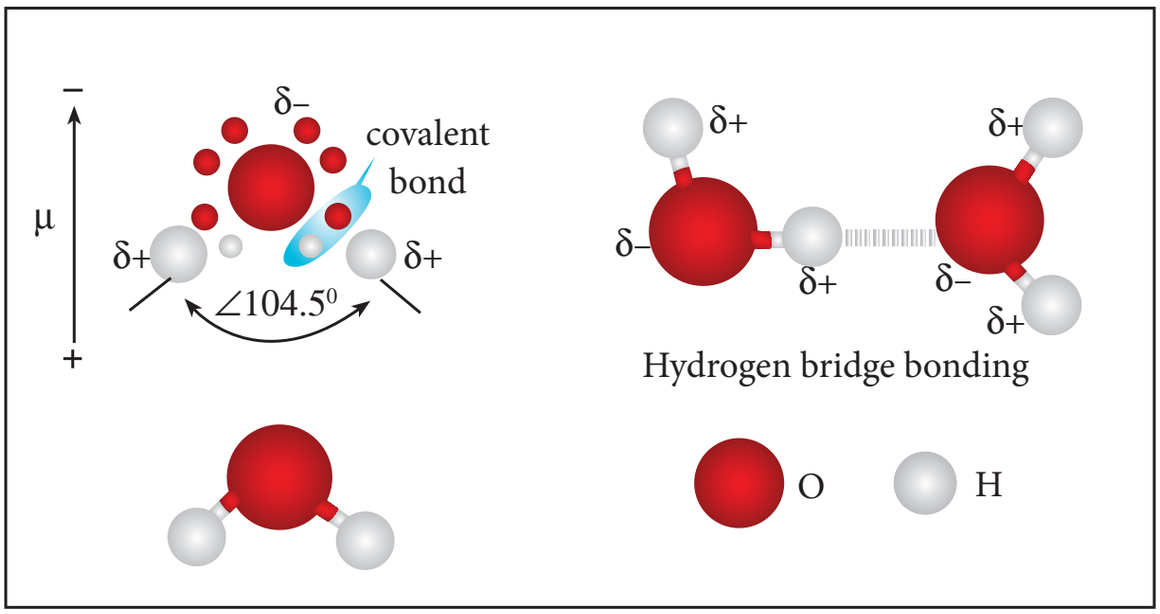

Figure 4.7 (b) Hydrogen bonding in water

Hydrogen bond occurs not only in simple molecules but also in complex biomolecules such as proteins, and they are crucial for biological processes. For example, hydrogen bonds play an important role in the structure of deoxyribonucleic acid (DNA), since they hold together the two helical nucleic acid chains (strands).

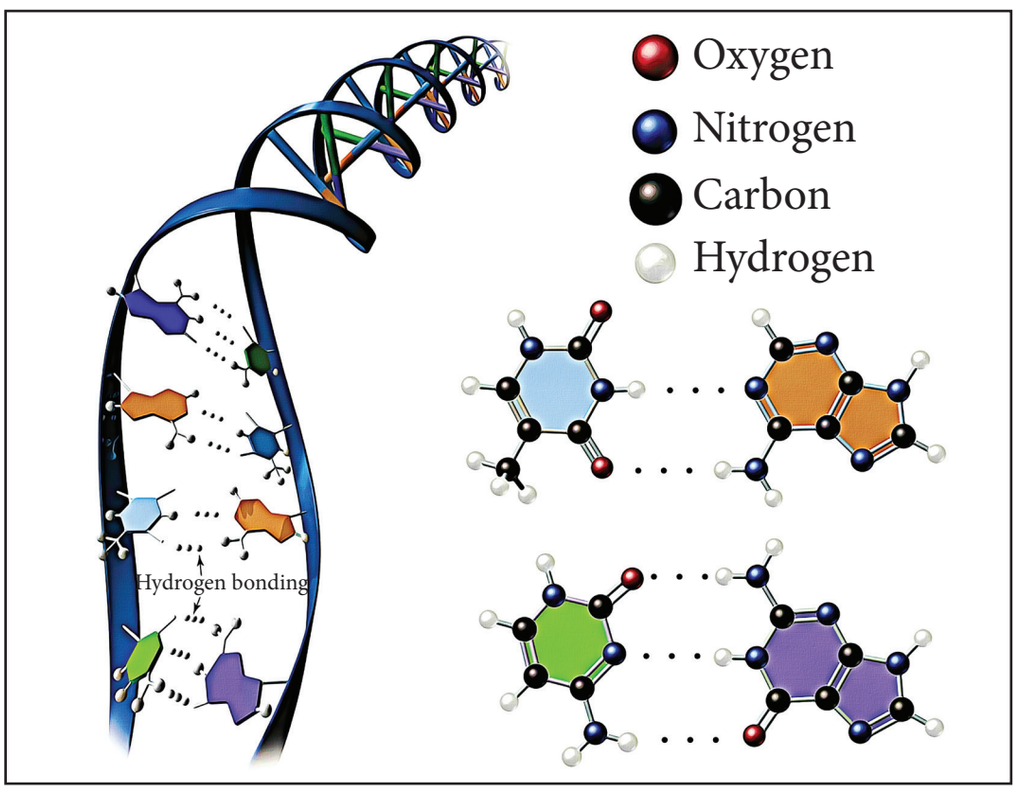

Figure 4.8 Hydrogen bonding in DNA molecules

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Significant developments related to hydrogen

1670	Robert Boyle produced flammable gas by reacting metals with acid.
1700	Nicolas Lemery showed that the gas produced in the sulphuric acid/iron reaction was explosive in air.
1766	Henry Cavendish, discovered of hydrogen by reacting zinc metal with hydrochloric acid and isolated a gas.
1780	Felice Fontana discovered the water-gas shift reaction
1783	Antoine Lavoisier named the element hydrogen (Greek meaning – water former).
1800	William Nicholson and Anthony Carlisle decomposed water into hydrogen and oxygen by electrolysis.
1801	Humphrey Davy discovered the concept of the Fuel Cell.
1806	François I. de Rivaz built the first internal combustion engine powered by a mixture of hydrogen and oxygen.
1811	Humphrey Davy discovered gas hydrates ($Cl_2 \cdot 7H_2O$).
1818	J.L. Thenard recognized and prepared hydrogen peroxide from BaO_2.
1834	Michael Faraday published Faraday's laws of electrolysis
1866	T. Graham discovered solubility/ absorption of hydrogen on palladium.
1897	Paul Sabatier facilitated the use of hydrogenation with the discovery of the Sabatier reaction.
1898	James Dewar liquefied hydrogen.
1909	S.P.L. Sorensen introduced the pH scale for hydrogen ion concentration.
1910	Fritz Haber patented the Haber process.
1913	Niels Bohr explained the Rydberg formula for the spectrum of hydrogen by imposing a quantization condition on classical orbits of the electron in hydrogen
1924	R. Mecke discovered ortho- and para-hydrogen.
1931	Harold C. Urey discovered deuterium.
1932	Harold C. Urey discovered heavy water
1932	L.P. Hammett proposed acidity function (H0) for very strong acids.
1934	Ernest Rutherford, Mark Oliphant, and Paul Harteck discovered tritium.
1935	Eugene Wigner and H.B. Huntington predicted metallic hydrogen.
1947	A.E. Finholt, A.C. Bond and H.I. Schlesinger discovered $LiAlH_4$ and subsequently shown to be a versatile reducing agent.
1950	V. Faltings and P. Harteckdetected first tritium in atmosphere.
1967	Akira Fujishima discovered the phenomenon of photocatalytic water decomposition.
1971	Alexandar I. Kloss and Boris I. Tsenter patented the Nickel-Hydrogen battery.
1990	Solar-Wasserstoff-Bayern, The first solar-powered hydrogen production plant became operational.
2000	Peter Toennies demonstrated superfluidity of hydrogen at 0.15 K.

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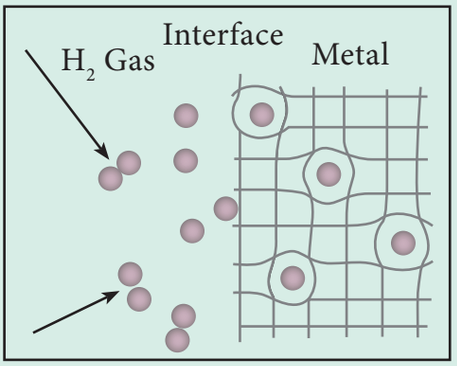
METAL HYDRIDE (HYDROGEN SPONGE)





The best studied binary hydrides are the palladium-hydrogen system. Hydrogen interacts with palladium in a unique way, and forms a limiting monohydride, PdH. Upon heating, H atoms diffuse through the metal to the surface and recombine to form molecular hydrogen. Since no other gas behaves this way with palladium, this process has been used to separate hydrogen gas from other gases:

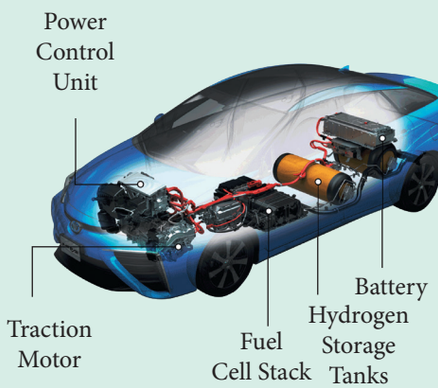
$$2\ Pd\ (s) + H_2\ (g) \leftarrow 2\ PdH\ (s).$$

The hydrogen molecule readily adsorb on the palladium surface, where it dissociates into atomic hydrogen. The dissociated atoms dissolve into the interstices or voids (octahedral/tetrahedral) of the crystal lattice.

Technically, the formation of metal hydride is by chemical reaction but it behaves like a physical storage method, i.e., it is absorbed and released like a water sponge. Such a reversible uptake of hydrogen in metals and alloys is also attractive for hydrogen storage and for rechargeable metal hydride battery applications.

The Hydrogen – Future Fuel





The depletion of fossil fuel reserves and the threat of global warming make the world to shift toward alternative fuels. In this regard, hydrogen is often considered as a potential candidate for this purpose as it is a clean burning fuel as it does not produce any pollutants upon burning. Hence, hydrogen can directly be used as a fuel and can replace existing gasoline (petrol)/diesel/kerosene powered engines, and/or indirectly be used with oxygen in fuel cells to generate electricity. However, there are some difficulties needs to be overcome. The production cost is high and also uses more fossil fuels. Due to its volatile and flammable nature in its native form, it is difficult to store and transport. Being the smallest molecule it is prone to leakage.

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SUMMARY

Hydrogen is the simplest atom which contains one electron and one proton. It has three isotopes namely protium, deuterium and tritium. The hydrogen exists as diatomic gaseous molecule. The molecule has two nuclear spin isomers namely ortho and para-hydrogen. Elemental hydrogen having an electronic configuration of $1s^1$, has properties similar to alkali metals as well as halogens. Based on its electronic configuration and existence of the +1 oxidation state in most of the compounds it is placed in group 1 along with alkali metals.

Hydrogen is prepared by the action of metal with mineral acids in laboratory. In industrial scale, hydrogen is produced by the steam-reforming of hydrocarbons. Deuterium can be synthesized by the electrolysis of heavy water, while the radioactive tritium is prepared by the nuclear transmutation reaction of lithium with slow neutrons.

Hydrogen reacts with nonmetals like oxygen and halogens to form water and hydrogen halides respectively. It reacts with metals to form metal hydrides. It acts as good reducing agent. Deuterium undergoes exchange reactions with hydrogen. Tritium with a half-life period of 12.3 years and emits β-particles spontaneously. Hydrogen has many uses including in the preparation of ammonia, methanol, and hydrogenation of oils and reduction of metal oxides. It can also be used as fuel.

Water is an important amphoteric oxide of hydrogen and used a universal solvent. It hydrolyses oxides and forms metal hydroxides with metals such as sodium and barium. Due to the presence of soluble salts of calcium and magnesium in water, the water shows hardness. Clark's method can be used to remove temporary hardness. Like water, another important oxide is hydrogen peroxide. It is used as a mild antiseptic and as a bleaching agent in textile and paper industries. Hydrogen bound to strong electronegative atoms such as fluorine, nitrogen or oxygen atoms, forms a peculiar type of electrostatic interactions with another strong electronegative atom. This is called hydrogen bond. This is one of important interactions observed in many biological molecules such as proteins, DNA etc…

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EVALUATION

I. Choose the best answer

1. Which of the following statements about hydrogen is incorrect ? (NEET - 2016)

   a) Hydrogen ion, H_3O^+ exists freely in solution.

   b) Dihydrogen acts as a reducing agent.

   c) Hydrogen has three isotopes of which tritium is the most common.

   d) Hydrogen never acts as cation in ionic salts.

2. Water gas is

   a) H_2O (g) b) $CO + H_2O$ c) $CO + H_2$ d) $CO + N_2$

3. Which one of the following statements is incorrect with regard to ortho and para dihydrogen ?

   a) They are nuclear spin isomers

   b) Ortho isomer has zero nuclear spin whereas the para isomer has one nuclear spin

   c) The para isomer is favoured at low temperatures

   d) The thermal conductivity of the para isomer is 50% greater than that of the ortho isomer.

4. Ionic hydrides are formed by

   a) halogens b) chalcogens c) inert gases d) group one elements

5. Tritium nucleus contains

   a) 1p + 0 n b) 2 p + 1n c) 1p + 2n d) none of these

6. Non-stoichiometric hydrides are formed by

   a) palladium, vanadium b) carbon, nickel

   c) manganese, lithium d) nitrogen, chlorine

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7. Assertion : Permanent hardness of water is removed by treatment with washing soda.

Reason : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false

d) Both assertion and reason are false

8. If a body of a fish contains 1.2 g hydrogen in its total body mass, if all the hydrogen is replaced with deuterium then the increase in body weight of the fish will be

a) 1.2 g b) 2.4 g c) 3.6 g d) $\sqrt{4.8}$ g

9. The hardness of water can be determined by volumetrically using the reagent

a) sodium thio sulphate b) potassium permanganate

c) hydrogen peroxide d) EDTA

10. The cause of permanent hardness of water is due to

a) $Ca(HCO_3)_2$ b) $Mg(HCO_3)_2$ c) $CaCl_2$ d) $MgCO_3$

11. Zeolite used to soften hardness of water is, hydrated

a) Sodium aluminium silicate b) Calcium aluminium silicate

c) Zinc aluminium borate d) Lithium aluminium hydride

12. A commercial sample of hydrogen peroxide marked as 100 volume H_2O_2, it means that

a) 1 ml of H_2O_2 will give 100 ml O_2 at STP

b) 1 L of H_2O_2 will give 100 ml O_2 at STP

c) 1 L of H_2O_2 will give 22.4 L O_2

d) 1 ml of H_2O_2 will give 1 mole of O_2 at STP

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13. When hydrogen peroxide is shaken with an acidified solution of potassium dichromate in presence of ether, the ethereal layer turns blue due to the formation of

a) Cr_2O_3 b) CrO_4^{2-} c) $CrO(O_2)_2$ d) none of these

14. For decolourisation of 1 mole of acidified $KMnO_4$, the moles of H_2O_2 required is

a) $\frac{1}{2}$ b) $\frac{3}{2}$ c) $\frac{5}{2}$ d) $\frac{7}{2}$

15. Volume strength of 1.5 N H_2O_2 is

a) 1.5 b) 4.5 c) 16.8 d) 8.4

16. The hybridisation of oxygen atom is H_2O and H_2O_2 are, respectively

a) sp and sp^3 b) sp and sp c) sp and sp^2 d) sp^3 and sp^3

17. The reaction $H_3PO_2 + D_2O \rightarrow H_2DPO_2 + HDO$ indicates that hypo-phosphorus acid is

a) tribasic acid b) dibasic acid c) mono basic acid d) none of these

18. In solid ice, oxygen atom is surrounded

a) tetrahedrally by 4 hydrogen atoms

b) octahedrally by 2 oxygen and 4 hydrogen atoms

c) tetrahedrally by 2 hydrogen and 2 oxygen atoms

d) octahedrally by 6 hydrogen atoms

19. The type of H-bonding present in ortho nitro phenol and p-nitro phenol are respectively

a) inter molecular H-bonding and intra molecular H-bonding

b) intra molecular H-bonding and inter molecular H-bonding

c) intra molecular H - bonding and no H - bonding

d) intra molecular H - bonding and intra molecular H - bonding

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20. Heavy water is used as

a) moderator in nuclear reactions b) coolant in nuclear reactions

c) both (a) and (b) d) none of these

21. Water is a

a) basic oxide b) acidic oxide

c) amphoteric oxide d) none of these

II. Write brief answer to the following questions:

22. Explain why hydrogen is not placed with the halogen in the periodic table.

23. Discuss the three types of Covalent hydrides.

24. Predict which of the following hydrides is a gas on a solid (a) HCl (b) NaH. Give your reason.

25. Write the expected formulas for the hydrides of 4th period elements. What is the trend in the formulas? In what way the first two members of the series different from the others ?

26. Write chemical equation for the following reactions.

i) reaction of hydrogen with tungsten (VI) oxide on heating.

ii) hydrogen gas and chlorine gas.

27. Complete the following chemical reactions and classify them in to (a) hydrolysis (b) redox (c) hydration reactions.

i) $KMnO_4 + H_2O_2 \rightarrow$

ii) $CrCl_3 + H_2O \rightarrow$

iii) $CaO + H_2O \rightarrow$

28. Hydrogen peroxide can function as an oxidising agent as well as reducing agent. substantiate this statement with suitable examples.

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29. Do you think that heavy water can be used for drinking purposes ?

30. What is water-gas shift reaction ?

31. Justify the position of hydrogen in the periodic table ?

32. What are isotopes? Write the names of isotopes of hydrogen.

33. Give the uses of heavy water.

34. Explain the exchange reactions of deuterium.

35. How do you convert para hydrogen into ortho hydrogen ?

36. Mention the uses of deuterium.

37. Explain preparation of hydrogen using electrolysis.

38. A group-1 metal (A) which is present in common salt reacts with (B) to give compound (C) in which hydrogen is present in –1 oxidation state. (B) on reaction with a gas (C) to give universal solvent (D). The compound (D) on reacts with (A) to give (E), a strong base. Identify A, B, C, D and E. Explain the reactions.

39. An isotope of hydrogen (A) reacts with diatomic molecule of element which occupies group number 16 and period number 2 to give compound (B) is used as a moderator in nuclear reaction. (A) adds on to a compound (C), which has the molecular formula C_3H_6 to give (D). Identify A, B, C and D.

40. NH_3 has exceptionally high melting point and boiling point as compared to those of the hydrides of the remaining element of group 15 - Explain.

41. Why interstitial hydrides have a lower density than the parent metal.

42. How do you expect the metallic hydrides to be useful for hydrogen storage ?

43. Arrange NH_3, H_2O and HF in the order of increasing magnitude of hydrogen bonding and explain the basis for your arrangement.

44. Compare the structures of H_2O and H_2O_2.

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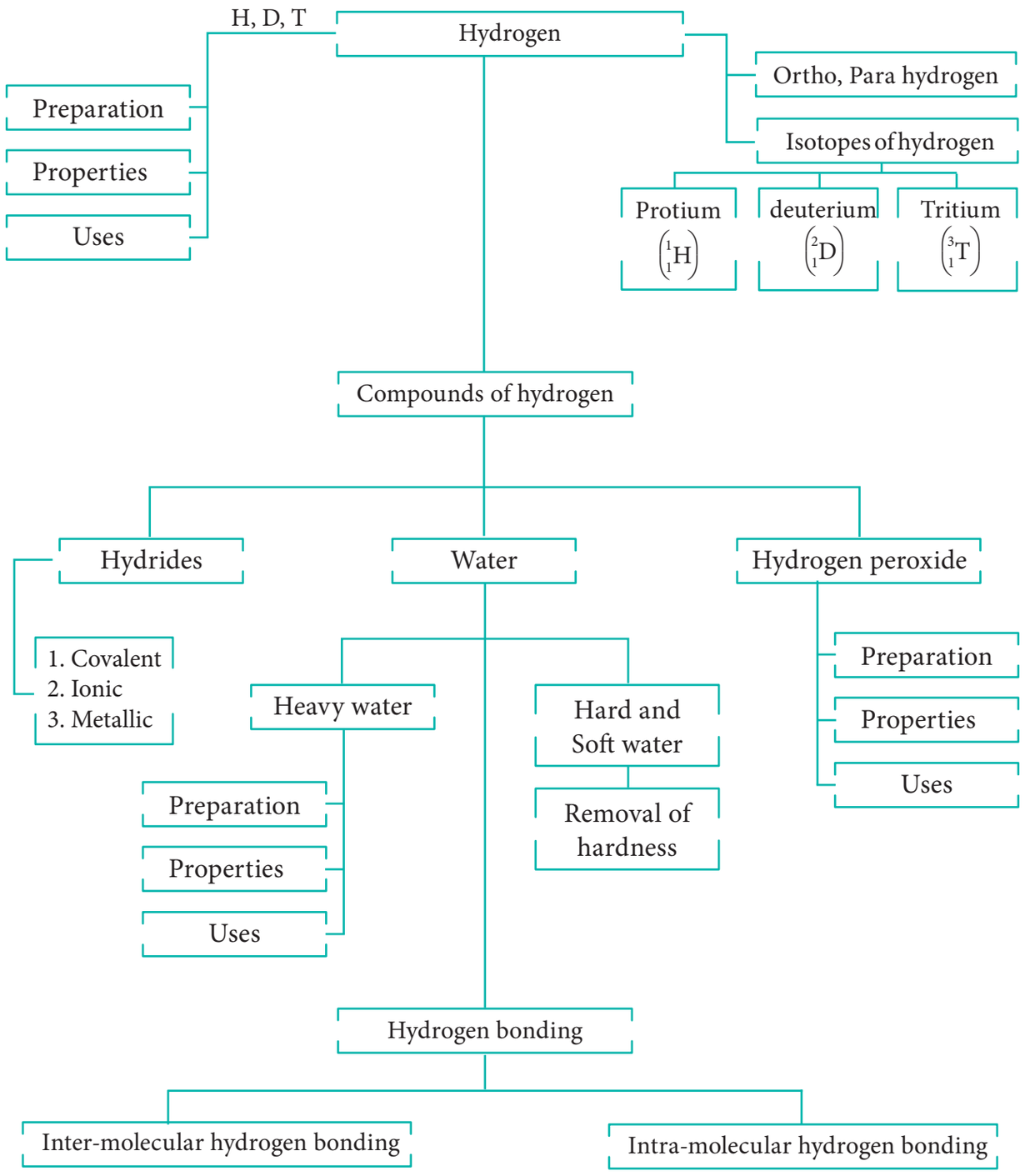
CONCEPT MAP



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Unit 5

Alkali and Alkaline Earth Metals

Learning Objectives

After studying this unit, students will be able to

- Explain the properties of alkali metals and alkaline earth metals
- Recognise the anomalous properties of Li and Be
- List the uses of alkali metals and alkaline earth metals
- Describe the general characteristics of compounds of alkali metals and alkaline earth metals
- Appreciate the biological importance of sodium and potassium, Magnesium and Calcium
- Explain the preparation, properties and uses of calcium oxide, calcium hydroxide, gypsum and plaster of paris.



Rock salt



Sylvite



Spodumene

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5.1 s-Block Elements:

The elements belonging to the group 1 and 2 in the modern periodic table are called s-block elements. The elements belonging to these two groups are commonly known as alkali and alkaline earth metals respectively. In this unit, we study their properties, uses, important compounds and biological importance.

5.2 Alkali metals:

The word "alkali" is derived from the word al-qalīy meaning the plant ashes, referring to the original source of alkaline substances. A water-extract of burnt plant ashes, called potash contain mainly potassium carbonate. Alkali metal group consists of the elements: lithium, sodium, potassium, rubidium, caesium and francium. They are all metals, generally soft and highly reactive. They form oxides and hydroxides and these compounds are basic in nature.

5.2.1 General characteristics of alkali metals:

Alkali metals are highly reactive and are found in nature only as compounds. Rubidium and caesium are found associated in minute quantities with minerals of other alkali metals. Francium is radioactive and does not occur appreciably in nature. Francium is highly radioactive; its longest-lived isotope has a half-life of only 21 minutes.

Table 5.1 Abundance of important alkali metals and their sources

Elements	Abundance in earth crust (%)	Relative Abundance	Mineral source
Lithium	0.0018	35	Spodumene [$LiAl(SiO_3)$]
Sodium	2.27	7	Rock Salt [NaCl]
Potassium	1.84	8	Sylvite [KCl]
Rubidium	0.0078	23	No convenient Source (obtained as by product of lithium processing)
Cesium	0.00026	46	



Figure 5.1 Alkali metals Li, Na and K stored under oil

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Electronic configuration

The general valence shell electronic configuration of alkali metals is ns^1, where 'n' represents the period number.

Table 5.2 Electronic configuration of alkali metals

Element	Symbol	Atomic No.	Electronic configuration
Lithium	Li	3	$[He]2s^1$
Sodium	Na	11	$[Ne]3s^1$
Potassium	K	19	$[Ar]4s^1$
Rubidium	Rb	37	$[Kr]5s^1$
Caesium	Cs	55	$[Xe]6s^1$
Francium	Fr	87	$[Rn]7s^1$

Common oxidation state

All these elements are highly electropositive in nature. They readily lose their valence electron to give monovalent cations (M^+). Alkali metals have only one oxidation state which is +1.

Atomic and ionic radii

Being the first element of each period, alkali metals have the largest atomic and ionic radii in their respective periods. On moving down the group, there is an increase in the number of shells and, therefore, atomic and ionic radii increase. The monovalent ions (M^+) are smaller than the respective parent atoms as expected.

Table 5.3 Physical properties of alkali metals

Physical property	Li	Na	K	Rb	Cs
Atomic radius / Metallic radius (Å)	1.52	1.86	2.27	2.48	2.65
Ionic radius (Å)	0.76	1.02	1.38	1.52	1.67
Melting point (^{0} C)	181	98	63	39	28.5
Boiling point (^{0} C)	1347	881	766	688	705
First ionization enthalpy (kJ mol^{-1})	520.2	495.8	418.8	403.0	375.7
Electronegativity (Paulings scale)	1.0	0.9	0.8	0.8	0.7
Density (g cm^{-3})	0.54	0.97	0.86	1.53	1.90
Standard potential E^0 for M^+/M (V)	-3.04	-2.71	-2.92	-2.93	-2.93
Hydration enthalpy (kJ mol^{-1})	-506	-406	-330	-310	-276

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Ionisation enthalpy

Alkali metals have the lowest ionisation enthalpy compared to other elements present in the respective period. As we go down the group, the ionisation enthalpy decreases due to the increase in atomic size. In addition, the number of inner shells also increases, which in turn increases the magnitude of screening effect and consequently, the ionisation enthalpy decreases down the group.

The second ionisation enthalpies of alkali metals are very high. The removal of an electron from the alkali metals gives monovalent cations having stable electronic configurations similar to the noble gas. Therefore, it becomes very difficult to remove the second electron from the stable configurations already attained.

Hydration enthalpy

Lithium salts are more soluble than the salts of other metals of group 1. eg. $LiClO_4$ is upto 12 times more soluble than $NaClO_4$. Other salts $KClO_4$, $RbClO_4$ and $CsClO_4$ have solubilities only 10^{-3} times of that of $LiClO_4$. The high solubility of Li salts is due to strong solvation of small size Li^+ ion.

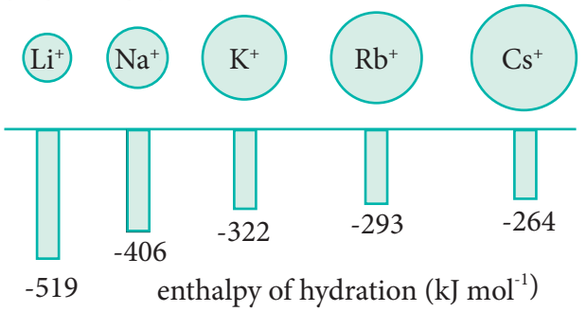

Figure 5.2 Hydration enthalpy of alkali metals

Electronegativity:

Alkali metals have comparatively smaller value of electronegativity than the other elements in the respective period. When they react with other elements, they usually produce ionic compounds. For example, they react with halogens to form ionic halides.

Flame colour and the spectra:

When the alkali metal salts moistened with concentrated hydrochloric acid are heated on a platinum wire in a flame, they show characteristic coloured flame as shown below.

Table 5.4 Flame colour and wavelength

Element	Colour	Wavelength (nm)
Lithium	Crimson red	670.8
Sodium	Yellow	589.2
Potassium	Lilac (violet)	766.5
Rubidium	Reddish violet	780.0
Caesium	Blue	455.5

The heat in the flame excites the valence electron to a higher energy level. When it drops back to its actual energy level, the excess energy is emitted as light, whose wavelength is in the visible region as shown in the above table.

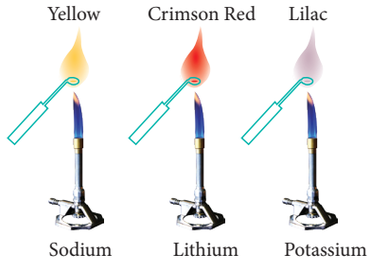

Figure 5.3 Flame colours of alkali metal salts

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5.2.2 Distinctive behavior of lithium

The distinctive behaviour of Li^+ ion is due to its exceptionally small size, high polarising power, high hydration energy and non availability of d-orbitals.

Table 5.5 Comparison of properties of lithium with other elements of the group:

Lithium	Other elements of the family
Hard, high melting and boiling point	Soft and Lower melting and boiling point
Least reactive (For example it reacts with oxygen to form normal oxide, forms peroxides with great difficulty and its higher oxides are unstable)	More reactive
Reacts with nitrogen to give Li_3N $6Li + N_2 \rightarrow 2Li_3N$	No reaction
Reacts with bromine slowly	React violently
Reacts directly with carbon to form ionic carbides. For example $2Li + 2C \rightarrow Li_2C_2$	Do not react with carbon directly, but can react with carbon compounds. $2Na + C_2H_2 \rightarrow Na_2C_2 + H_2$
Lithium nitrate decomposes to give an oxide	Decompose to give nitrites

Table 5.6 Similarities between lithium and Magnesium

S.No.	Properties
1	Both lithium and magnesium are harder than other elements in the respective groups
2	Lithium and magnesium react slowly with water. Their oxides and hydroxides are much less soluble and their hydroxides decompose on heating.
3	Both form a nitride, Li_3N and Mg_3N_2, by direct combination with nitrogen
4	They do not give any superoxides and form only oxides, Li_2O and MgO
5	The carbonates of lithium and magnesium decompose upon heating to form their respective oxides and CO_2.
6	Lithium and magnesium do not form bicarbonates.
7	Both LiCl and $MgCl_2$ are soluble in ethanol and are deliquescent. They crystallise from aqueous solution as hydrates, $LiCl{\cdot}2H_2O$ and $MgCl_2{\cdot}8H_2O$

Diagonal Relationship:

Similarity between the first member of group 1 (Li) and the diagonally placed second element of group 2 (Mg) is called diagonal relationship. It is due to similar size (r_{Li^+} = 0.766 Å and $r_{Mg^{2+}}$ = 0.72 Å) and comparable electronegativity values (Li = 1.0; Mg = 1.2).

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5.2.3 Chemical properties of alkali metals

Alkali metals exhibit high chemical reactivity. The reactivity of alkali metals increases from Li to Cs, since the ionisation energy decreases down the group. All alkali metals are highly reactive towards the more electronegative elements such as oxygen and halogens. Some characteristic chemical properties of alkali metals are described below.

Reaction with oxygen

All the alkali metals on exposure to air or oxygen burn vigorously, forming oxides on their surface. Lithium forms only monoxide, sodium forms the monoxide and peroxide and the other elements form monoxide, peroxide, and superoxides. These oxides are basic in nature.

$4\ Li + O_2 \longrightarrow 2Li_2O$ (simple oxide)

$2\ Na + O_2 \longrightarrow Na_2O_2$ (peroxide)

$M + O_2 \longrightarrow MO_2$ (superoxide)
(M= K, Rb,Cs)

Reaction with hydrogen

All alkali metals react with hydrogen at about 673 K (lithium at 1073 K) to form the corresponding ionic hydrides. Reactivity of alkali metals with hydrogen decreases from Li to Cs.

$2M + H_2 \longrightarrow 2\ M^+H^-$
(M = Li, Na, K, Rb, Cs)

The ionic character of the hydrides increases from Li to Cs and their stability decreases. The hydrides behave as strong reducing agents and their reducing nature increases down the group.

Reaction with halogen

Alkali metals combine readily with halogens to form ionic halides MX. Reactivity of alkali metals with halogens increases down the group because of corresponding decrease in ionisation enthalpy.

$2M + X_2 \longrightarrow 2\ MX$
(M= Li, Na, K, Rb, Cs) (X= F, Cl, Br, I)

All metal halides are ionic crystals. However Lithium iodide shows covalent character, as it is the smallest cation that exerts high polarising power on the iodide anion. Additionally, the iodide ion being the largest can be polarised to a greater extent by Li^+ ion.

Reaction with liquid ammonia:

Alkali metals dissolve in liquid ammonia to give deep blue solutions that are conducting in nature. The conductivity is similar to that of pure metals (The specific conductivity of Hg is $10^4\ \Omega^{-1}$ and for sodium in liquid ammonia is $0.5 \times 10^4\ \Omega^{-1}$). This happens because the alkali metal atom readily loses its valence electron in ammonia solution. Both the cation and the electron are ammoniated to give ammoniated cation and ammoniated electron.

$M + (x + y)NH_3 \rightarrow$

$[M(NH_3)_x]^+ + [e(NH_3)_y]^-$

The blue colour of the solution is due to the ammoniated electron which

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absorbs energy in the visible region of light and thus imparts blue colour to the solution. The solutions are paramagnetic and on standing slowly liberate hydrogen resulting in the formation of an amide.

$$M^+ + e^- + NH_3 \rightarrow MNH_2 + \tfrac{1}{2}H_2$$

In concentrated solution, the blue colour changes to bronze colour and become diamagnetic.

Reaction with water:

Alkali metals react with water to give corresponding hydroxides with the liberation of hydrogen.

$$2\ Li + 2\ H_2O \rightarrow 2\ LiOH + H_2$$

They also react with alcohol, and alkynes which contain active hydrogens.

$$2\ Na + 2\ C_2H_5OH \rightarrow 2\ C_2H_5ONa + H_2$$

$$H\text{-}C \equiv C\text{-}H \xrightarrow{Na} H\text{-}C \equiv C\text{-}Na \xrightarrow{Na} Na\text{-}C \equiv C\text{-}Na$$

Reducing activity:

Alkali metals can lose their valence electron readily hence they act as good reducing agents.

$$M_{(s)} \rightarrow M^+_{(g)} + e^-$$

Reaction with carbon:

Lithium directly reacts with carbon to form the ionic compound, lithium carbide. Other metals do not react with carbon directly. However, when they are treated with compounds like acetylene they form acetelydes.

$$2\ Li + 2C \rightarrow Li_2C_2$$

5.2.4 Uses of alkali metals:

i. Lithium metal is used to make useful alloys. For example with lead it is used to make 'white metal' bearings for motor engines, with aluminium to make aircraft parts, and with magnesium to make armour plates. It is used in thermonuclear reactions.

ii. Lithium is also used to make electrochemical cells.

iii. Sodium is used to make Na/Pb alloy needed to make $Pb(Et)_4$ and $Pb(Me)_4$. These organolead compounds were earlier used as anti-knock additives to petrol, but nowadays lead-free petrol in use.

iv. Liquid sodium metal is used as a coolant in fast breeder nuclear reactors.

v. Potassium has a vital role in biological systems.Potassium chloride is used as a fertilizer.

vi. Potassium hydroxide is used in the manufacture of soft soap. It is also used as an excellent absorbent of carbon dioxide.

vii. Caesium is used in devising photoelectric cells.

5.3 General characteristics of the compounds of alkali metals

All the common compounds of the alkali metals are generally ionic in nature. General characteristics of some of their compounds are discussed here.

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Oxides and Hydroxides

On combustion in excess of air, alkali metals forms normal oxides with formula M_2O. They react with water to form corresponding hydroxides which are basic in nature.

$$M_2O + H_2O \rightarrow 2\ MOH$$

Alkali metals apart from lithium form peroxides in addition to normal oxides upon combustion with excess air. These peroxides produce hydroxides and H_2O_2 upon reacting with water.

$$M_2O_2 + 2\ H_2O \rightarrow 2MOH + H_2O_2$$

(M = Na, K, Rb, Cs)

Except lithium and sodium, all the other alkali metals form superoxides also. These superoxides also gives basic hydroxides upon treatment with water.

$$2\ MO_2 + 2\ H_2O \rightarrow 2\ MOH + H_2O_2 + O_2$$

(M = K, Rb, Cs)

Under appropriate conditions pure compounds M_2O, M_2O_2 or MO_2 may be prepared.

Properties of oxides and hydroxides:

The oxides and the peroxides are colourless when pure, but the superoxides are yellow or orange in colour. The peroxides are diamagnetic while the superoxides are paramagnetic. Sodium peroxide is widely used as an oxidising agent. The hydroxides which are obtained by the reaction of the oxides with water are all white crystalline solids. The alkali metal hydroxides are strong bases. They dissolve in water with evolution of heat on account of intense hydration.

Halides:

The alkali metal halides, MX, (X=F, Cl, Br, I) are colourless crystalline solids with high melting points. They can be prepared by the reaction of the appropriate oxide, hydroxide or carbonate with aqueous hydrohalic acid (HX). As the electropositive character of alkali metal increases from Li to Cs, the ease with which the metals form halides increases from Li to Cs. All halides are ionic in nature except LiBr and LiI. Except LiF, all other halides are soluble in water. The low solubility of LiF in water is due to its high lattice enthalpy (small size of Li^+ and F^-). Due to the presence of covalent nature both LiBr and LiI are soluble in organic solvents.

Salts of oxo-acids

Alkali metals form salts with all the oxo-acids. Most of these salts are soluble in water and are thermally stable. As the electropositive character increases down the group, the stability of the carbonates and bicarbonates increases. This is due to the decrease in polarising power of alkali metal cations. The carbonates (M_2CO_3) of alkali metals are remarkably stable up to 1273 K, above which they first melt and then eventually decompose to form oxides. However, Li_2CO_3 is considerably less stable and decomposes readily.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

This is presumably due to large size difference between Li^+ and CO_3^{-2} which

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makes the crystal lattice unstable. Being strongly basic, alkali metals except lithium form solid bicarbonates. No other metal forms solid bicarbonates.

$M_2CO_3 + CO_2 + H_2O \rightarrow 2\ MHCO_3$

(M = Na, K, Rb, Cs)

All the carbonates and bicarbonates are soluble in water and their solubilities increase rapidly on descending the group. This is due to the reason that lattice energies decrease more rapidly than their hydration energies on moving down the group.

5.3.1 Important compounds of alkali metals:

Sodium Carbonate $Na_2CO_3.10H_2O$ (Washing soda):

Sodium carbonate is one of the important inorganic compounds used in industries. It is prepared by Solvay process. In this process, ammonia is converted into ammonium carbonate which then converted to ammonium bicarbonate by passing excess carbon dioxide in a sodium chloride solution saturated with ammonia. The ammonium bicarbonate thus formed reacts with the sodium chloride to give sodium bicarbonate and ammonium chloride. As sodium bicarbonate has poor solubility, it gets precipitated. The sodium bicarbonate is isolated and is heated to give sodium carbonate. The equations involved in this process are,

$2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2CO_3$

$(NH_4)_2CO_3 + H_2O + CO_2 \rightarrow 2\ NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$

The ammonia used in this process can be recovered by treating the resultant ammonium chloride solution with calcium hydroxide. Calcium chloride is formed as a by-product.

Properties:

Sodium carbonate, commonly known as washing soda, crystallises as decahydrate which is white in colour. It is soluble in water and forms an alkaline solution. Upon heating, it looses the water of crystallisation to form monohydrate. Above 373 K, the monohydrate becomes completely anhydrous and changes to a white powder called soda ash.

$Na_2CO_3 \cdot 10H_2O \rightarrow Na_2CO_3 \cdot H_2O + 9H_2O$

$Na_2CO_3 \cdot H_2O \rightarrow Na_2CO_3 + H_2O$

Uses:

i. Sodium carbonate known as washing soda and is used mainly for laundering.

ii. It is also used in water treatment to convert the hard water to soft water.

iii. It is used in the manufacturing of glass, paper, paint etc...

Sodium chloride NaCl (Cooking salt or Table salt):

Sodium chloride is isolated by evaporation from sea water which contains

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2.7 to 2.9% by mass. Approximately 50 lakh tons of salt are produced annually in India by solar evaporation. Crude sodium chloride can be obtained by crystallisation of brine solution which contains sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride as impurities. Pure sodium chloride can be obtained from crude salt as follows. Firstly removal of insoluble impurities by filtration from the crude salt solution with minimum amount of water. Sodium chloride can be crystallised by passing HCl gas into this solution. Calcium and magnesium chloride, being more soluble than sodium chloride, remain in solution.

Sodium chloride melts at 1081K. It has a solubility of 36.0 g in 100 g of water at 273 K. The solubility does not increase appreciably with increase in temperature.

Uses :

(i) It is used as a common salt or table salt for domestic purpose.

(ii) It is used for the preparation of many inorganic compounds such as NaOH and Na_2CO_3

Sodium hydroxide:

Sodium hydroxide is prepared commercially by the electrolysis of brine solution in Castner-Kellner cell using a mercury cathode and a carbon anode. Sodium metal is discharged at the cathode and combines with mercury to form sodium amalgam. Chlorine gas is evolved at the anode. The sodium amalgam thus obtained is treated with water to give sodium hydroxide.

At cathode : $Na^+ + e^- \rightarrow Na(amalgam)$

At anode : $Cl^- \rightarrow \frac{1}{2} Cl_2 \uparrow + e^-$

$2Na(amalgam) + 2H_2O \rightarrow 2NaOH + 2Hg + H_2\uparrow$

Sodium hydroxide is a white, translucent and deliquescent solid, that dissolves in water to give a strong alkaline solution. It melts at 591 K. The sodium hydroxide solution at the surface reacts with the CO_2 in the atmosphere to form Na_2CO_3

Uses:

- Sodium hydroxide is used in the purification of bauxite (ore of Aluminium) and petroleum refining
- It is used in the textile industries for mercerising cotton fabrics
- It is used in the manufacture of soap, paper and artificial silks.

Sodium bicarbonate $NaHCO_3$ (Baking soda):

Sodium hydrogen carbonate or sodium bicarbonate is used in baking cakes pastries etc. It is called so because it decomposes on heating to generate bubbles of carbon dioxide, leaving holes in cakes or pastries and making them light and fluffy. This compound is prepared by saturating a solution of sodium carbonate with carbon dioxide. The white crystalline powder of sodium bicarbonate, being less soluble, precipitated out.

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Uses:

- Primarily used as an ingredient in baking.
- Sodium hydrogen carbonate is a mild antiseptic for skin infections.
- It is also used in fire extinguishers.

5.4 Biological importance of sodium and potassium

Monovalent sodium and potassium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction. A typical 70 kg man contains about 90 g of sodium and 170 g of potassium compared with only 5 g of iron and 0.06 g of copper.

Sodium ions are found primarily on the outside of cells, being located in blood plasma and in the interstitial fluid which surrounds the cells. These ions participate in the transmission of nerve signals, in regulating the flow of water across cell membranes and in the transport of sugars and amino acids into cells. Sodium and potassium, although so similar chemically, differ quantitatively in their ability to penetrate cell membranes, in their transport mechanisms and in their efficiency to activate enzymes. Thus, potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

Sodium–potassium pump play an important role in transmitting nerve signals.

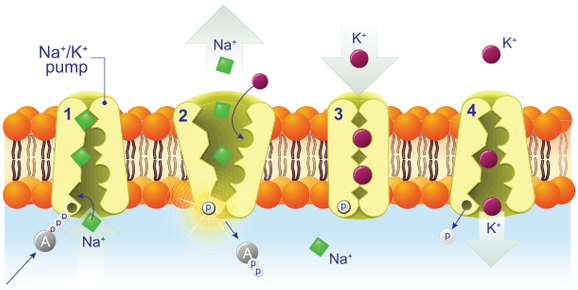

Figure 5.4 Sodium–potassium pump

5.5 Alkaline earth metals

Group 2 in the modern periodic table contains the elements beryllium, magnesium, calcium, strontium, barium and radium. These elements with the exception of beryllium are commonly known as the alkaline earth metals because their oxides and hydroxides are alkaline in nature and these metal oxides are found in the earth's crust.



Figure 5.5 Alkaline earth metals

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Table 5.7 Abundance of important alkaline earth metals and their sources

Element	Abundance in Earth crust by weight (ppm)	Mineral source
Be	2.0	beryl $Be_3Al_2Si_6O_{18}$
Mg	27640	Carnallite ($KCl.MgCl_2.6H_2O$) Dolomite $MgCO_3$ $CaCO_3$
Ca	1.84	Fluorapatite $Ca_5(PO_4)_3$ F
Sr	384	Celestite $SrSO_4$
Ba	390	barytes $BaSO_4$

5.5.1 General characteristics of alkaline earth metals

Physical state

Beryllium is rare and radium is the rarest of all comprising only 10 % of igneous rocks. Magnesium and calcium are very common in the earth's crust, with calcium the fifth-most-abundant element, and magnesium the eighth. Magnesium and calcium are found in many rocks and minerals: magnesium in carnallite, magnesite, dolomite and calcium in chalk, limestone, gypsum. Most strontium is found in the minerals celestite and strontianite. Barium is slightly less common, much of it in the mineral barite. Radium, being a decay product of uranium, is found in all uranium-bearing ores.



FIREWORK



Many alkaline and alkaline earth metals are used in creating colours, such as strontium and barium, are the colourful stars of a fireworks show. Combined with the element chlorine, barium sends up a green spark, calcium gives orange and lithium gives medium red. Strontium carbonate gives a bright red colour Nitrates of sodium gives orange, potassium and rubidium gives violet colour and caesium gives indigo colour. The burning "excites" the electrons, pushing them into higher than normal energy level; they release their extra energy as a colourful burst of light

The blue fireworks are the hardest to make, since the compound copper chloride breaks down in a hot flame. In recent years, fireworks experts have used magnalium- a mixture of the alkaline earth metal magnesium and aluminium - to boost all firework colours. Magnalium has made the blues brighter, but pyro technicians are still searching for a blue as brilliant as the red, green and yellow colours.

Electronic configuration

These elements have two electrons in the valence shell of their atoms, preceded by the noble gas configuration. Their general electronic configuration is written

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as [Noble gas]ns^2 where 'n' represents the valence shell.

Table 5.8 Electronic configuration of alkaline earth metals

Element	Atomic No.	Electronic configuration
Be	4	$[He]2s^2$
Mg	12	$[Ne]3s^2$
Ca	20	$[Ar]4s^2$
Sr	38	$[Kr]5s^2$
Ba	56	$[Xe]6s^2$
Ra	88	$[Rn]7s^2$

Atomic and ionic radii

The atomic and ionic radii of alkaline earth metals are smaller than the corresponding members of the alkali metals. This is due to the fact the Group 2 elements having a higher nuclear charge that allows electrons to be attracted more strongly towards the nucleus. On moving down the group, the radii increases due to gradual increase in the number of the shells and the screening effect.

Common oxidation state

The group 2 elements have two electrons in their valence shell and by losing these electrons, they acquire the stable noble gas configuration. So these elements exhibit +2 oxidation state in their compounds.

Ionisation enthalpy

Due to a fairly large size of the atoms, alkaline earth metals have low ionisation enthalpies when compared to 'p' block elements. Down the group the ionisation enthalpy decreases as atomic size increases. This is due to the addition of new shells as well as increase in the magnitude of the screening effect of inner shell electrons. Members of group 2 have higher ionization enthalpy values than group 1 because of their smaller size, with electrons being more attracted towards the nucleus of the atoms. Correspondingly they are less electropositive than alkali metals.

Table 5.9 Physical properties of alkaline earth metals

Physical property	Be	Mg	Ca	Sr	Ba
Atomic radius -non bonded (Å)	1.12	1.60	1.97	2.15	2.22
Ionic radius (Å)	0.27(0.31)	0.72	1.00	1.18	1.35
First ionization energy (kJ mol^{-1})	899.5	737.8	589.8	549.5	502.9
Second ionization energy (kJ mol^{-1})	1757.1	1450.7	1145.5	1064.2	965.2
Hydration enthalpy (kJ mol^{-1})	– 2494	– 1921	–1577	– 1443	– 1305
Melting Point (^{0} C)	1287	651	851	789	729
Boiling Point (^{0} C)	2472	1090	1494	1382	1805
Density (g cm^{-3})	1.84	1.74	1.55	2.63	3.59
Standard Potential $E^{\ominus}$ for M^+/M (V)	-1.97	-2.36	-2.84	-2.89	-2.92
Electronegativity (Paulings scale)	1.6	1.2	1.0	1.0	0.9

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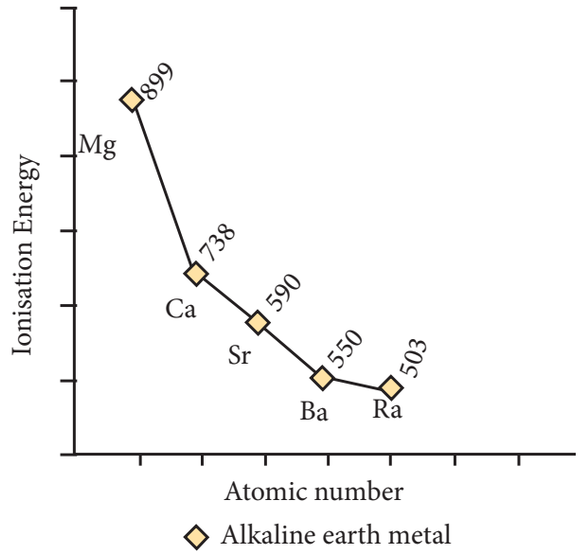

Figure 5.6 Variation of ionisation energy - Alkaline earth metals.

Although IE_1 values of alkaline earth metals are higher than that of alkali metals, the IE_2 values of alkaline earth metals are much smaller than those of alkali metals. This occurs because in alkali metals the second electron is to be removed from a cation, which has already acquired a noble gas configuration. In the case of alkaline earth metals, the second electron is to be removed from a monovalent cation, which still has one electron in the outermost shell. Thus, the second electron can be removed more easily in the case of group 2 elements than in group 1 elements.

Hydration Enthalpies

Compounds of alkaline earth metals are more extensively hydrated than those of alkali metals, because the hydration enthalpies of alkaline earth metal ions are larger than those of alkali metal ions. Like alkali metal ions, the hydration enthalpies of alkaline earth metal ions also decrease with increase in ionic size down the group.

$$Be > Mg > Ca > Sr > Ba$$

e.g., Magnesium chloride and calcium chloride exist as their hydrated crystals $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$ respectively. whereas NaCl and KCl do not form such hydrates.

Electronegativity

In alkaline earth metals the electronegativity values decrease as we go down the group as seen in the alkali metals.

Flame colour and the spectra:

When the alkaline earth metal salts moistened with concentrated hydrochloric acid are heated on a platinum wire in a flame, they show characteristic coloured flame as shown below.

Table 5.10 Flame Colour and wavelength

Element	Colour	Wavelength (nm)
Calcium	Brick - Red	622
Strontium	Crimson- Red	689
Barium	Apple Green	554

The heat in the flame excites the valence electron to a higher energy level. when it drops back to its actual energy level, the excess energy is emitted as light, whose wavelength is in the visible region as shown in the above table.

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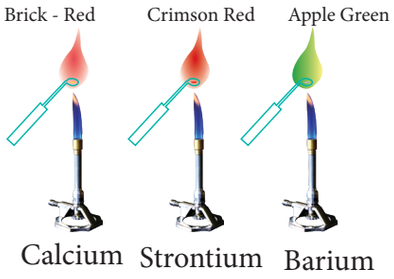

Figure 5.7: Flame colours of alkaline earth metal salts

5.5.2 Distinctive behavior of beryllium

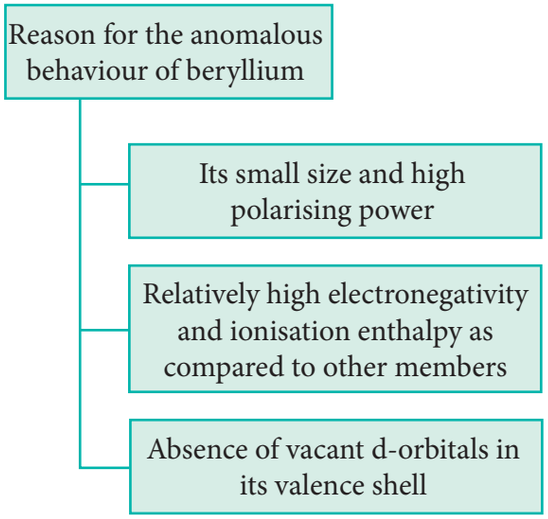

Figure 5.8 Distinctive behaviour of beryllium

The anomalous properties of beryllium is mainly due to its small size, high electronegativity, high ionisation energy and high polarising power compared to the other elements in the block. The anomalous properties of beryllium compared to other elements of the group are mentioned in Table 5.11

Table 5.11 Comparison of Properties of Beryllium with other elements of the group

Beryllium	Other elements of the family
Forms covalent compounds	form ionic compounds
High melting and boiling point	Low melting and boiling point
Does not react with water even at elevated temperature	React with water
Does not combine directly with hydrogen	Combine directly with hydrogen
Does not combine directly with halogens. Halides are covalent.	Combine directly with halogens Halides are electrovalent.

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Hydroxide and oxides of beryllium are amphoteric in nature	Basic in nature.
It is not readily attacked by acids because of the presence of an oxide film	Readily attacked by acids
Beryllium carbide evolves methane with water.	evolve acetylene with water.
Salts of Be are extensively hydrolysed	Hydrolysed

Diagonal Relationship:

As observed in alkali metals, beryllium (the first member of group 2) shows a diagonal relationship with aluminium. In this case, the size of these ions ($r_{Be^{2+}}$ = 0.45 Å and $r_{Al^{3+}}$ = 0.54 Å) is not as close. However, their charge per unit area is closer (Be^{2+} = 2.36 and Al^{3+} = 2.50). They also have same electronegativity values (Be = 1.5; Al = 1.5).

Table 5.12 Similarities between Beryllium and Aluminium

S.No.	Properties
1	Beryllium chloride forms a dimeric structure like aluminium chloride with chloride bridges. Beryllium chloride also forms polymeric chain structure in addition to dimer. Both are soluble in organic solvents and are strong Lewis acids.
2	Beryllium hydroxide dissolves in excess of alkali and gives beryllate ion and $[Be(OH)_4]^{2-}$ and hydrogen as aluminium hydroxide which gives aluminate ion, $[Al(OH)_4]^-$.
3	Beryllium and aluminium ions have strong tendency to form complexes, BeF_4^{2-}, AlF_6^{3-}.
4	Both beryllium and aluminium hydroxides are amphoteric in nature.
5	Carbides of beryllium (Be_2C) like aluminium carbide (Al_4C_3) give methane on hydrolysis.
6	Both beryllium and aluminium are rendered passive by nitric acid.

5.5.3 Chemical properties of alkaline earth metals

The alkaline earth metals are less reactive than the alkali metals. The reactivity of these elements increases on going down the group.

Reactivity towards the halogens:

All the alkaline earth metals combine with halogen at elevated temperatures to form their halides.

$M + X_2 \rightarrow MX_2$

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(M= Be, Mg, Ca, Sr, Ba, Ra ,
X = F, Cl, Br, I)

Thermal decomposition of $(NH_4)_2BeF_4$ is the best route for the preparation of BeF_2. $BeCl_2$ is conveniently made from the oxide.

$$BeO + C + Cl_2 \xrightarrow{600 - 800K} BeCl_2 + CO$$

Reactivity towards hydrogen:

All the elements except beryllium, combine with hydrogen on heating to form their hydrides with general formula MH_2. BeH_2 can be prepared by the reaction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \rightarrow 2BeH_2 + LiCl + AlCl_3$$

5.5.4 Uses of alkaline earth metals

Uses of beryllium

1. Because of its low atomic number and very low absorption for X-rays, it is used as radiation windows for X-ray tubes and X-ray detectors.
2. The sample holder in X-ray emission studies usually made of beryllium
3. Since beryllium is transparent to energetic particles, it is used to build the 'beam pipe' in accelerators.
4. Because of its low density and diamagnetic nature, it is used in various detectors.

Uses of magnesium

1. Removal of sulphur from iron and steel.
2. Used as photoengrave plates in printing industry.
3. Magnesium alloys are used in aeroplane and missile construction.
4. Mg ribbon is used in synthesis of Grignard reagent in organic synthesis.
5. It alloys with aluminium to improve its mechanical, fabrication and welding property.
6. As a desiccant .
7. As sacrificial anode in controlling galvanic corrosion.

Uses of calcium

1. As a reducing agent in the metallurgy of uranium, zirconium and thorium.
2. As a deoxidiser, desulphuriser or decarboniser for various ferrous and non-ferrous alloys.
3. In making cement and mortar to be used in construction.
4. As a getter in vacuum tubes.
5. In dehydrating oils
6. In fertilisers, concrete and plaster of paris.

Uses of strontium

1. ^{90}Sr is used in cancer therapy.
2. ^{87}Sr / ^{86}Sr ratios are commonly used

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in marine investigations as well as in teeth, tracking animal migrations or in criminal forensics.

3. Dating of rocks.

4. As a radioactive tracer in determining the source of ancient archaeological materials such as timbers and coins.

Uses of Barium

1. Used in metallurgy, its compounds are used in pyrotechnics, petroleum mining and radiology.

2. Deoxidiser in copper refining.

3. Its alloys with nickel readily emits electrons hence used in electron tubes and in spark plug electrodes.

4. As a scavenger to remove last traces of oxygen and other gases in television and other electronic tubes.

5. An isotope of barium ^{133}Ba, used as a source in the calibration of gamma ray detectors in nuclear chemistry.

Uses of Radium

Used in self-luminous paints for watches, nuclear panels, aircraft switches, clocks and instrument dials.

5.6. General characteristics of the compounds of the alkaline earth metals

The dipositive oxidation state (M^{2+}) is the predominant valence of group 2 elements. The alkaline earth metals form compounds which are predominantly ionic. However, they are less ionic than the corresponding compounds of alkali metals. This is due to increased nuclear charge and smaller size. The general characteristics of some of the compounds of alkaline earth metals are described below.

(a) Oxides

Generally alkaline earth metals form monoxides and peroxides.

Monoxides

Monoxides are obtained by heating the metals in oxygen. BeO and MgO are almost insoluble in water. On the other hand, oxides of other elements form hydroxides. BeO is amphoteric; MgO is weakly basic while CaO, SrO and BaO are strongly basic.

BeO oxide is covalent due to the small size of Be^{2+}ion,while other oxides are ionic in nature.

Peroxides

Except beryllium, all the remaining metals form peroxides. It is prepared by heating monoxides with oxygen at high temperature.

$$2\ BaO + O_2 \longrightarrow 2\ BaO_2$$

b)Hydroxides:

All the oxides except BeO are basic in nature and react with water to form sparingly soluble hydroxides.

$$MO + H_2O \rightarrow M(OH)_2$$

The solubility, thermal stability

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and the basic character of the hydroxides increase down the group. The alkaline earth metal hydroxides are, however, less basic and less stable than alkali metal hydroxides. Beryllium hydroxide is amphoteric in nature as it reacts with both acid and alkali.

$$Be(OH)_2 + 2\ NaOH \rightarrow Na_2BeO_2 + 2H_2O$$

$$Be(OH)_2 + 2HCl \rightarrow BeCl_2 + 2H_2O$$

c) Halides:

Alkaline earth metals form halides with general formula MX_2. They can be prepared by heating metals with halogens on heating.

$$M + X_2 \longrightarrow MX_2$$

Beryllium halides are covalent on account of smaller size of Be^{+2}. Beryllium halides are hygroscopic, fume in moist air and soluble in organic solvents. Beryllium chloride has a chain structure in the solid state as shown in figure 5.9 (structure-a). In the vapour phase $BeCl_2$ tends to form a chloro-bridged dimer (structure-c) which dissociates into the linear monomer at high temperatures of the order of 1200 K. (structure-b).

Except beryllium halides, all the other halides of alkaline earth metals are ionic in nature. Chloride and fluorides of the other metals are ionic solids. These are good conductors of electricity in fused state and in aqueous solutions. The tendency to form halide hydrates gradually decreases (for example, $MgCl_2.8H_2O$, $CaCl_2.6H_2O$, $SrCl_2.6H_2O$ and $BaCl_2.2H_2O$) down the group.

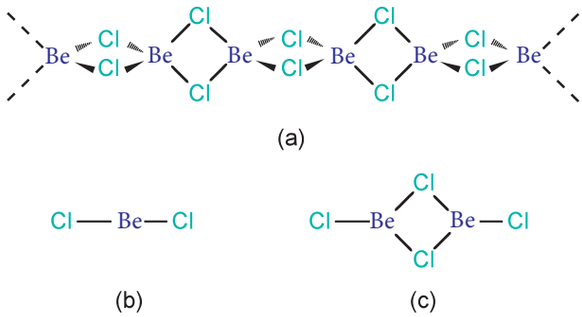

Figure 5.9 Structure of beryllium chloride

Salts of oxo acids

The alkaline earth metals form salts of oxo acids. Some of these are given below:

Carbonates:

All the carbonates decompose on heating to give carbon dioxide and the oxide.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

- The solubility of carbonates in water decreases down the group.
- The thermal stability increases down the group with increasing cationic size.

Table 5.13 Decomposition temperature of alkaline metal carbonates and sulphates

Element	Decomposition temp for carbonates (in °C)	Decomposition temp for sulphates (in °C)
Be	25	500
Mg	540	895
Ca	900	1149
Sr	1290	1374
Ba	1360	-

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Sulphates:

The sulphates of the alkaline earth metals are all white solids and stable to heat. $BeSO_4$, and $MgSO_4$ are readily soluble in water; the solubility decreases from $CaSO_4$ to $BaSO_4$. The greater hydration enthalpies of Be^{2+} and Mg^{2+} ions overcome the lattice enthalpy factor and therefore their sulphates are soluble in water.

Nitrates:

The nitrates are made by dissolution of the carbonates in dilute nitric acid. Magnesium nitrate crystallises with six molecules of water, whereas barium nitrate crystallises as the anhydrous salt. This again shows a decreasing tendency to form hydrates with increasing size. All of them decompose on heating to give the oxide.

5.6.1 Important compounds of calcium

Quick lime, CaO

Preparation

It is produced on a commercial scale by heating limestone in a lime kiln in the temperature range 1070-1270K.

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

The reaction being reversible, carbon dioxide is removed as soon as it is produced to enable the reaction to proceed to completion.

Properties

Calcium oxide is a white amorphous solid.

It has a melting point of 2870 K.

(i)It absorbs moisture and carbon dioxide on exposure to atmosphere.

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

$$CaO + CO_2 \rightarrow CaCO_3$$

(ii)The addition of limited amount of water breaks the lump of lime. This process is called slaking of lime and the product is slaked lime.

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

(iii)The mixtureof Quick lime(CaO) and sodium hydroxide is called soda lime.

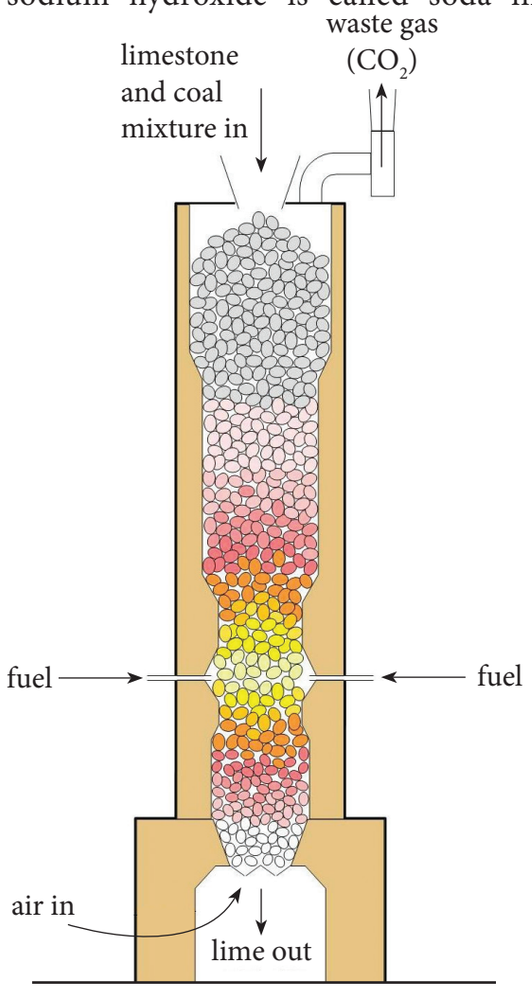

Figure 5.10 Preparation of Quick Lime

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(iv)It combines with acidic oxides such as SiO_2 and P_4O_{10} to form $CaSiO_3$ and $Ca_3(PO_4)_2$, respectively.

$CaO + SiO_2 \rightarrow CaSiO_3$

$6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$

Uses

Calcium oxide is used

(i) to manufacture cement, mortar and glass.

(ii) in the manufacture of sodium carbonate and slaked lime.

(iii) in the purification of sugar.

(iv) as a drying agent.

5.6.2 Calcium hydroxide

Preparation

Calcium hydroxide is prepared by adding water to quick lime, CaO.

Properties

It is a white powder. It is sparingly soluble in water. The aqueous solution is known as lime water and a suspension of slaked lime in water is known as milk of lime.

When carbon dioxide is passed through lime water, it turns milky due to the formation of calcium carbonate.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

On passing excess of carbon dioxide, the precipitate dissolves to form calcium hydrogen carbonate.

$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$2Ca(OH)_2 + 2Cl_2 \rightarrow$

$CaCl_2 + Ca(OCl)_2 + 2H_2O$

Uses:

Calcium hydroxide is used

(i) in the preparation of mortar, a building material.

ii) in white wash due to its disinfectant nature.

(iii) in glass making, in tanning industry, in the preparation of bleaching powder and for the purification of sugar.

5.6.3 Gypsum ($CaSO_4.2H_2O$)

Gypsum beds were formed due to the evaporation of water from the massive prehistoric sea basins. When water evaporates, the minerals present in it become concentrated, and crystallise.



Figure 5.11 A Gypsum Quarry

Properties of Gypsum

- Gypsum is a soft mineral, which is moderately soluble in water. The solubility of this mineral in water is

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affected by temperature. Unlike other salts, gypsum becomes less soluble in water as the temperature increases. This is known as retrograde solubility, which is a distinguishing characteristic of gypsum.

- Gypsum is usually white, colorless, or gray in color. But sometimes, it can also be found in the shades of pink, yellow, brown, and light green, mainly due to the presence of impurities.

- Gypsum crystals are sometimes found to occur in a form that resembles the petals of a flower. This type of formation is referred to as 'desert rose', as they mostly occur in arid areas or desert terrains.

- Gypsum is known to have low thermal conductivity, which is the reason why it is used in making drywalls or wallboards. Gypsum is also known as a natural insulator.

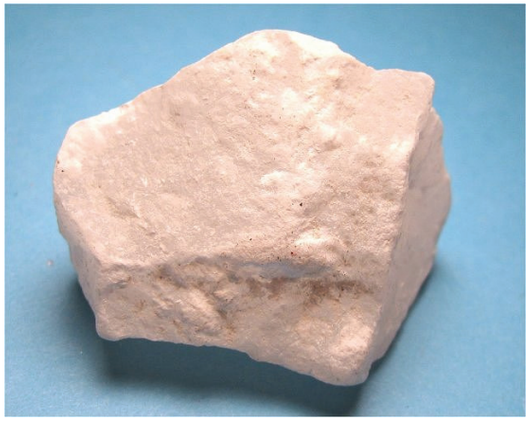

Figure 5.12 -**The Alabaster Variety of Gypsum**

- Alabaster is a variety of gypsum, that is highly valued as an ornamental stone. It has been used by the sculptors for centuries. Alabaster is granular and opaque.

- Gypsum has hardness between 1.5 to 2 on Moh's Hardness Scale. Its specific gravity is 2.3 to 2.4.

Uses of Gypsum

- The alabaster variety of gypsum was used in ancient Egypt and Mesopotamia by the sculptors. The ancient Egyptians knew how to turn gypsum into plaster of Paris about 5,000 years ago. Today, gypsum has found a wide range of uses and applications in human society, some of which are enlisted below.

- Gypsum is used in making drywalls or plaster boards. Plaster boards are used as the finish for walls and ceilings, and for partitions.

- Another important use of gypsum is the production of plaster of Paris. Gypsum is heated to about 300 degree Fahrenheit to produce plaster of Paris, which is also known as gypsum plaster. It is mainly used as a sculpting material.

- Gypsum is used in making surgical and orthopedic casts, such as surgical splints and casting moulds.

- Gypsum plays an important role in agriculture as a soil additive, conditioner, and fertilizer. It helps loosen up compact or clay soil, and provides calcium and sulphur, which are essential for the healthy growth of a plant. It can also be used for removing sodium ion from soils having excess salinity.

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- Gypsum is used in toothpastes, shampoos, and hair products, mainly due to its binding and thickening properties.

- Gypsum is a component of Portland cement, where it acts as a hardening retarder to control the speed at which concrete sets.

- To sum up, gypsum is one of the most abundant minerals that have endless uses and applications. Mining of gypsum is simple and easy, as the mineral occurs in large thick beds near the Earth's surface. However, large-scale mining of gypsum involves considerable damage to the environment. Gypsum can also be recycled, but not much importance has been given to recycle this mineral due to its abundance.

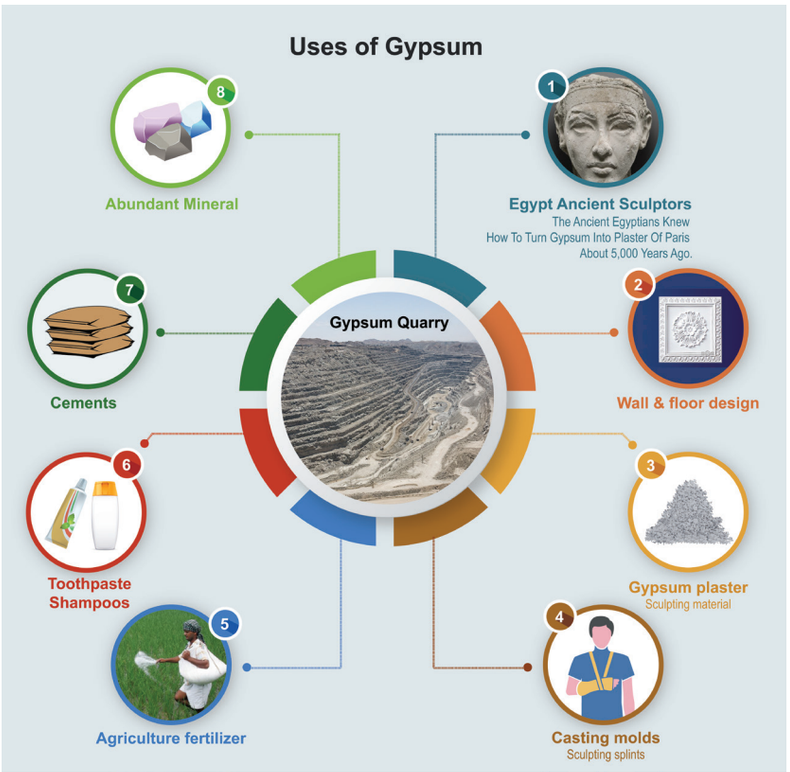

Figure 5.13 -**Uses of Gypsum**

5.6.4 Plaster of paris

Calcium Sulphate hemihydrate : $CaSO_4 \cdot ½\ H_2O$ (Plaster of Paris)

It is a hemihydrate of calcium sulphate. It is obtained when gypsum, $CaSO_4 \cdot 2H_2O$, is heated to 393 K.

$$2CaSO_4 \,.\, 2H_2O(s) \rightarrow 2\,CaSO_4 \,.\, ½\,H_2O + 3H_2O$$

Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate, $CaSO_4$ is formed. This is known as 'dead burnt plaster'.

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It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes.

Uses:

Plaster of Paris is used as/in,

1. The building industry as well as plasters.
2. For immobilising the affected part of organ where there is a bone fracture or sprain.
3. Employed in dentistry, in ornamental work and for making casts of statues and busts.



5.7 Biological importance of magnesium and calcium

Magnesium and calcium also plays a vital role in biological functions. A typical adult human body contains about 25 g of magnesium and 1200 g of calcium. Magnesium plays an important role in many biochemical reactions catalysed by enzymes. It is the co-factor of all enzymes that utilize ATP in phosphate transfer and energy release. It also essential for DNA synthesis and is responsible for the stability and proper functioning of DNA. It is also used for balancing electrolytes in our body. Deficiency of magnesium results into convulsion and neuromuscular irritation.

Calcium is a major component of bones and teeth. It is also present in in blood and its concentration is maintained by hormones (calcitonin and parathyroid hormone). Deficiency of calcium in blood causes it to take longer time to clot. It is also important for muscle contraction.

The main pigment that is responsible for photosynthesis, chlorophyll, contains magnesium which plays an important role in photosynthesis.

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SUMMARY

The elements belonging to groups 1 and 2 of the modern periodic table are called s-block elements. They are called so because the valence electron occupies the s orbitals. The group 1 elements have a general outer electronic configuration ns^1 and are called alkali metals. The group 2 elements have a general outer electronic configuration ns^2 and these are called alkaline earth metals as they are found in earth's crust and their oxides and hydroxides are alkaline in nature. Elements belonging to group 1 and 2 are highly reactive and forms M^+ and M^{2+} cations respectively. Their physical and chemical properties of both groups show a regular trend as we move down the group. The atomic and ionic radii increase as we move down the group while their ionisation enthalpies decrease.

The first element in each of these groups, lithium in Group 1 and beryllium in Group 2 shows some difference in behaviour with the elements in rest of their groups and show similarities in properties to the second member of the next group. This behaviour is known as the 'diagonal relationship' in the periodic table.

The alkali metals are soft and silvery white in colour with low melting points. They are highly reactive. The compounds of alkali metals are predominantly ionic. They form metal hydrides and halides with hydrogen and halogens respectively. Their oxides and hydroxides are soluble in water forming strong alkalies. Important compounds of sodium include sodium carbonate, sodium chloride, sodium hydroxide and sodium hydrogen carbonate. Sodium hydroxide is manufactured by Castner-Kellner process and sodium carbonate by Solvay process.

The chemistry of alkaline earth metals is similar to alkali metals. However, we observe some differences because of their reduced atomic and ionic sizes and increased cationic charges. Their oxides and hydroxides are less basic than the alkali metal oxides and hydroxides. They also form hydrides and halides with hydrogen and halogens respectively. Industrially important compounds of calcium include calcium oxide (lime), calcium hydroxide (slaked lime), calcium sulphate hemihydrate (Plaster of Paris), calcium carbonate (limestone) and cement. Portland cement is an important constructional material. It is manufactured by heating a pulverised mixture of limestone and clay in a rotary kiln. The clinker thus obtained is mixed with some gypsum (2-3%) to give a fine powder of cement. All these substances find variety of uses in different areas.

Monovalent sodium and potassium ions and divalent magnesium and calcium ions are found in large proportions in biological fluids. These ions perform important biological functions such as maintenance of ion balance and nerve impulse conduction.

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EVALUATION

1. For alkali metals, which one of the following trends is incorrect ?

   a) Hydration energy : Li > Na > K > Rb

   b) Ionisation energy : Li > Na > K > Rb

   c) Density : Li < Na < K < Rb

   d) Atomic size : Li < Na < K < Rb

2. Which of the following statements is incorrect ?

   a) Li^+ has minimum degree of hydration among alkali metal cations.

   b) The oxidation state of K in KO_2 is +1

   c) Sodium is used to make Na / Pb alloy

   d) $MgSO_4$ is readily soluble in water

3. Which of the following compounds will not evolve H_2 gas on reaction with alkali metals ?

   a) ethanoic acid b) ethanol

   c) phenol d) none of these

4. Which of the following has the highest tendency to give the reaction $M^+(g) \xrightarrow[\text{Medium}]{\text{Aqueous}} M^+(aq)$

   a) Na b) Li c) Rb d) K

5. sodium is stored in

   a) alcohol b) water c) kerosene d) none of these

6. RbO_2 is

   a) superoxide and paramagnetic b) peroxide and diamagnetic

   c) superoxide and diamagnetic d) peroxide and paramagnetic

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7. Find the wrong statement

a) sodium metal is used in organic qualitative analysis

b) sodium carbonate is soluble in water and it is used in inorganic qualitative analysis

c) potassium carbonate can be prepared by solvay process

d) potassium bicarbonate is acidic salt

8. Lithium shows diagonal relationship with

a) sodium b) magnesium c) calcium d) aluminium

9. Incase of alkali metal halides, the ionic character increases in the order

a) MF < MCl < MBr < MI

b) MI < MBr < MCl < MF

c) MI < MBr < MF < MCl

d) none of these

10. In which process, fused sodium hydroxide is electrolysed for extraction of sodium ?

a) Castner's process b) Cyanide process

c) Down process d) All of these

11. The product obtained as a result of a reaction of nitrogen with CaC_2 is (NEET - Phase I)

a) $Ca(CN)_3$ b) CaN_2 c) $Ca(CN)_2$ d) Ca_3N_2

12. Which of the following has highest hydration energy

a) $MgCl_2$ b) $CaCl_2$ c) $BaCl_2$ d) $SrCl_2$

13. Match the flame colours of the alkali and alkaline earth metal salts in the bunsen burner

(p) Sodium (1) Brick red

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(q) Calcium	(2)	Yellow
(r) Barium	(3)	Lilac (violet)
(s) Strontium	(4)	Apple green
(t) Cesium	(5)	Crimson red
(u) Potassium	(6)	Blue

a) p - 2, q - 1, r - 4, s - 5, t - 6, u - 3

b) p - 1, q - 2, r - 4, s - 5, t - 6, u - 3

c) p - 4, q - 1, r - 2, s - 3, t - 5, u - 6

d) p - 6, q - 5, r - 4, s - 3, t - 1, u - 2

14. Assertion : Generally alkali and alkaline earth metals form superoxides

Reason : There is a single bond between O and O in superoxides.

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

d) both assertion and reason are false

15. Assertion : $BeSO_4$ is soluble in water while $BaSO_4$ is not

Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant.

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

d) both assertion and reason are false

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16. Which is the correct sequence of solubility of carbonates of alkaline earth metals ?

a) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$

b) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

c) $CaCO_3 > BaCO_3 > SrCO_3 > MgCO_3$

d) $BaCO_3 > CaCO_3 > SrCO_3 > MgCO_3$

17. In context with beryllium, which one of the following statements is incorrect ? (NEET Phase - 2)

a) It is rendered passive by nitric acid

b) It forms Be_2C

c) Its salts are rarely hydrolysed

d) Its hydride is electron deficient and polymeric

18. The suspension of slaked lime in water is known as (NEET Phase - II)

a) lime water b) quick lime

c) milk of lime d) aqueous solution of slaked lime

19. A colourless solid substance (A) on heating evolved CO_2 and also gave a white residue, soluble in water. Residue also gave CO_2 when treated with dilute HCl.

a) Na_2CO_3 b) $NaHCO_3$ c) $CaCO_3$ d) $Ca(HCO_3)_2$

20. The compound (X) on heating gives a colourless gas and a residue that is dissolved in water to obtain (B). Excess of CO_2 is bubbled through aqueous solution of B, C is formed. Solid (C) on heating gives back X. (B) is

a) $CaCO_3$ b) $Ca(OH)_2$ c) Na_2CO_3 d) $NaHCO_3$

21. Which of the following statement is false ? (NEET - Phase - I)

a) Ca^{2+} ions are not important in maintaining the regular beating of the heart

b) Mg^{2+} ions are important in the green parts of the plants

c) Mg^{2+} ions form a complex with ATP

d) Ca^{2+} ions are important in blood clotting

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22. The name 'Blue John' is given to which of the following compounds ?

a) CaH_2 b) CaF_2 c) $Ca_3(PO_4)_2$ d) CaO

23. Formula of Gypsum is

a) $CaSO_4 . 2H_2O$ b) $CaSO_4 . ½ H_2O$

c) $3 CaSO_4 . H_2O$ d) $2CaSO_4 . 2H_2O$

24. When CaC_2 is heated in atmospheric nitrogen in an electric furnace the compound formed is

a) $Ca(CN)_2$ b) CaNCN

c) CaC_2N_2 d) $CaNC_2$

25. Among the following the least thermally stable is

(a) K_2CO_3 b) Na_2CO_3

(c) $BaCo_3$ d) Li_2CO_3

II. Write brief answer to the following questions:

26. Why sodium hydroxide is much more water soluble than sodium chloride?

27. Write the chemical equations for the reactions involved in solvay process of preparation of sodium carbonate.

28. An alkali metal (x) forms a hydrated sulphate, $X_2SO_4. 10H_2O$. Is the metal more likely to be sodium (or) potassium.

29. Write balanced chemical equation for each of the following chemical reactions.

(i) Lithium metal with nitrogen gas

(ii) heating solid sodium bicarbonate

(iii) Rubidum with oxygen gas

(iv) solid potassium hydroxide with CO_2

(v) heating calcium carbonate

(vi) heating calcium with oxygen

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30. Discuss briefly the similarities between Lithium and Magnesium.

31. Give the systematic names for the following

(i) milk of magnesia (ii) lye (iii) lime (iv) Caustic potash

(v) washing soda (vi) soda ash (v) trona

32. Substantiate Lithium fluoride has the lowest solubility among group one metal fluorides.

33. Mention the uses of plaster of paris

34. Beryllium halides are covalent whereas magnesium halides are ionic why?

35. Alkaline earth metal (A), belongs to 3rd period reacts with oxygen and nitrogen to form compound (B) and (C) respectively. It undergoes metal displacement reaction with $AgNO_3$ solution to form compound (D). Identify A, B, C and D.

36. Write balanced chemical equation for the following processes

(a) heating calcium in oxygen

(b) heating calcium carbonate

(c) evaporating a solution of calcium hydrogen carbonate

(d) heating calcium oxide with carbon

37. Explain the important common features of Group 2 elements.

38. Discuss the similarities between beryllium and aluminium.

39. Why alkaline earth metals are harder than alkali metals.

40. How is plaster of paris prepared?

41. Give the uses of gypsum.

42. Describe briefly the biological importance of Calcium and magnesium.

43. Which would you expect to have a higher melting point, magnesium oxide or magnesium fluoride? Explain your reasoning.

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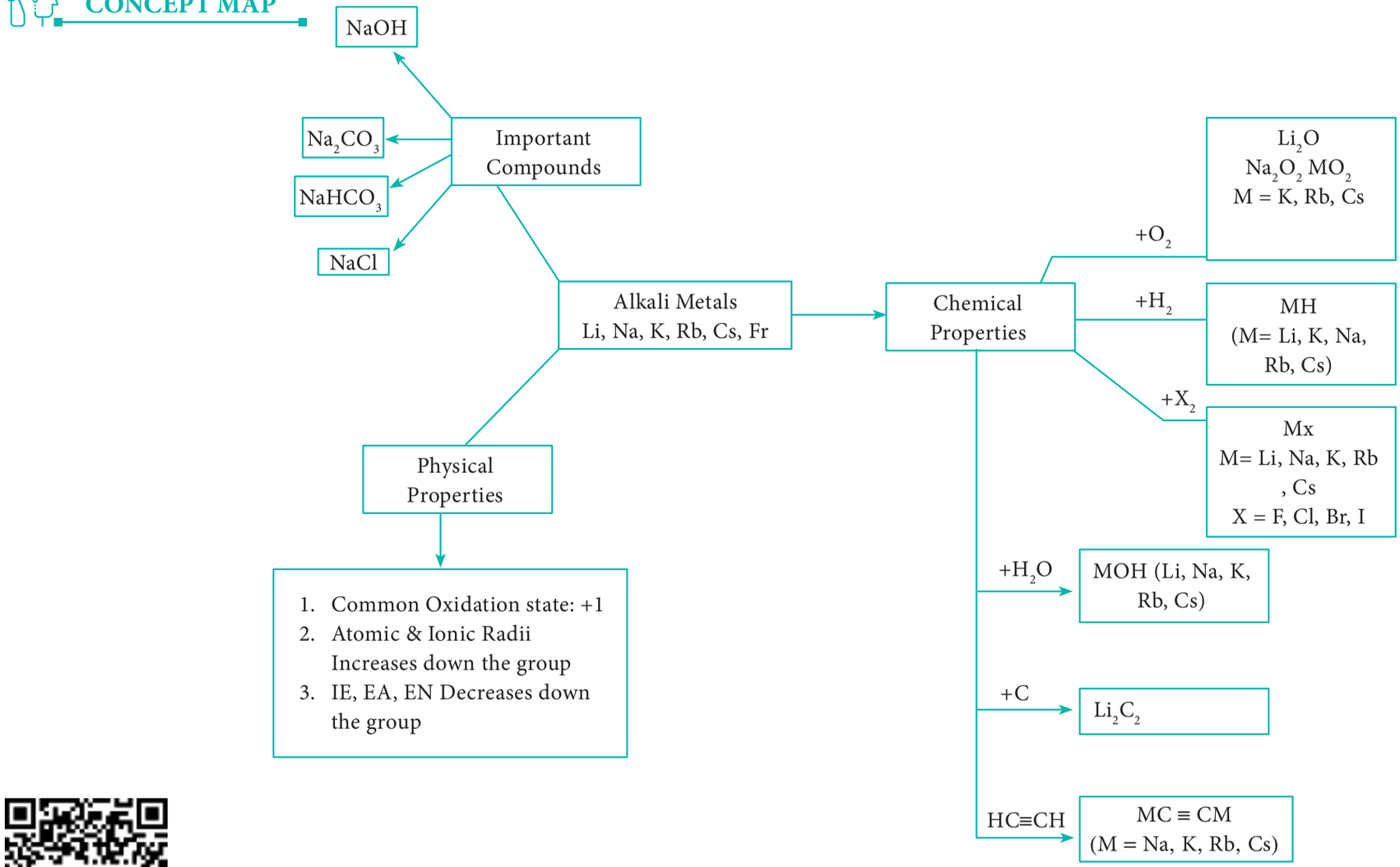
CONCEPT MAP



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ICT Corner

Flame test of alkali and alkaline earth elements (Virtual Lab)

By using this virtual lab you can perform the flame test of different alkali and alkali earth metals and see the colour of the flame produced.

Please go to the URL https://www.newpathonline.com/free-curriculumresources/virtual_lab/Flame_Test/9/12,13,14/1914
(or)
Scan the QR code on the right side

FHQ7U

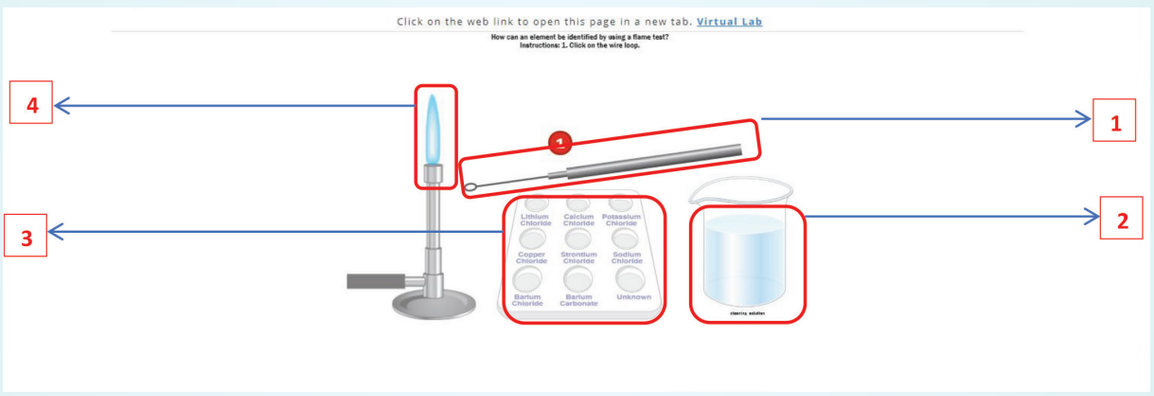
Step – 1

Open the Browser and type the URL given (or) Scan the QR Code. Just click the view button on the Flame test panel. This will open a flame test window as shown in the figure.

Step – 2

Follow the instrutions to perform a virtual flame test.

1. Click on the wire loop (1).
2. Move the wire loop to the cleaning solution (2). Click on the cleaning solution. The wire must be cleaned before each test to ensure there is no other salt on the loop.
3. Move the wire loop to the salt solution you want to test (3). Click on the salt solution.
4. Move the wire loop to the flame (4) and click on it.
5. You will see the characteristic colour change in the flame with respect to the metal ion



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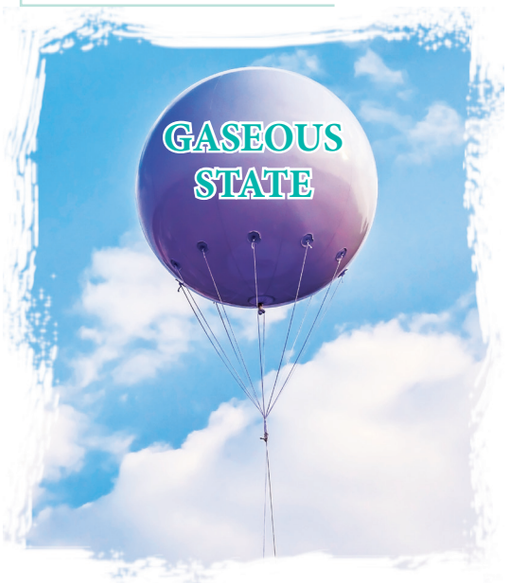
Unit 6

GASEOUS STATE

So many properties of properties of matter, especially when in gaseous form, can be deduced from hypothesis that their minute parts are in rapid motion, the velocity increasing with temperature, that the precise nature of this motion becomes a subject of rational curiosity.

James Clerk Maxwell





Jacques Charles
(1746-1823)

Learning Objectives

After studying this unit, students will be able to

- State the laws governing an ideal gas
- Demonstrate gas laws in various real life situations
- Derive ideal gas equation and perform calculations using it.
- State the deviations from ideal behavior
- Derive van der Waals equation.
- Define Graham's law of diffusion
- Define compressibility factor
- Explain critical phenomena
- Derive critical constants in terms of van der Waal's constants
- Explain Andrew's isotherms of carbon dioxide
- Describe Joule – Thomson effect and liquefaction of gases.

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6.1. Introduction

We can survive for weeks without food, days without water, but only minutes without air. Thus, we inhale a lungful of air every few seconds, keep some of the molecules for our own end, and some of the molecules that our body no longer needs, and exhale the mixture back into the surrounding air. The air around us is in the gaseous state, which is the simplest of the states of matter. Although the chemical behaviour of gases depends on their composition, all the gases have remarkably similar physical behaviour.

DO YOU KNOW?

Do you know the difference between gas and vapour?

Gas is a substance that is normally in a gaseous state at room temperature and 1 atm pressure, while vapour is the gaseous form of any substance that is a liquid or solid at room temperature and 1 atm pressure.

Earth is surrounded by an atmosphere of air whose composition in volume percentage is roughly 78 % nitrogen, 21 % oxygen and 1 % other gases. Of the known elements, only eleven are gases under normal atmospheric conditions. The elements hydrogen (H_2), nitrogen (N_2), oxygen (O_2), fluorine (F_2) and chlorine (Cl_2) exist as gaseous diatomic molecules. Another form of oxygen, namely, ozone (O_3) is also a gas at room temperature. The noble gases, namely, helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) of 18th group are monatomic gases. Compounds such as carbon monoxide (CO), carbon dioxide (CO_2), nitrogen dioxide (NO_2) and nitric oxide (NO) also exist in gaseous state under normal atmospheric conditions. In this unit you will learn the properties of gases and other related phenomena.

6.2. The Gas Laws

The gas laws have played a major role in the development of chemistry. The physical properties of all gases are governed by the gas laws that were formulated based on the studies of the properties like pressure, volume, etc., as a function of temperature. Before studying the gas laws in detail, let us understand an important parameter, namely, the pressure.

Pressure is defined as force divided by the area to which the force is applied. The SI unit of pressure is pascal which is defined as 1 Newton per square meter (Nm^{-2}). There are other units that are commonly used and their relation with the SI unit is as follows.

$$\text{Pressure} = \frac{\text{Force (N or kg m s}^{-2})}{\text{Area (m}^2)}$$

Table 6.1 Units of pressure

Unit	Symbol	Value (Nm^{-2} or $kgm^{-1}s^{-2}$)
pascal	Pa	1 Pa = 1 Nm^{-2}
atmosphere	atm	1 atm = 101325 Pa
millimeter of mercury	mmHg	1 mmHg = 133.322 Pa
bar	bar	1 bar = 10^5 Pa
torr	Torr	1 Torr = 133.322 Pa
pound per square inch	psi	1 psi = 6894.76 pa

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6.2.1 Boyle's Law: Pressure-Volume Relationship

Robert Boyle performed a series of experiments to study the relation between the pressure and volume of gases. The schematic of the apparatus used by him is shown in figure 6.1.

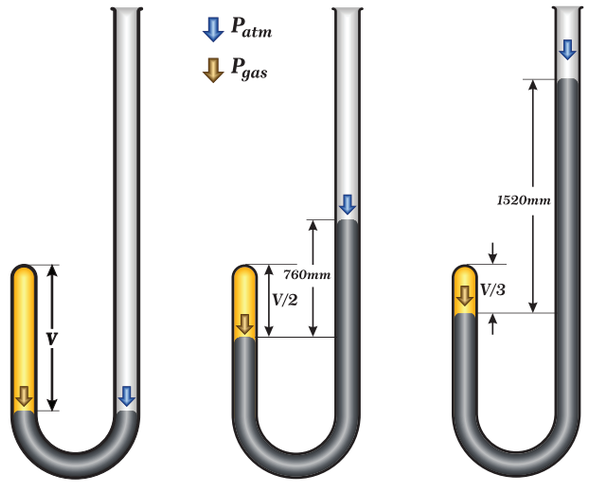

Figure. 6.1 Boyle's law experiment

Mercury was added through the open end of the apparatus such that the mercury level on both ends are equal as shown in the figure 6.1(a). Add more amount of mercury until the volume of the trapped air is reduced to half of its original volume as shown in figure 6.1(b). The pressure exerted on the gas by the addition of excess mercury is given by the difference in mercury levels of the tube. Initially the pressure exerted by the gas is equal to 1 atm as the difference in height of the mercury levels is zero. When the volume is reduced to half, the difference in mercury levels increases to 760 mm. Now the pressure exerted by the gas is equal to 2 atm. It led him to conclude that at a given temperature the volume occupied by a fixed mass of a gas is inversely proportional to its pressure.

Mathematically, the Boyle's law can be written as

$$V \propto \frac{1}{P} \quad \text{------- (6.1)}$$

(T and n are fixed, T-temperature, n- number of moles)

$$V = k \times \frac{1}{P} \quad \text{------- (6.2)}$$

k – proportionality constant

When we rearrange equation 6.2.

$PV = k$ ------ (6.2a)(at constant temperature and mass)

Boyle's law is applicable to all gases regardless of their chemical identity (provided the pressure is low). Therefore, for a given mass of a gas under two different sets of conditions at constant temperature we can write

$$P_1V_1 = P_2V_2 = k \quad \text{------ (6.3)}$$

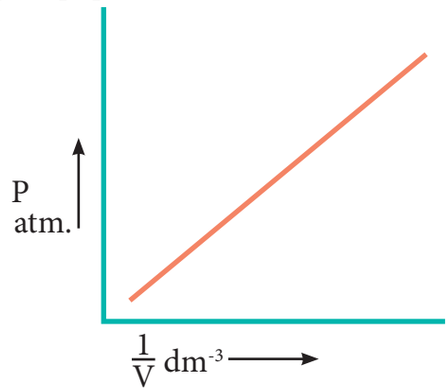

Figure. 6.2 a Graphical representation of Boyle's law (equation 6.2)

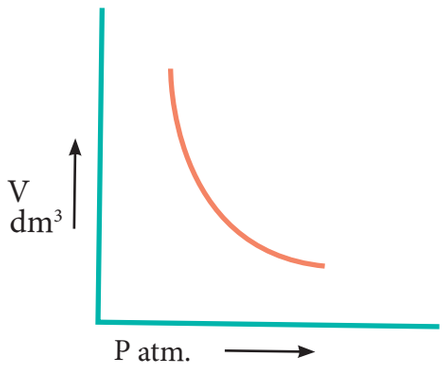

Figure. 6.2 b Graphical representation of Boyle's law (equation 6.2 a)

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The PV relationship can be understood as follows. The pressure is due to the force of the gas particles on the walls of the container. If a given amount of gas is compressed to half of its volume, the density is doubled and the number of particles hitting the unit area of the container will be doubled. Hence, the pressure would increase twofold.

Consequence of Boyle's law

The pressure-density relationship can be derived from the Boyle's law as shown below.

$$P_1V_1 = P_2V_2 \quad \text{(Boyle's law)}$$

$$P_1 \frac{m}{d_1} = P_2 \frac{m}{d_2}$$

where "m" is the mass, d_1 and d_2 are the densities of gases at pressure P_1 and P_2.

$$\frac{P_1}{d_1} = \frac{P_2}{d_2} \quad \text{------ (6.4)}$$

In other words, the density of a gas is directly proportional to pressure.



All the passenger aeroplane cabins have to be artificially pressurised. do you know why?

Most commercial aeroplanes fly at about 30,000 feet altitude. The pressure decreases with the increase in altitude as there are fewer molecules per unit volume of air. Hence, while at air, the pressure around the aeroplane will be so low that one could pass out for lack of oxygen. For this reason aeroplanes cabins are artificially pressurized.

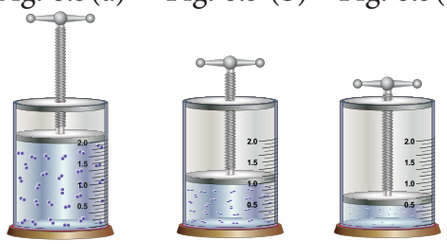


Similarly, the effect of drop in pressure is felt as a little pain in the ears by a person while ascending a mountain in a plain. Though the external pressure drops, the internal pressure within the ear cavities remains the same. This creates an imbalance. The greater internal pressure forces the eardrum to bulge outward causing pain. The excess air within the ear cavities escapes after some time and with the help of yawning and thereby equalizing the internal and external pressure to relieve the pain.

Underwater divers are advised not to hold the breath unnecessarily while diving. Do you know why?

In figure (6.3) let us find the missing parameters (volume in 6.3 (b) and pressure in 6.3(c))

Fig. 6.3(a) Fig. 6.3 (b) Fig. 6.3(c)



P_1 = 1 atm.	P_2=2 atm.	P_3=? atm.
V_1 = 1 dm^3	V_2 = ? dm^3	V_3 = 0.25dm^3
T = 298 K	T = 298 K	T = 298 K

Figure. 6.3 Effect of pressure on volume of the gas to verify Boyle's law

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Solution:

According to Boyle's law, at constant temperature for a given mass of gas at constant temperature,

$P_1V_1 = P_2V_2 = P_3V_3$

$1\ atm \times 1\ dm^3 = 2\ atm \times V_2 = P_3 \times 0.25\ dm^3$

$\Psi\ 2\ atm \times V_2 = 1\ atm \times 1\ dm^3$

$$V_2 = \frac{1\ \cancel{atm} \times 1\ dm^3}{2\ \cancel{atm}}$$

$\boxed{V_2 = 0.5\ dm^3}$

and $P_3 \times 0.25\ dm^3 = 1\ atm \times 1\ dm^3$

$$P_3 = \frac{1\ atm \times 1\ \cancel{dm^3}}{0.25\ dm^3}$$

$\boxed{P_3 = 4\ atm}$

Evaluate Yourself

1. Freon-12, the compound widely used in the refrigerator system as coolant causes depletion of ozone layer. Now it has been replaced by eco-friendly compounds. Consider 1.5 dm^3 sample of gaseous Freon at a pressure of 0.3 *atm*. If the pressure is changed to 1.2 *atm*. at a constant temperature, what will be the volume of the gas increased or decreased?

2. Inside a certain automobile engine, the volume of air in a cylinder is 0.375 dm^3, when the pressure is 1.05 *atm*. When the gas is compressed to a volume of 0.125 dm^3 at the same temperature, what is the pressure of the compressed air?

6.2.2 Charles Law (Volume-temperature relationship)

The relationship between volume of a gas and its temperature was examined by J. A. C. Charles. He observed that for a fixed mass of a gas at constant pressure, the volume is directly proportional to its temperature (K). Mathematically it can be represented as (at constant P and n)

$$V = kT \quad \text{------- (6.5)}$$

$$\text{or} \quad \frac{V}{T} = \text{Constant}$$

If the temperature of the gas increases, the volume also increases in direct proportion, so that $\frac{V}{T}$ is a constant. For the same system at constant pressure, one can write

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{Constant} \quad \text{----- (6.6)}$$

For example, if a balloon is moved from an ice cold water bath to a boiling water bath, the temperature of the gas increases. As a result, the gas molecules inside the balloon move faster and gas expands. Hence, the volume increases.



Ice water Boiling water

Figure. 6.4 Air filled balloon in ice cold and hot water

Variation of volume with temperature at constant pressure

The plot of the volume of the gas against its temperature at a given pressure

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is shown in the figure 6.5. From the graph it is clear that the volume of the gas linearly increases with temperature at a given pressure. Such lines are called isobars. It can be expressed by the following straight line equation.

V = mT + C where T is the temperature in degree Celsius and m & C are constants.

When T= 0 °C the volume becomes V_0. Hence, V_0 = C and slope of the straight line m is equal to ΔV / ΔT. Therefore the above equation can be written in the following form.

$$V = \left(\frac{\Delta V}{\Delta T}\right)T + V_0 \quad \text{-------- (6.7)}$$

(n, P are constant)

Divide the equation 6.7 by V_o

$$\frac{V}{V_0} = \frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right)T + 1 \quad \text{-------- (6.8)}$$

Charles and Gay Lussac found that under constant pressure, the relative increase in volume per degree increase in temperature is same for all gases. The relative increase in volume per ° C (α)is equal to $\frac{1}{V_0}\left(\frac{\Delta V}{\Delta T}\right)$.

Therefore

$$\frac{V}{V_0} = \alpha T + 1$$

$$V = V_0(\alpha T + 1) \text{ ------ (6.9)}$$

Charles found that the coefficient of expansion is approximately equal to 1/273. It means that at constant pressure for a given mass, for each degree rise in temperature, all gases expand by 1/273 of their volume at 0 °C

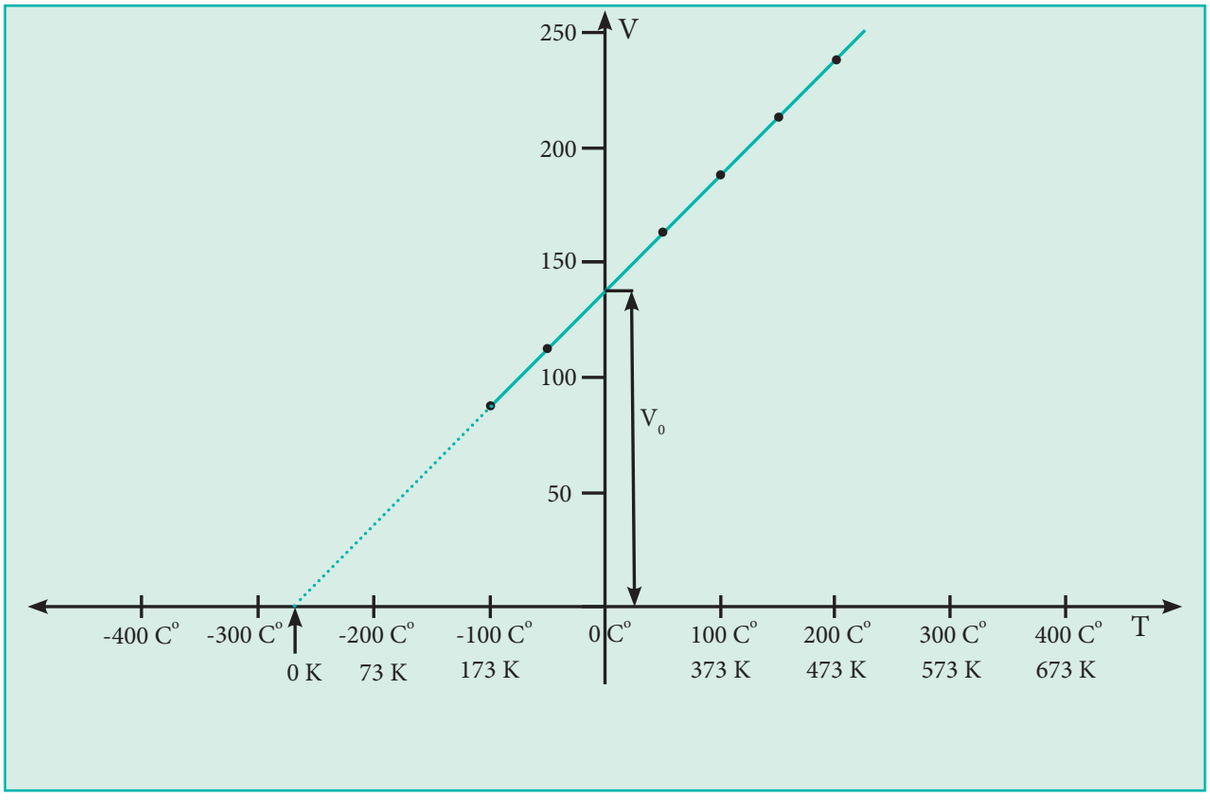

Figure. 6.5 Plot of volume vs temperature for an ideal gas

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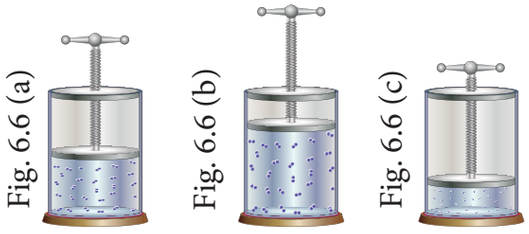
If we extrapolate the straight line in the figure 6.5 beyond the experimental measurements, the straight line intersects the temperature axis (x-axis) at -273⁰ C. This shows that the volume of the gas becomes zero at -273⁰ C, more precisely this temperature is -273.15⁰ C. Beyond this temperature the gas would have a negative volume which is physically impossible. For this reason, this temperature was defined as absolute zero by Kelvin and he proposed a new temperature scale with absolute zero as starting point which is now called Kelvin scale. The only difference between the Kelvin scale of temperature and Celsius scale of temperature is that the zero position is shifted. The boiling and freezing point of water in both scales are given below.

	Kelvin Scale	Celsius scale
Absolute Zero	0 K	-273.15 °C
Freezing point of water	273.15 K	0 °C
Boiling point of water	373.15 K	100 °C

Example:

In figure 6.6 let us find the missing parameters (volume in 6.6 (b) and temperature in 6.6(c))



P = 1 atm.	P = 1 atm.	P = 1 atm.
V_1 = 0.3 dm^3	V_2 = ? dm^3	V_3 = 0.15 dm^3
T_1 = 200 K	T_2 = 300 K	T_3 = ? K

Fig. 6.6. Effect of temperature on volume of the gas to verify Charles law

Solution:

According to Charles law,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \frac{V_3}{T_3}$$

$$\frac{0.3\ dm^3}{200\ K} = \frac{V_2}{300\ K} = \frac{0.15\ dm^3}{T_3}$$

$$\frac{V_2}{300\ K} = \frac{0.3\ dm^3}{200\ K}$$

$$V_2 = \frac{1.5}{\cancel{300\ K} \times 0.3\ dm^3}{\cancel{200\ K}}$$

V_2 = 0.45 dm^3 and

$$\frac{0.15 dm^3}{T_3} = \frac{0.3\ dm^3}{200\ K}$$

$$T_3 = \frac{0.5}{\cancel{0.15 dm^3} \times 200\ K}{\cancel{0.3\ dm^3}}$$

T_3 = 100 K

Evaluate Yourself

3. A sample of gas has a volume of 3.8 dm^3 at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume gets reduced to 2.27 dm^3. What is its initial temperature?

6.2.3 Gay-Lussac's Law (Pressure-temperature relationship)

Joseph Gay-Lussac stated that, at constant volume the pressure of a fixed mass of a gas is directly proportional to temperature.

$P \alpha T$

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or $\frac{P}{T} = \text{Constant } k$

If P_1 and P_2 are the pressures at temperatures T_1 and T_2, respectively, then from Gay Lussac's law

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Activity -1

The table below contains the values of pressure measured at different temperatures for 1 mole of an ideal gas. Plot the values in a graph and verify the Gay Lussac's law. [Lines in the pressure vs temperature graph are known as iso chores (constant volume) of a gas.]

Temperature (in deg celcius)	32	69	94	130	154	191
Pressure in 50 L container (atm)	0.51	0.56	0.6	0.66	0.7	0.76
Pressure in 75 L container (atm)	0.34	0.37	0.40	0.44	0.47	0.51

6.2.4 Avogadro's Hypothesis

Avogadro hypothesised that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. The mathematical form of Avogadro's hypothesis may be expressed as

$V \alpha n$,

$$\frac{V_1}{n_1} = \frac{V_2}{n_2} = \text{constant} \text{ -------- } (6.10)$$

where V_1 & n_1 are the volume and number of moles of a gas and V_2 & n_2 are a different set of values of volume and number of moles of the same gas at same temperature and pressure.

Evaluate Yourself

4. An athlete in a kinesiology research study has his lung volume of 7.05 dm^3 during a deep inhalation. At this volume the lungs contain 0.312 mole of air. During exhalation the volume of his lung decreases to 2.35 dm^3. How many moles of air does the athlete exhale during exhalation? (assume pressure and temperature remain constant)

6.3. Ideal gas equation

The gaseous state is described completely using the following four variables T, P, V and n and their relationships were governed by the gas laws studied so far.

Boyle's law $V \alpha \frac{1}{P}$

Charles law $V \alpha T$

Avogadro's law $V \alpha n$

We can combine these equations into the following general equation that describes the physical behaviour of all gases.

$$V \alpha \frac{nT}{P}$$

$$V = \frac{nRT}{P}$$

where, R is the proportionality

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constant called universal gas constant.

The above equation can be rearranged to give the ideal gas equation

PV = nRT. ------ (6.11)

We already know that pressure is expressed in many different units (Table 6.1) hence it is important to know the values of gas constant R in different units as well.

We can calculate R using the equation,

$$R = \frac{PV}{nT}$$

For Conditions in which P is 1 *atm*., volume 22.414 dm^3. for 1 mole at 273.15 K.

$$R = \frac{1\,atm. \times 22.414\,dm^3}{1\,mol. \times 273.15\,K}$$

$$= \mathbf{0.0821\ dm^3\ atm.\ mol^{-1}\ K^{-1}}$$

Under standard conditions (STP) Where P = 1 bar (10^5 pascal), V= 22.71 × 10^{-3} m^3 for 1 mole of a gas at 273.15 K

$$R = \frac{10^5\ Pa \times 22.71 \times 10^{-3}\ m^3}{1\,mol. \times 273.15\,K}$$

$$= \mathbf{8.314\ Pa\ m^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-5}\ bar\ m^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-2}\ bar\ dm^3\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314 \times 10^{-2}\ bar\ L\ K^{-1}\ mol^{-1}}$$

$$= \mathbf{8.314\ J\ K^{-1}\ mol^{-1}}$$

The ideal gas equation is a relationship between four variables (P, V, T, n). Since it describes the state of any gas, it is referred to as the equation of state of gases.

Let us calculate the pressure exerted by 2 moles of sulphur hexafluoride in a steel vessel of volume 6 dm^3 at 70 °C assuming it is an ideal gas.

We will use the ideal gas equation for this calculation as below:

$$P = \frac{nRT}{V} = \frac{2\ mol \times 0.0821\ L\ atm.\ K^{-1}.mol^{-1} \times (70 + 273\ K)}{6\ dm^3}$$

= 9.39 atm.

Evaluate Yourself

5. A small bubble rises from the bottom of a lake where the temperature and pressure are 8° C and 6.4 *atm.* to the water surface, where the temperature is 25°C and pressure is 1 *atm*. Calculate the final volume in (mL) of the bubble, if its initial volume is 2.1 mL.

6.4 Mixture of gases - Dalton's law of partial pressures

Studies of non-reacting gaseous mixtures showed that in a gaseous mixture each component behaves independently. For a gaseous mixture, it is important to know, how the pressure of individual component contributes to the total pressure of the mixture.

John Dalton stated that "the total

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pressure of a mixture of non-reacting gases is the sum of partial pressures of the gases present in the mixture" where the partial pressure of a component gas is the pressure that it would exert if it were present alone in the same volume and temperature. This is known as *Dalton's law of partial pressures*.

i.e., for a mixture containing three gases 1, 2 and 3 with partial pressures p_1, p_2 and p_3 in a container with volume V, the total pressure P_{total} will be give by

$$P_{total} = p_1 + p_2 + p_3 \text{ ------- } (6.12)$$

Assuming that the gases behave ideally,

$$p_1 = n_1 \frac{RT}{V}\,;\, p_2 = n_2 \frac{RT}{V}\,;\, p_3 = n_3 \frac{RT}{V}$$

$$P_{Total} = n_1 \frac{RT}{V} + n_2 \frac{RT}{V} + n_3 \frac{RT}{V}$$

$$= (n_1 + n_2 + n_3) \frac{RT}{V}$$

$$P_{Total} = n_{Total} \left(\frac{RT}{V}\right) ------ (6.13)$$

The partial pressure can also be expressed as

$\left(\frac{RT}{V}\right)$ can be expressed as $\frac{p_1}{n_1}$ or $\frac{p_2}{n_2}$ or $\frac{p_3}{n_3}$

or in general $\frac{p_i}{n_i}$

Therefore

$$P_{Total} = n_{Total} \frac{p_i}{n_i} = \frac{n_{Total}}{n_i} p_i$$

$$\Rightarrow p_i = \frac{n_i}{n_{Total}} P_{Total} = x_i P_{Total} \text{ ------- } (6.14)$$

where x_i is the mole fraction of the ith component.

Application of Dalton's law

In a reaction involving the collection of gas by downward displacement of water, the pressure of dry vapor collected can be calculated using Dalton's law.

$$P_{\text{dry gas collected}} = p_{total} - p_{\text{water vapour}}$$

$p_{\text{water vapour}}$ is generally referred as aqueous tension and its values are available for air at various temperatures.

Let us understand Dalton's law by solving this problem. A mixture of gases contains 4.76 mole of Ne, 0.74 mole of Ar and 2.5 mole of Xe. Calculate the partial pressure of gases, if the total pressure is 2 *atm*. at a fixed temperature.

Solution:

$$p_{Ne} = x_{Ne}\, P_{Total}$$

$$x_{Ne} = \frac{n_{Ne}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{4.76}{4.76 + 0.74 + 2.5} = 0.595$$

$$x_{Ar} = \frac{n_{Ar}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{0.74}{4.76 + 0.74 + 2.5} = 0.093$$

$$x_{Xe} = \frac{n_{Xe}}{n_{Ne} + n_{Ar} + n_{Xe}}$$

$$= \frac{2.5}{4.76 + 0.74 + 2.5} = 0.312$$

$$P_{Ne} = x_{Ne}\, P_{Total} = 0.595 \times 2$$

$$= 1.19 \text{ atm.}$$

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$P_{Ar} = x_{Ar} P_{Total}$ $= 0.093 \times 2$

$= 0.186$ atm.

$P_{Xe} = x_{Xe} P_{Total}$ $= 0.312 \times 2$

$= 0.624$ atm.

Evaluate Yourself

6. (a) A mixture of He and O_2 were used in the 'air' tanks of underwater divers for deep dives. For a particular dive 12 dm^3 of O_2 at 1 *atm*. and 46 dm^3 of He, at 1 *atm*. were both pumped into a 5 dm^3 tank. Calculate the partial pressure of each gas and the total pressure in the tank at 298 K

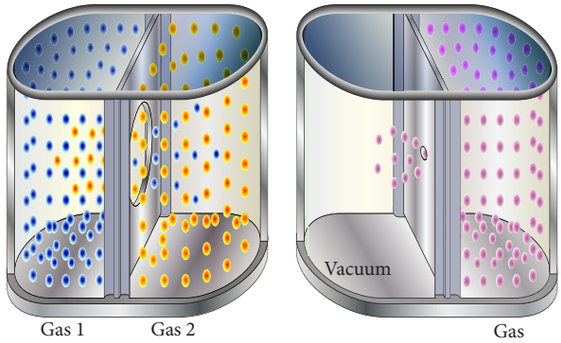
(b) A sample of solid $KClO_3$ (potassium chlorate) was heated in a test tube to obtain O_2 according to the reaction

$$2KClO_3 \rightarrow 2KCl + 3O_2$$

The oxygen gas was collected by downward displacement of water at 295 K. The total pressure of the mixture is 772 mm of Hg. The vapour pressure of water is 26.7 mm of Hg at 300K. What is the partial pressure of the oxygen gas?

6.4.1 Graham' s Law of Diffusion

Gases have a tendency to occupy all the available space. When two non -reactive gases are allowed to mix, the gas molecules migrate from region of higher concentration to a region of lower concentration. This property of gas which involves the movement of the gas molecules through another gases is called diffusion. Effusion is another process in which a gas escapes from a container through a very small hole.



Diffusion Effusion

Figure. 6.7 Diffusion and effusion of gases

The rate of diffusion or effusion is inversely proportional to the square root of molar mass. This statement is called Graham's law of diffusion/effusion.

$$\text{Mathematically, rate of diffusion } \alpha \frac{1}{\sqrt{M}}$$

Otherwise

$$\frac{r_A}{r_B} = \sqrt{\frac{M_B}{M_A}} \text{ -------- (6.15)}$$

When diffusing gases are at different pressures (P_A, P_B),

$$\frac{r_A}{r_B} = \frac{P_A}{P_B}\sqrt{\frac{M_B}{M_A}} \text{ ------(6.16)}$$

where r_A and r_B are the rates of diffusion of A and B and the M_A and M_B are their respective molar masses.



Graham's Law forms the basis of the process of enriching the isotopes of U^{235} from other isotopes.

Example:

1. An unknown gas diffuses at a rate of 0.5 time that of nitrogen at the same

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temperature and pressure. Calculate the molar mass of the unknown gas

Solution:

$$\frac{\text{rate}_{\text{unknown}}}{\text{rate } N_2} = \sqrt{\frac{M_{N_2}}{M_{\text{unknown}}}}$$

$$0.5 = \sqrt{\frac{28\ \text{g mol}^{-1}}{M_{\text{unknown}}}}$$

Squaring on both sides

$$(0.5)^2 = \frac{28\ \text{g mol}^{-1}}{M_{\text{unknown}}}$$

$$\Rightarrow M_{\text{unknown}} = \frac{28}{0.25} = 112\ \text{g mol}^{-1}$$

Evaluate Yourself



7. A flammable hydrocarbon gas of particular volume is found to diffuse through a small hole in 1.5 minutes. Under the same conditions of temperature and pressure an equal volume of bromine vapour takes 4.73 min to diffuse through the same hole. Calculate the molar mass of the unknown gas and suggest what this gas might be.

(Given that molar mass of bromine = 159.8 g/mole)

6.5 Deviation from ideal gas behaviour

The kinetic theory of gases (postulates of kinetic theory of gases are described in physics text book) which is the basis for the gas equation (PV=nRT), assumes that the individual gas molecules occupy negligible volume when compared to the total volume of the gas and there is no attractive force between the gas molecules. Gases whose behaviour is consistent with these assumptions under all conditions are called ideal gases. But in practice both these assumptions are not valid under all conditions. For example, the fact that gases can be liquefied shows that the attractive force exists among molecules. Hence, there is no gas which behaves ideally under all conditions. The non-ideal gases are called real gases. The real gases tend to approach the ideal behaviour under certain conditions.

6.5.1 Compressibility factor Z

The deviation of real gases from ideal behaviour is measured in terms of a ratio of PV to nRT. This is termed as compressibility factor. Mathematically,

$$Z = \frac{PV}{nRT}$$

For ideal gases PV = nRT, hence the compressibility factor, Z = 1 at all temperatures and pressures. For these gases the plot of Z vs P should be a straight line parallel to the pressure axis. When a gas deviates from ideal behaviour, its Z value deviates from unity. For all gases, at very low pressures and very high temperature the compressibility factor approaches unity and they tend to behave ideally. The plot of the compressibility factor vs pressure for some common gases are shown in Figure 6.8.

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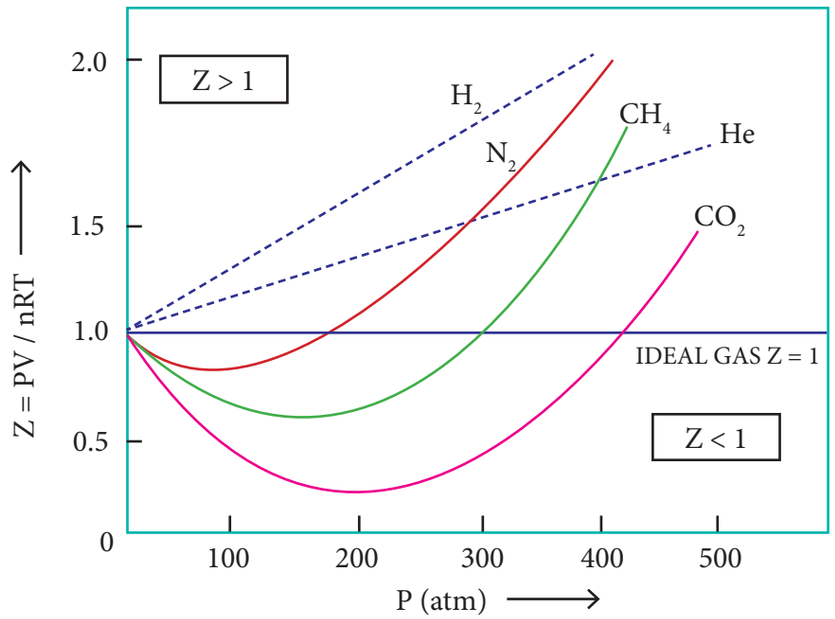

Figure. 6.8 Plot of compressibility factor(Z) vs pressure for some common gases

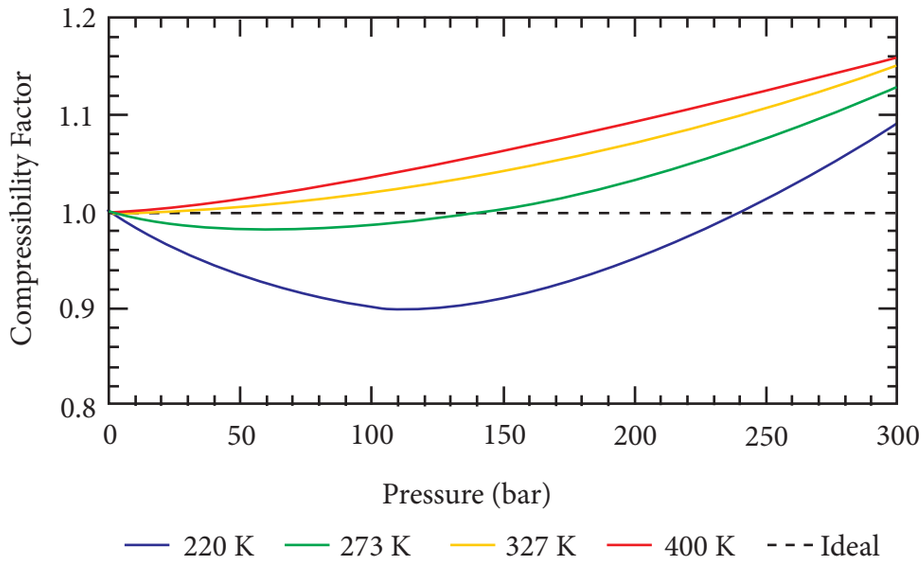

Figure. 6.9 Compressibility factor vs pressure at different temperatures for Nitrogen

When the pressure is low, the volume of the container is very large compared to the volume of the gas molecules so that individual volume of the gas molecules can be neglected. In addition, the molecule in a gas are far apart and attractive forces are negligible. As the pressure increases, the density of gas also increases and the molecules are much closer to one another. Hence, the intermolecular force becomes significant enough to affect the motion of the molecules and the gas will not behave ideally.

At high temperatures the average kinetic energy of the molecules is very high and hence inter moleclular attractions will become insignificant. As the temperature

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decreases, the average kinetic energy of molecules also decreases, hence the molecular attraction is enhanced. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point. The Boyle point varies with the nature of the gas. Above the Boyle point, for real gases, $Z > 1$, ie., the real gases show positive deviation. Below the Boyle point, the real gases first show a decrease for Z, reaches a minimum and then increases with the increase in pressure. So, it is clear that at low pressure and at high temperature, the real gases behave as ideal gases.

6.5.2 Compressibility factor for real gases

The compressibility factor Z for real gases can be rewritten

$$Z = \frac{PV_{real}}{nRT} \quad -----(6.17)$$

$$V_{ideal} = \frac{nRT}{P} \quad ------(6.18)$$

Substituting 6.18 in 6.17

$$Z = \frac{V_{real}}{V_{ideal}} \text{ ---------- } (6.19)$$

Where V_{real} is the molar volume of the real gas and V_{ideal} is the molar volume of it when it behaves ideally.

6.5.3 Van der Waals Equation

J. D. Van der Waals made the first mathematical analysis of real gases. His treatment provides us an interpretation of real gas behaviour at the molecular level. He modified the ideal gas equation PV = nRT by introducing two correction factors, namely, pressure correction and volume correction.

Pressure Correction:

The pressure of a gas is directly proportional to the force created by the bombardment of molecules on the walls of the container. The speed of a molecule moving towards the wall of the container is reduced by the attractive forces exerted by its neighbours. Hence, the measured gas pressure is lower than the ideal pressure of the gas. Hence, van der Waals introduced a correction term to this effect.

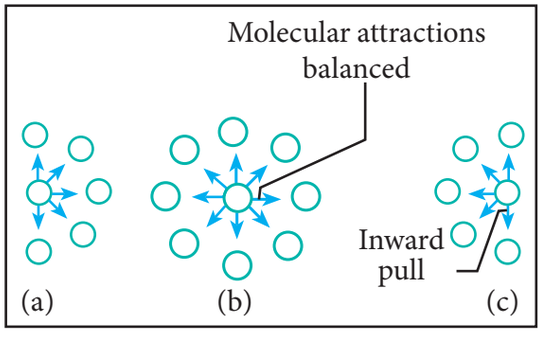

Figure. 6.10 Inter-molecular forces of attraction

Van der Waals found out the forces of attraction experienced by a molecule near the wall are directly proportional to the square of the density of the gas.

$$P' \alpha \rho^2$$

$$\rho = \frac{n}{V}$$

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where n is the number of moles of gas and V is the volume of the container

$$\Rightarrow P' \alpha \frac{n^2}{V^2}$$

$$\Rightarrow P' = a \frac{n^2}{V^2}$$

where a is proportionality constant and depends on the nature of gas

Therefore,

$$P_{ideal} = P + \frac{an^2}{V^2} \quad \text{------ (6.20)}$$

Volume Correction

As every individual molecule of a gas occupies a certain volume, the actual volume is less than the volume of the container, V. Van der Waals introduced a correction factor V' to this effect. Let us calculate the correction term by considering gas molecules as spheres.

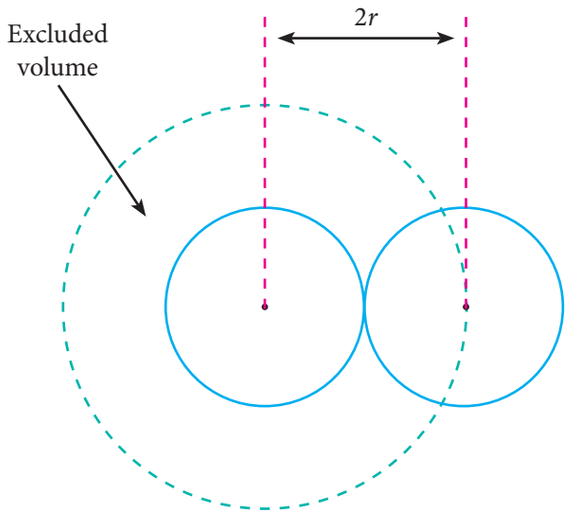

Figure. 6.11 Excluded volume

V = excluded volume

Excluded volume for two molecules

$$= \frac{4}{3}\pi(2r)^3$$

$$= 8\left(\frac{4}{3}\pi r^3\right) = 8\ V_m$$

where v_m is a volume of a single molecule

Excluded volume for single molecule

$$= \frac{8\ V_m}{2} = 4\ V_m$$

Excluded volume for n molecule

$$= n\ (4\ V_m) = nb$$

Where b is van der waals constant whch is equal to $4\ V_m$

$$\Rightarrow V' = nb$$

$$V_{ideal} = V - nb \text{ ----- (6.21)}$$

Replacing the corrected pressure and volume in the ideal gas equation PV=nRT we get the van der Waals equation of state for real gases as below,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT \text{ . ----(6.22)}$$

The constants *a* and *b* are van der Waals constants and their values vary with the nature of the gas. It is an approximate formula for the non-ideal gas.

6.6 Pressure-Volume isotherms of Carbon dioxide

Andrew's isotherm

Thomas Andrew gave the first complete data on pressure-volume-temperature of a substance in the gaseous and liquid states. He plotted isotherms of carbon dioxide at different temperatures which is shown in Figure. 6.12. From the plots we can infer the following.

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At low temperature isotherms, for example, at 13⁰ C as the pressure increases, the volume decreases along AB and is a gas until the point B is reached. At B, a liquid separates along the line BC, both the liquid and gas co-exist and the pressure remains constant. At C, the gas is completely converted into liquid. If the pressure is higher than at C, only the liquid is compressed so, there is no significant change in the volume. The successive isotherms shows similar trend with the shorter flat region. i.e. The volume range in which the liquid and gas coexist becomes shorter. At the temperature of 31.1 ⁰C the length of the shorter portion is reduced to zero at point P. In other words, the CO_2 gas is liquefied completely at this point. This temperature is known as the liquefaction temperature or critical temperature of CO_2. At this point the pressure is 73 atm. Above this temperature CO_2 remains as a gas at all pressure values. It is then proved that many real gases behave in a similar manner to carbon dioxide.

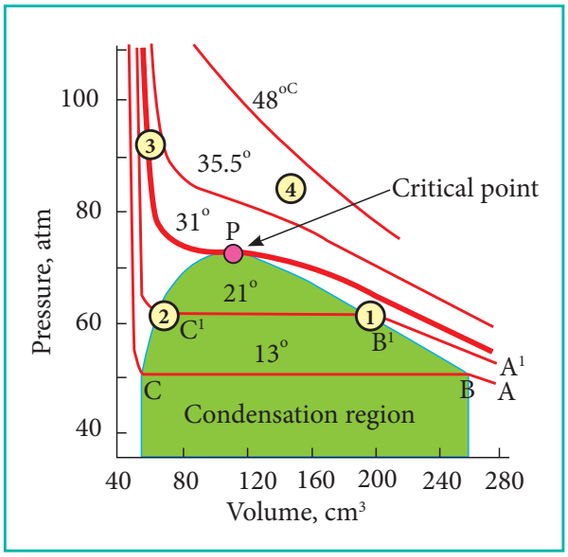

Figure. 6.12 Isotherms of Carbon dioxide at different tempeartures

Though the nature of isotherm remains similar, the critical temperature, the corresponding pressure and volume are characteristics of a particular gas.

Now we can define the critical constants as follows. Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied even at high pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure. The critical constants of some common gases are given in Table 6.2

Table 6.2 Critical constants of some gases

Name of the Gas	Critical Temperature (T_c) in K	Critical Pressure (P_c) in atm	Critical Volume (V_c) cm^3 mol^{-1}
Helium (He)	5.2	2.26	57.8
Carbon dioxide (CO_2)	304.2	72.9	94.0
Oxygen (O_2)	154.8	50.14	78.0
Nitrogen (N_2)	126.3	33.54	90.1
Hydrogen (H_2)	33.2	12.80	65
Water (H_2O)	647.4	218.3	55.3
Ammonia (NH_3)	405.5	111.3	72.5
Hydrogen Chloride (HCl)	324.7	81.5	81.0
Methane (CH_4)	190.6	45.6	98.7
Ethylene (C_2H_4)	283.1	50.50	124

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Evaluate Yourself

8. Critical temperature of H_2O, NH_3, and CO_2 are 647.4, 405.5 and 304.2 K, respectively. When we start cooling from a temperature of 700 K which will liquefy first and which will liquefy finally?

6.6.1 Derivation of critical constants from van der Waals constant:

The van der Waals equation for n moles is

$$\left(P+\frac{a\,n^2}{V^2}\right)(V-nb)=nRT \quad \text{---------- (6.22)}$$

For 1 mole

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \quad \text{---------- (6.23)}$$

From the equation we can derive the values of critical constants P_c, V_c and T_c in terms of a and b, the van der Waals constants, On expanding the above equation

$$PV+\frac{a}{V}-Pb-\frac{ab}{V^2}-RT=0 \quad \text{------- (6.24)}$$

Multiply equation (6.24) by V^2 / P

$$\frac{V^2}{P}\left(PV+\frac{a}{V}-Pb-\frac{ab}{V^2}-RT\right)=0$$

$$V^3+\frac{aV}{P}+-bV^2-\frac{ab}{P}-\frac{RTV^2}{P}=0 \text{---} (6.25)$$

When the above equation is rearranged in powers of V

$$V^3-\left[\frac{RT}{P}+b\right]V^2+\left[\frac{a}{P}\right]V-\left[\frac{ab}{P}\right]=0 \text{---} (6.26)$$

The equation (6.26) is a cubic equation in V. On solving this equation, we will get three solutions. At the critical point all these three solutions of V are equal to the critical volume V_C. The pressure and temperature becomes P_c and T_c respectively

i.e., $V = V_C$

$$V - V_C = 0$$

$$(V - V_C)^3 = 0$$

$$V^3 - 3V_CV^2 + 3V_C^2V - V_C^3 = 0 \quad \text{---- (6.27)}$$

As equation (6.26) is identical with equation (6.27), we can equate the coefficients of V^2, V and constant terms in (6.26) and (6.27).

$$-3V_CV^2=-\left[\frac{RT_C}{P_C}+b\right]V^2$$

$$3V_C=\frac{RT_C}{P_C}+b \quad \text{---- (6.28)}$$

$$3V_C^2=\frac{a}{P_C} \quad \text{---- (6.29)}$$

$$V_C^3=\frac{ab}{P_C} \quad \text{---- (6.30)}$$

Divide equation (6.30) by equation (6.29)

$$\frac{V_C^3}{3V_C^2}=\frac{ab/P_C}{a/P_C}$$

$$\frac{V_C}{3}=b$$

i.e. $V_C = 3b$ ------- (6.31)

when equation (6.31) is substituted in (6.29)

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$$3V_C^2 = \frac{a}{P_C}$$

$$P_C = \frac{a}{3V_C^2} = \frac{a}{3(3b^2)} = \frac{a}{3 \times 9b^2} = \frac{a}{27\,b^2}$$

$$P_C = \frac{a}{27b^2} \quad \text{------ (6.32)}$$

substituting the values of V_c and P_c in equation (6.28),

$$3V_C = b + \frac{R\,T_C}{P}$$

$$3\,(3\,b) = b + \frac{R\,T_C}{\left(a/27\,b^2\right)}$$

$$9\,b - b = \left(\frac{R\,T_C}{a}\right) 27\,b^2$$

$$8\,b = \frac{T_C\,R\,27b^2}{a}$$

$$\therefore \quad T_C = \frac{8\,a\,b}{27\,R\,b^2} = \frac{8\,a}{27\,R\,b}$$

$$T_C = \frac{8\,a}{27\,R\,b} \quad \text{------ (6.33)}$$

The critical constants can be calculated using the values of van der waals constant of a gas and vice versa.

$$a = 3\,V_C^2\,P_C \quad \text{and} \quad b = \frac{V_C}{3}$$

6.7 Liquefaction of gases

For important commercial operations such as LPG and rocket fuels, we require gases in their liquid state. The liquefication methods are based on the Joule-Thomson effect. He observed appreciable cooling when the compressed gas is forced through an orifice plug into a low-pressure region. This phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect. This effect is observed only below a certain temperature, which is a characteristic one for each gas. This temperature below which a gas obeys Joule-Thomson effect is called inversion temperature (T_i). This value is given using van der waals constants *a* and *b*.

$$T_i = \frac{2a}{Rb} \quad \text{--------- (6.34)}$$

Gases like O_2, He, N_2 and H_2 have very low T_c, hence Joule-Thomson effect can be applied for cooling effectively. At the inversion temperature, no rise or fall in temperature of a gas occurs while expanding. But above the inversion temperature, the gas gets heated up when allowed to expand through a hole.

There are different methods used for liquefaction of gases:

1) In **Linde's method,** Joule-Thomson effect is used to get liquid air or any other gas.

2) In **Claude's process,** the gas is allowed to perform mechanical work in addition to Joule-Thomson effect so that more cooling is produced.

3) In **Adiabatic process,** cooling is produced by removing the magnetic property of magnetic material such as gadolinium sulphate. By this method, a temperature of 10^{-4} K i.e. as low as 0 K can be achieved.

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SUMMARY

The state of a gas is defined by a relationship between the four independent variables pressure (P), volume (V), temperature (T) and number of moles (n). The relationship between these parameters is governed by different gas laws as summarised below.

LAW	Expression	Conditions	Expression for two differnt states
Boyle's law	PV = constant	n and T are constant	$P_1V_1 = P_2V_2$
Charle's law	$\frac{V}{T}$ = constant	P and n are constant	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Gay Lussac's law	$\frac{P}{T}$ = constant	V and n are constant	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Combined gas law	$\frac{PV}{T}$ = constant	n is constant	$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
Avogadro's Hypothesis	$\frac{V}{n}$ = constant	T and P are constant	$\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Dalton's law of partial pressure	$P_{Total} = p_1+p_2+p_3+....$	T and V are constant	
Graham's law of diffusion	$r \alpha \frac{1}{\sqrt{M}}$	T and P are constant	$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$

Gases that obey the equation PV=nRT under all conditions are called ideal gases. But in practice there is no ideal gas. Gases tend to behave ideally at high temperatures and at low pressures. For real gases, van der Waals modified the ideal gas equation as

$$\left(P + \frac{a\,n^2}{V^2}\right)(V - nb) = nRT$$

Critical temperature (T_c) of a gas is defined as the temperature above which it cannot be liquefied at any pressure. Critical pressure (P_c) of a gas is defined as the minimum pressure required to liquefy 1 mole of a gas at its critical temperature. Critical volume (V_c) is defined as the volume occupied by 1 mole of a gas at its critical temperature and critical pressure.

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The critical constants are related to Van der Waals constants as follows

$$T_C = \frac{8\,a}{27\,R\,b}, \quad P_C = \frac{a}{27b^2} \text{ and } V_C = 3b$$

When a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, the temperature of the gas is reduced rapidly and this is known as Joule-Thomson effect. This effect is used in the liquefication of gases.

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EVALUATION

I. Choose the best answer

1. Gases deviate from ideal behavior at high pressure. Which of the following statement(s) is correct for non-ideality?

   a) at high pressure the collision between the gas molecule become enormous

   b) at high pressure the gas molecules move only in one direction

   c) at high pressure, the volume of gas become insignificant

   d) at high pressure the intermolecular interactions become significant

2. Rate of diffusion of a gas is

   a) directly proportional to its density

   b) directly proportional to its molecular weight

   c) directly proportional to its square root of its molecular weight

   d) inversely proportional to the square root of its molecular weight

3. Which of the following is the correct expression for the equation of state of van der Waals gas?

   (a) $\left(P + \frac{a}{n^2V^2}\right)(V - nb) = nRT$ (b) $\left(P + \frac{na}{n^2V^2}\right)(V - nb) = nRT$

   (c) $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$ (d) $\left(P + \frac{n^2a^2}{V^2}\right)(V - nb) = nRT$

4. When an ideal gas undergoes unrestrained expansion, no cooling occurs because the molecules

   a) are above inversion temperature

   b) exert no attractive forces on each other

   c) do work equal to the loss in kinetic energy

   d) collide without loss of energy

5. Equal weights of methane and oxygen are mixed in an empty container at 298 K. The fraction of total pressure exerted by oxygen is

   (a) $1/3$ (b) $1/2$ (c) $2/3$ (d) $1/3 \times 273 \times 298$

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6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called

a) Critical temperature b) Boyle temperature

c) Inversion temperature d) Reduced temperature

7. In a closed room of 1000 m^3 a perfume bottle is opened up. The room develops a smell. This is due to which property of gases?

a) Viscosity b) Density

c) Diffusion d) None

8. A bottle of ammonia and a bottle of HCl connected through a long tube are opened simultaneously at both ends. The white ammonium chloride ring first formed will be

a) At the center of the tube

b) Near the hydrogen chloride bottle

c) Near the ammonia bottle

d) Throughout the length of the tube

9. The value of universal gas constant depends upon

a) Temperature of the gas b) Volume of the gas

c) Number of moles of the gas d) units of Pressure and volume.

10. The value of the gas constant R is

a) 0.082 $dm^3 atm.$ b) 0.987 cal mol^{-1} K^{-1}

c) 8.3 J $mol^{-1}K^{-1}$ d) 8 erg $mol^{-1}K^{-1}$

11. Use of hot air balloon in sports and meteorological observation is an application of

a) Boyle's law b) Newton's law c) Kelvin's law d) Brown's law

12. The table indicates the value of van der Waals constant 'a' in $(dm^3)^2 atm.\ mol^{-2}$

Gas	O_2	N_2	NH_3	CH_4
a	1.360	1.390	4.170	2.253

The gas which can be most easily liquefied is

a) O_2 b) N_2 c) NH_3 d) CH_4

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13. Consider the following statements

i) Atmospheric pressure is less at the top of a mountain than at sea level

ii) Gases are much more compressible than solids or liquids

iii) When the atmospheric pressure increases the height of the mercury column rises
Select the correct statement

a) I and II b) II and III c) I and III d) I, II and III

14. Compressibility factor for CO_2 at 400 K and 71.0 bar is 0.8697. The molar volume of CO_2 under these conditions is

a) 22.04 dm^3 b) 2.24 dm^3 c) 0.41 dm^3 d) 19.5dm^3

15. If temperature and volume of an ideal gas is increased to twice its values, the initial pressure P becomes

a) 4P b) 2P c) P d) 3P

16. At identical temperature and pressure, the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. What is the value of n ?

a) 8 b) 4 c) 3 d) 1

17. Equal moles of hydrogen and oxygen gases are placed in a container, with a pin-hole through which both can escape what fraction of oxygen escapes in the time required for one-half of the hydrogen to escape. (NEET phase I)

a) $\frac{3}{8}$ b) $\frac{1}{2}$ c) $\frac{1}{8}$ d) $\frac{1}{4}$

18. The variation of volume V, with temperature T, keeping pressure constant is called the coefficient of thermal expansion ie $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. For an ideal gas α is equal to

a) T b) $\frac{1}{T}$ c) P d) none of these

19. Four gases P, Q, R and S have almost same values of 'b' but their 'a' values (a, b are Vander Waals Constants) are in the order Q < R < S < P. At a particular temperature, among the four gases the most easily liquefiable one is

a) P b) Q c) R d) S

20. Maximum deviation from ideal gas is expected from (NEET)

a) $CH_4(g)$ b) $NH_3(g)$ c) $H_2(g)$ d) $N_2(g)$

21. The units of Vander Waals constants 'b' and 'a' respectively

a) mol L^{-1} and L atm^2 mol^{-1} b) mol L and L atm mol^2
c) mol^{-1}L and L^2 atm mol^{-2} d) none of these

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22. Assertion : Critical temperature of CO_2 is 304K, it can be liquefied above 304K.

Reason : For a given mass of gas, volume is to directly proportional to pressure at constant temperature

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

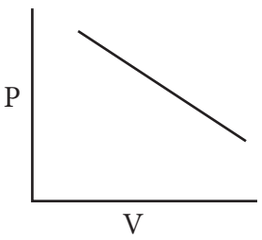
d) both assertion and reason are false

23. What is the density of N_2 gas at 227°C and 5.00 atm pressure? (R = 0.082 L atm K–1 mol^{-1})

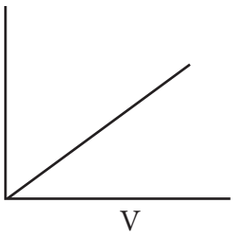
a) 1.40 g/L b) 2.81 g/L c) 3.41 g/L d) 0.29 g/L

24. Which of the following diagrams correctly describes the behaviour of a fixed mass of an ideal gas ? (T is measured in K)

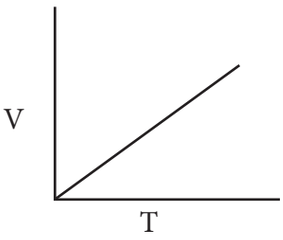
a)



b) PV



c)



d) All of these

25. 25g of each of the following gases are taken at 27°C and 600 mm Hg pressure. Which of these will have the least volume ?

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

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II. Write brief answer to the following questions:

26. State Boyle's law.
27. Name two items that can serve as a model for Gay Lusaac' law and explain.
28. Give the mathematical expression that relates gas volume and moles.
29. What are ideal gases? In what way real gases differ from ideal gases.
30. Can a Van der Waals gas with a=0 be liquefied? explain.
31. Suppose there is a tiny sticky area on the wall of a container of gas. Molecules hitting this area stick there permanently. Is the pressure greater or less than on the ordinary area of walls?
32. Explain the following observations
    a) Aerated water bottles are kept under water during summer
    b) Liquid ammonia bottle is cooled before opening the seal
    c) The tyre of an automobile is inflated to slightly lesser pressure in summer than in winter
    d) The size of a weather balloon becomes larger and larger as it ascends up into larger altitude
33. Give suitable explanation for the following facts about gases.
    a) Gases don't settle at the bottom of a container
    b) Gases diffuse through all the space available to them
34. Suggest why there is no hydrogen (H_2) in our atmosphere. Why does the moon have no atmosphere?
35. Explain whether a gas approaches ideal behavior or deviates from ideal behaviour if
    a) it is compressed to a smaller volume at constant temperature.
    b) the temperature is raised while keeping the volume constant
    c) more gas is introduced into the same volume and at the same temperature
36. Which of the following gases would you expect to deviate from ideal behaviour under conditions of low temperature F_2, Cl_2 or Br_2? Explain.
37. Distinguish between diffusion and effusion.
38. Aerosol cans carry clear warning of heating of the can. Why?
39. Would it be easier to drink water with a straw on the top of Mount Everest?
40. Write the Van der Waals equation for a real gas. Explain the correction term for pressure and volume
41. Derive the values of critical constants in terms of van der Waals constants.
42. Why do astronauts have to wear protective suits when they are on the surface of moon?
43. When ammonia combines with HCl, NH_4Cl is formed as white dense fumes. Why do more fumes appear near HCl?

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44. A sample of gas at 15 °C at 1 atm. has a volume of 2.58 dm^3. When the temperature is raised to 38 °C at 1 atm does the volume of the gas increase? If so, calculate the final volume.

45. A sample of gas has a volume of 8.5 dm^3 at an unknown temperature. When the sample is submerged in ice water at 0 °C, its volume gets reduced to 6.37 dm^3. What is its initial temperature?

46. Of two samples of nitrogen gas, sample A contains 1.5 moles of nitrogen in a vessel of volume of 37.6 dm^3 at 298K, and the sample B is in a vessel of volume 16.5 dm^3 at 298K. Calculate the number of moles in sample B.

47. Sulphur hexafluoride is a colourless, odourless gas; calculate the pressure exerted by 1.82 moles of the gas in a steel vessel of volume 5.43 dm^3 at 69.5 °C, assuming ideal gas behaviour

48. Argon is an inert gas used in light bulbs to retard the vaporization of the tungsten filament. A certain light bulb containing argon at 1.2 atm and 18°C is heated to 85°C at constant volume. Calculate its final pressure in atm.

49. A small bubble rises from the bottom of a lake where the temperature and pressure are 6°C and 4 atm. to the water surface, where the temperature is 25°C and pressure is 1 atm. Calculate the final volume in (mL) of the bubble, if its initial volume is 1.5 mL.

50. Hydrochloric acid is treated with a metal to produce hydrogen gas. Suppose a student carries out this reaction and collects a volume of 154.4×10^{-3} dm^3 of a gas at a pressure of 742 mm of Hg at a temperature of 298 K. What mass of hydrogen gas (in mg) did the student collect?

51. It takes 192 sec for an unknown gas to diffuse through a porous wall and 84 sec for N_2 gas to effuse at the same temperature and pressure. What is the molar mass of the unknown gas?

52. A tank contains a mixture of 52.5 g of oxygen and 65.1 g of CO_2 at 300 K the total pressure in the tanks is 9.21 atm. Calculate the partial pressure (in atm.) of each gas in the mixture.

53. A combustible gas is stored in a metal tank at a pressure of 2.98 atm at 25 °C. The tank can withstand a maximum pressure of 12 atm after which it will explode. The building in which the tank has been stored catches fire. Now predict whether the tank will blow up first or start melting? (Melting point of the metal = 1100 K).

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CONCEPT MAP



Gaseous State

IDEAL GASES

obey following gas laws under all conditions

1. Boyle's Law $P \alpha \frac{1}{V}$ (T, n constant)
2. Charles Law - $V \alpha T$ (P, n constant)
3. Gay Lusaac - $P \alpha T$ (V, n constant)
4. Avogadro's Hypothesis - $V \alpha n$ (T, P constant)
5. Ideal gas equation $PV = nRT$

REAL GASES

obey Van der Waals equation

$$\left(P + \frac{a n^2}{V^2}\right)(V - nb) = nRT$$

↓

Critical constant

$$T_C = \frac{8a}{27 R b}, \quad P_C = \frac{a}{27 b^2}$$

and $V_C = 3b$

Gases

Diffusion → Graham's Law of diffusion

Critical phenomenon → Critical temperature, Critical volume, Critical pressure

Liquefaction of gases → Joule-Thomson effect

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ICT Corner

Properties of Gases

By using this tool you will be able to understand the relationship between T, P of V gases and verify the gas laws.

Please go to the URL https://phet.colorado.edu/en/simulation/gas-properties
(or)
Scan the QR code on the right side

DLWZX

Step – 1

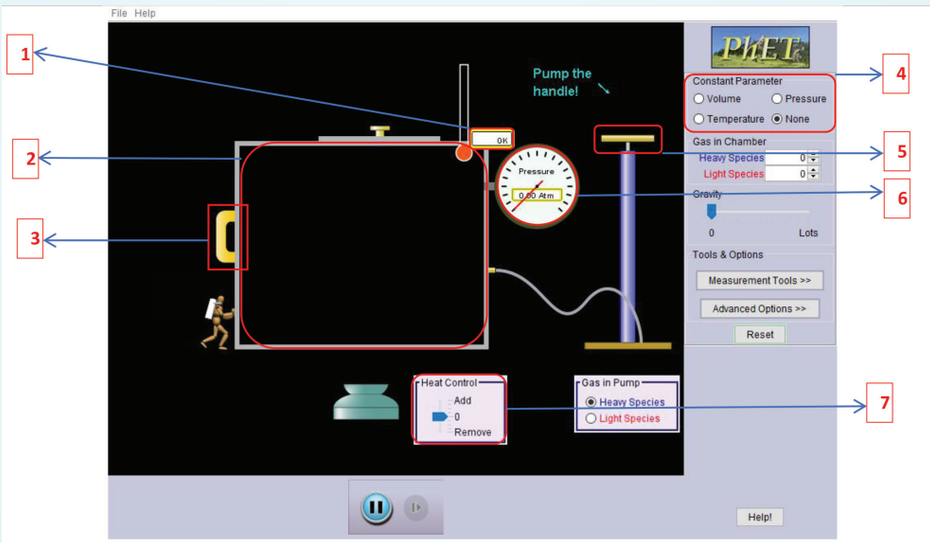
Open the Browser and type the URL given (or) Scan the QR Code. In the website click the gas properties applet, then you will see a Java applet named 'gas properties' opening up as shown in the figure.

Set up instructions:

- In the chamber (2) you can pump some gas molecules by using the pump handle (5).
- The temperature (1) and pressure (6) of the gas molecules in the chamber can be monitored by using the corresponding gauges.
- The volume of the chamber can be altered by moving the left side wall (3).
- The temperature of the chamber can be altered by heating or cooling using the slider (7)
- Any of the three properties can be kept as constant by making appropriate selections in the box (4)

Verifying the gas laws:

By using the above instructions you can understand the gas laws. To understand the Boyle's law, keep the temperature constant (4) and pump few molecules of gas (5) and keep it as constant. Now reduce the volume by pushing the left side wall (3) then you can see that the pressure of the gas increases. Similarly the other two gas laws can also be verified.



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Unit 7

THERMODYNAMICS

Classical thermodynamics... is the only physical theory of universal physical theory of universal content which I am convinced... will never be overthrown.

Albert Einstein



Rudolf Clausius
(1822-1888)

Learning Objectives:

After studying this unit, students will be able to

- distinguish between the system and surroundings
- define closed, open and isolated systems
- distinguish between state and path functions
- describe the relation between internal energy, work and heat
- state four laws of thermodynamics
- correlate internal energy change (ΔU) and enthalpy change (ΔH)and their measurement.
- calculate enthalpy changes for various types of reactions
- apply Hess's law to calculate lattice energy of crystals
- define spontaneous and non spontaneous processes
- establish the relationship between thermodynamic state functions enthalpy (H), entropy (S) and Gibbs free energy (G)
- list the factors that determines spontaneity of the process
- establish the link between ΔG and spontaneity, and the relationship between ΔG^0 and equilibrium constant

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7.1 Introduction

The term 'Thermodynamics' means flow of heat and is derived from the Greek `Thermos' (heat) and `dynamics' (flow), In our daily life, we come across many useful reactions such as burning of fuel to produce heat energy, flow of electrons through circuit to produce electrical energy, metabolic reactions to produce the necessary energy for biological functions and so on. Thermodynamics, the study of the transformation of energy, explains all such processes quantitatively and allows us to make useful predictions.

In the 19th century, scientists tried to understand the underlying principles of steam engine which were already in operation, in order to improve their efficiency. The basic problem of the investigation was the transformation of heat into mechanical work. However, over time, the laws of thermodynamics were developed and helped to understand the process of steam engine. These laws have been used to deduce powerful mathematical relationships applicable to a broad range of processes.

Thermodynamics evaluates the macroscopic properties (heat, work) and their inter relationships. It deals with properties of systems in equilibrium and is independent of any theories or properties of the individual molecules which constitute the system.

The principles of thermodynamics are based on three laws of thermodynamics. The first two laws (First and second law) summarise the actual experience of inter conversion of different forms of energy. The third law deals with the calculation of entropy and the unattainability of absolute zero Kelvin. Thermodynamics carries high practical values but bears certain limitations. It is independent of atomic and molecular structure and reaction mechanism. The laws can be used to predict whether a particular reaction is feasible or not under a given set of conditions, but they cannot give the rate at which the reaction takes place. In other words, thermodynamics deals with equilibrium conditions quantitatively, but does not take into account the kinetic approach to the equilibrium state.

7.2 System and Surrounding

Before studying the laws of thermodynamics and their applications, it is important to understand the meaning of a few terms used frequently in thermodynamics.

System:

The universe is divided into two parts, the system and its surroundings. The system is the part of universe which is under thermodynamic consideration. It is separated from the rest of the universe by real or imaginary boundaries.

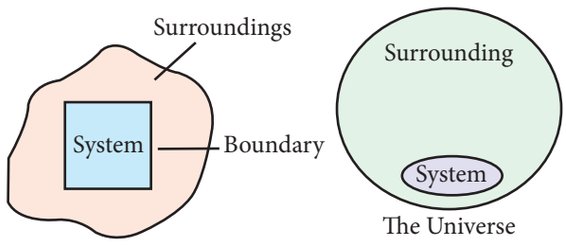

Figure 7.1 System, surrounding & boundary Homogeneous and heterogeneous systems

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Example:

The system may be water in a beaker, a balloon filled with air, an aqueous solution of glucose etc.

On the basis of physical and chemical properties, systems can be divided into two types.

A system is called homogeneous if the physical state of all its constituents are the same. Example: a mixture of gases, completely miscible mixture of liquids etc.

A system is called heterogeneous, if physical state of all its constituents is not the same.

Example: mixture of oil and water

Surrounding:

Everything in the universe that is not the part of the system is called surroundings.

Boundary:

Anything which separates the system from its surrounding is called boundary.

7.2.1 Types of systems:

There are three types of thermodynamic systems depending on the nature of the boundary.

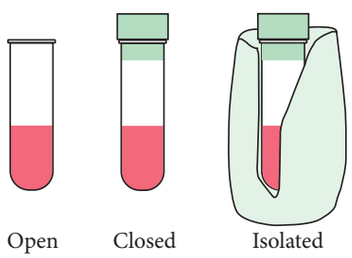

Figure 7.2 Types of Systems

Isolated system:

A system which can exchange neither matter nor energy with its surroundings is called an isolated system. Here boundary is sealed and insulated. Hot water contained in a thermos flask, is an example for an isolated system. In this isolated system both energy (heat) and matter (water vapour) neither enter nor leave the system.

Closed system:

A system which can exchange only energy but not matter with its surroundings is called a closed system. Here the boundary is sealed but not insulated. Hot water contained in a closed beaker is an example for a closed system. In this system energy (heat) is transferred to the surroundings but no matter (water vapour) can escape from this system. A gas contained in a cylinder fitted with a piston constitutes a closed system.

Open system:

A System which can exchange both matter and energy with its surrounding is called an open system. Hot water contained in an open beaker is an example for open system. In this system both matter (water vapour) and energy (heat) is transferred to the surrounding.

All living things and chemical reactions are open systems because they exchange matter and energy with the surroundings.

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7.2.2 Properties of the system:

Intensive and extensive properties

Some of the properties of a system depend on its mass or size whereas other properties do not depend on its mass or size. Based on this, the properties of a system are grouped as ***extensive*** property and ***intensive*** property.

Extensive properties:

The property that depends on the mass or the size of the system is called an extensive property.

Examples: Volume, Number of moles, Mass, Internal energy, etc.,

Intensive properties:

The property that is independent of the mass or the size of the system is called an intensive property.

Examples : Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume, etc.,

Table: 7.1 Typical List of Extensive and Intensive properties

Extensive properties	Intensive properties
volume, mass, amount of substance (mole), energy, enthalpy, entropy, free energy, heat capacity	molar volume, density, molar mass, molarity, mole fraction, molality, specific heat capacity

7.2.3 Thermodynamic processes

The method of operation which can bring about a change in the system is called thermodynamic process. Heating, cooling, expansion, compression, fusion, vaporization etc., are some examples of a thermodynamic process.

Types of processes:

A thermodynamic process can be carried out in different ways and under different conditions. The processes can be classified as follows:

Reversible process:

The process in which the system and surrounding can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process. There are two important conditions for the reversible process to occur. Firstly, the process should occur infinitesimally slowly and secondly throughout the process, the system and surroundings must be in equilibrium with each other.

Irreversible Process:

The process in which the system and surrounding cannot be restored to the initial state from the final state is called an irreversible process. All the processes occurring in nature are irreversible processes. During the irreversible process the system and surroundings are not in equilibrium with each other.

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Adiabatic process:

An adiabatic process is defined as one in which there is no exchange of heat (q) between the system and surrounding during the process. Those processes in which no heat can flow into or out of the system are called ***adiabatic processes.*** This condition is attained by thermally insulating the system. In an adiabatic process if work is done by the system its temperature decreases, if work is done on the system its temperature increases, because, the system cannot exchange heat with its surroundings.

For an adiabatic process q = 0

Isothermal process :

An isothermal process is defined as one in which the temperature of the system remains constant, during the change from its initial to final state. The system exchanges heat with its surrounding and the temperature of the system remains constant. For this purpose the experiment is often performed in a thermostat.

For an isothermal process $dT = 0$

Isobaric process

An isobaric process is defined as one in which the pressure of the system remains constant during its change from the initial to final state.

For an isobaric process $dP = 0$.

Isochoric process

An isochoric process is defined as the one in which the volume of system remains constant during its change from initial to final state. Combustion of a fuel in a bomb calorimeter is an example of an isochoric process.

For an isochoric process, $dV = 0$.

Cyclic process:

When a system returns to its original state after completing a series of changes, then it is said that a cycle is completed. This process is known as a cyclic process.

For a cyclic process dU = 0, dH = 0, dP=0, dV=0, dT=0

Table: 7.2 Overview of the process and its condition

Process	Condition
Adiabatic	q = 0
Isothermal	dT= 0
Isobaric	dP= 0
Isochoric	dV= 0
Cyclic	dE= 0, dH = 0, dP=0, dV=0 , dT=0

State functions, path functions:

State function

A thermodynamic system can be defined by using the variables P, V, T and `n'. A state function is a thermodynamic property of a system, which has a specific value for a given state and does not depend on the path (or manner) by which the particular state is reached.

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Example : Pressure (P), Volume (V), Temperature(T), Internal energy (U), Enthalpy (H), free energy (G) etc.

Path functions:

A path function is a thermodynamic property of the system whose value depends on the path by which the system changes from its initial to final states.

Example: Work (*w*), Heat (*q*).

Work (w) will have different values if the process is carried out reversibly or irreversibly.

Internal Energy (U)

The internal energy is a characteristic property of a system which is denoted by the symbol U. The internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The total energy of all molecules in a system is equal to the sum of their translational energy (U_t), vibrational energy (U_v), rotational energy (U_r), bond energy (U_b), electronic energy (U_e) and energy due to molecular interactions (U_i).

Thus:

$$U = U_t + U_v + U_r + U_b + U_e + U_i$$

The total energy of all the molecules of the system is called internal energy. In thermodynamics one is concerned only with the change in internal energy (ΔU) rather than the absolute value of energy.

Importance of Internal energy

The internal energy possessed by a substance differentiates its physical structure. For example, the allotropes of carbon, namely, graphite ($C_{graphite}$) and diamond ($C_{diamond}$), differ from each other because they possess different internal energies and have different structures.

Characteristics of internal energy (U):

- The internal energy of a system is an extensive property. It depends on the amount of the substances present in the system. If the amount is doubled, the internal energy is also doubled.
- The internal energy of a system is a state function. It depends only upon the state variables (T, P, V, n) of the system. The change in internal energy does not depend on the path by which the final state is reached.
- The change in internal energy of a system is expressed as $\Delta U = U_f - U_i$
- In a cyclic process, there is no internal energy change. $\Delta U_{(cyclic)} = 0$
- If the internal energy of the system in the final state (U_f) is less than the internal energy of the system in its initial state (U_i), then ΔU would be negative.

  $$\Delta U = U_f - U_i = -ve \quad (U_f < U_i)$$
- If the internal energy of the system in the final state (U_f) is greater than the internal energy of the system in its initial state(U_i), then ΔU would be positive.

  $$\Delta U = U_f - U_i = +ve \quad (U_f > U_i)$$

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HEAT(q)

The heat (q) is regarded as an energy in transit across the boundary separating a system from its surrounding. Heat changes lead to temperature differences between system and surrounding. Heat is a path function.

Units of heat:

The SI unit of heat is joule (J). Heat quantities are generally measured in calories (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1° C in the vicinity of 15° *C*.

Sign convention of heat:

The symbol of heat is *q*.

If heat flows into the system from the surrounding, energy of a system increases. Hence it is taken to be positive (+q).

If heat flows out of the system into the surrounding, energy of the system decreases. Hence, it is taken to be negative (–q).

Work(w)

Work is defined as the force (F) multiplied by the displacement(*x*).

$-w = F.\ x$ ----------(7.1)

The negative sign (–) is introduced to indicate that the work has been done by the system by spending a part of its internal energy.

The work,

(i) is a path function.

(ii) appears only at the boundary of the system.

(iii) appears during the change in the state of the system.

(iv) In thermodynamics, surroundings is so large that macroscopic changes to surroundings do not happen.

Units of work:

The SI unit of work is joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter (J= Nm). We often use kilojoule (*k*J) for large quantities of work. 1 kJ = 1000 J.

Sign convention of work:

The symbol of work is '*w*'.

If work is done by the system, the energy of the system decreases, hence by convention, work is taken to be negative (– w).

If work is done on the system, the energy of the system increases, hence by convention, the work is taken to be positive (+w).

Pressure - volume work

In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as pressure-volume work, PV work or expansion work.

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Work involved in expansion and compression processes:

In most thermodynamic calculations we are dealing with the evaluation of work involved in the expansion or compression of gases. The essential condition for expansion or compression of a system is that there should be difference between external pressure (P_{ext}) and internal pressure (P_{int}).

For understanding pressure-volume work, let us consider a cylinder which contains 'n' moles of an ideal gas fitted with a frictionless piston of cross sectional area A. The total volume of the gas inside is V_i and pressure of the gas inside is P_{int}.

If the external pressure P_{ext} is greater than P_{int}, the piston moves inward till the pressure inside becomes equal to P_{ext}. Let this change be achieved in a single step and the final volume be V_f.

In this case, the work is done on the system (+w). It can be calculated as follows

$$w = -F \cdot \Delta x \quad \text{---------- (7.2)}$$

where dx is the distance moved by the piston during the compression and F is the force acting on the gas.

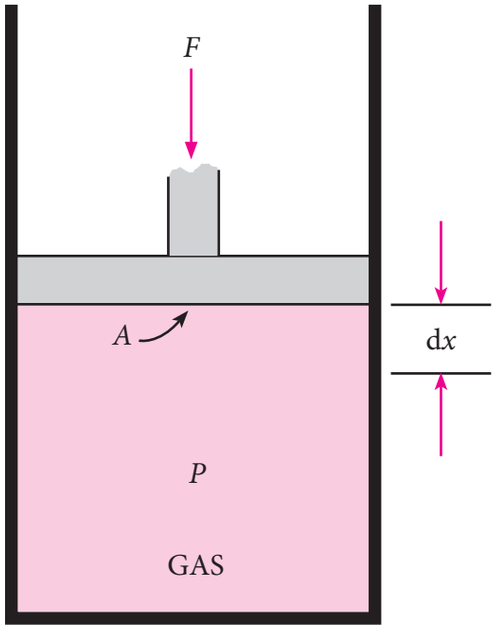

Figure 7.3 showing work involved in compression processes

$$F = P_{ext} A \text{---- } (7.3)$$

Substituting 7.3 in 7.2

$$w = -P_{ext} \cdot A \cdot \Delta x$$

$$A.\Delta x = \textit{change in volume} = V_f - V_i$$

$$w = -P_{ext} \cdot (V_f - V_i) \text{ ------ } (7.4)$$

$$w = -P_{ext} \cdot (-\Delta V) \text{ ------ } (7.5)$$

$$= P_{ext} \cdot \Delta V$$

Since work is done on the system, it is a positive quantity.

If the pressure is not constant, but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case we can calculate the work done on the gas by the relation

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$$w_{rev} = -\int_{V_i}^{V_f} P_{ext}\, dV$$

In a compression process, P_{ext} the external pressure is always greater than the pressure of the system.

i.e $P_{ext} = (P_{int} + dP)$.

In an expansion process, the external pressure is always less than the pressure of the system

i.e. $P_{ext} = (P_{int} - dP)$.

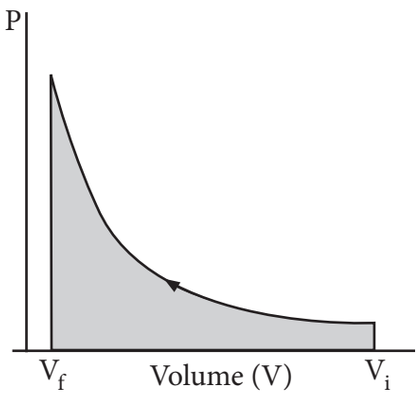

Figure 7.4

When pressure is not constant and changes in infinitesimally small steps (reversible conditions) during compression from V_i to V_f , the P-V plot looks like in fig 7.4 Work done on the gas is represented by the shaded area.

In general case we can write,

$P_{ext} = (P_{int} \pm dP)$. Such processes are called reversible processes. For a compression process work can be related to internal pressure of the system under reversible conditions by writing equation

$$w_{rev} = -\int_{V_i}^{V_f} P_{int}\, dV$$

For a given system with an ideal gas

$$P_{int}\, V = nRT$$

$$P_{int} = \frac{nRT}{V}$$

$$w_{rev} = -\int_{V_i}^{V_f} \frac{nRT}{V}\, dV$$

$$w_{rev} = -nRT \int_{V_i}^{V_f} \left(\frac{dV}{V}\right)$$

$$w_{rev} = -nRT \ln\left(\frac{V_f}{V_i}\right)$$

$$w_{rev} = -2.303\, nRT \log\left(\frac{V_f}{V_i}\right) \text{ ------ } 7.6$$

If $V_f > V_i$ (expansion), the sign of work done by the process is negative.

If $V_f < V_i$ (compression) the sign of work done on the process is positive.

Table: 7.3 Summary of sign conventions

1.	If heat is absorbed by the system	:	$+q$
2.	If heat is evolved by the system	:	$-q$
3.	work is done by the system	:	$-w$
4.	work is done on the system	:	$+w$

7.3 Zeroth law of thermodynamics:

The zeroth law of thermodynamics, also known as the law of thermal equilibrium, was put forward much after the establishment of the first and second laws of thermodynamics. It is placed

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before the first and second laws as it provides a logical basis for the concept of temperature of the system.

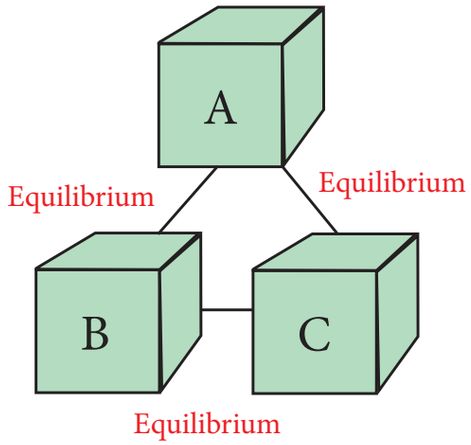

Figure : 7.5 Zeroth law of thermodynamics:

The law states that `If two systems are separately in thermal equilibrium with a third one, then they tend to be in thermal equilibrium with themselves'.

According to this law, if systems B and C separately are in thermal equilibrium with another system A, then systems B and C will also be in thermal equilibrium with each other. This is also the principle by which thermometers are used.

7.4 First Law of Thermodynamics:

The first law of thermodynamics, known as the law of conservation of energy, states that the total energy of an isolated system remains constant though it may change from one form to another.

When a system moves from state 1 to state 2, its internal energy changes from U_1 to U_2. Then change in internal energy

$$\Delta U = U_2 - U_1.$$

This internal energy change is brought about by the either absorption or evolution of heat and/or by work being done by/on the system.

Because the total energy of the system must remain constant, we can write the mathematical statement of the First Law as:

$$\Delta U = q + w \quad \text{----------(7.7)}$$

Where q - the amount of heat supplied to the system; w - work done on the system

Other statements of first law of thermodynamics

(1) Whenever an energy of a particular type disappears, an equivalent amount of another type must be produced.

(2) The total energy of a system and surrounding remains constant (or conserved)

(3) "Energy can neither be created nor destroyed, but may be converted from one form to another".

(4) "The change in the internal energy of a closed system is equal to the energy that passes through its boundary as heat or work".

(5) "Heat and work are two ways of changing a system's internal energy".

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7.4.1 Mathematical statement of the first law

The mathematical statement of the first law of thermodynamics is

$$\Delta U = q + w \quad \text{--------- (7.7)}$$

Case 1 : For a cyclic process involving isothermal expansion of an ideal gas,

$$\Delta U = 0.$$

eqn (7.7) $\Rightarrow \therefore q = -w$

In other words, during a cyclic process, the amount of heat absorbed by the system is equal to work done by the system.

Case 2 : For an isochoric process (no change in volume) there is no work of expansion. i.e. $\Delta V = 0$

$$\Delta U = q + w$$

$$= q - P\Delta V$$

$$\Delta V = 0$$

$$\Delta U = q_v$$

In other words, during an isochoric process, the amount of heat supplied to the system is converted to its internal energy.

Case 3 : For an adiabatic process there is no change in heat. i.e. q= 0. Hence

$$q = 0$$

eqn (7.7) $\Rightarrow \Delta U = w$

In other words, in an adiabatic process, the decrease in internal energy is exactly equal to the work done by the system on its surroundings.

Case 4 : For an isobaric process. There is no change in the pressure. P remains constant. Hence

$$\Delta U = q + w$$

$$\Delta U = q - P\,\Delta V$$

In other words, in an isobaric process a part of heat absorbed by the system is used for P-V expansion work and the remaining is added to the internal energy of the system.

Problem: 7.1

A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J of thermal energy from its surroundings. Determine the change in internal energy of system.

Solution:

Given data q = 400 J V_1=5L V_2 = 10L

Δu = q-w (heat is given to the system (+q); work is done by the system(-w)

$$\Delta u = q - PdV$$

$$= 400\ J - 1\ atm\ (10-5)L$$

$$= 400\ J - 5\ atm\ L$$

[$\therefore$1L atm = 101.33 J]

$$= 400\ J - 5 \times 101.33\ J$$

$$= 400\ J - 506.65\ J$$

$$= -106.65\ J$$

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7.5 Enthalpy (H)

The enthalpy (H), is a thermodynamic property of a system, is defined as the sum of the internal energy (*U*) of a system and the product of pressure and volume of the system. That is,

$H = U + PV$ ----------(7.8)

It reflects the capacity to do mechanical work and the capacity to release heat by the system. When a process occurs at constant pressure, the heat involved (either released or absorbed) is equal to the change in enthalpy.

Enthalpy is a state function which depends entirely on the state functions T, P and U. Enthalpy is usually expressed as the change in enthalpy (ΔH) for a process between initial and final states at constant pressure.

$\Delta H = \Delta U + P\Delta V$ ----------(7.9)

The change in enthalpy (*ΔH)* is equal to the heat supplied at the constant pressure to a system (as long as the system does no additional work).

$\Delta H = q_p$

In an endothermic reaction heat is absorbed by the system from the surroundings that is $q>0$ (positive). Therefore, ΔH is also positive. In an exothermic reaction heat is evolved by the system to the surroundings that is, $q<0$ (negative). If q is negative, then ΔH will also be negative.

7.5.1 Relation between enthalpy `H' and internal energy `U'

When the system at constant pressure undergoes changes from an initial state with H_1, U_1 and V_1 to a final state with H_2, U_2 and V_2 the change in enthalpy ΔH, can be calculated as follows:

$H=U + PV$

In the initial state

$$H_1=U_1 + PV_1 \text{-----(7.10)}$$

In the final state

$$H_2 = U_2 + PV_2 \text{----(7.11)}$$

change in enthalpy is (7.11) - (7.10)

$$(H_2-H_1) = (U_2-U_1) + P(V_2-V_1)$$

$$\Delta H=\Delta U + P\Delta V \text{ --------- (7.12)}$$

As per first law of thermodynamics,

$\Delta U = q+w$

Equation 7.12 becomes

$\Delta H = q + w + P\Delta V$

$w= -P\Delta V$

$\Delta H = q_p - P\Delta V + P\Delta V$

$\Delta H = q_p$ ---------- (7.13)

q_p – is the heat absorbed at constant pressure and is considered as heat content.

Consider a closed system of gases which are chemically reacting to form gaseous products at constant temperature

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and pressure with V_i and V_f as the total volumes of the reactant and product gases respectively, and n_i and n_f as the number of moles of gaseous reactants and products, then,

For reactants (initial state) :

$$PV_i = n_i RT \text{ --------- (7.14)}$$

For products (final state) :

$$PV_f = n_f RT \text{ --------- (7.15)}$$

(7.15) - (7.14)

$$P(V_f - V_i) = (n_f - n_i) RT$$

$$P\Delta V = \Delta n_{(g)} RT \text{ --------(7.16)}$$

Substituting in 7.16 in 7.12

$$\Delta H = \Delta U + \Delta n_{(g)} RT \text{--------(7.17)}$$

7.5.2 Enthalpy Changes for Different Types of Reactions and Phase Transitions:

The heat or enthalpy changes accompanying chemical reactions is expressed in different ways depending on the nature of the reaction. These are discussed below.

Standard heat of formation

The standard heat of formation of a compound is defined as "the change in enthalpy that takes place when one mole of a compound is formed from its elements, present in their standard states (298 K and 1 bar pressure)". By convention the standard heat of formation of all elements is assigned a value of zero.

$Fe(s) + S(s) \rightarrow FeS(s)$

$$\Delta H_f^0 = -100.42 \text{ kJ mol}^{-1}$$

$2C(s) + H_2(g) \rightarrow C_2H_2(g)$

$$\Delta H_f^0 = +222.33 \text{ kJ mol}^{-1}$$

$$\frac{1}{2} Cl_2(g) + \frac{1}{2} H_2(g) \rightarrow HCl(g)$$

$$\Delta H_f^0 = -92.4 \text{ kJ mol}^{-1}$$

The standard heats of formation of some compounds are given in Table 7.4.

Table: 7.4 standard heat of formation of some compounds

Substance	ΔH_f^0 (kJ mol^{-1})	Substance	ΔH_f^0 (kJ mol^{-1})
$H_2O(l)$	−242	$CH_4(g)$	-74.85
HCl(g)	−92.4	$C_2H_6(g)$	−84.6
HBr(g)	−36.4	$C_6H_6(g)$	+49.6
NH3(g)	−46.1	$C_2H_2(g)$	+222.33
$CO_2(g)$	-393.5	$CH_3OH(l)$	−239.2

7.6 Thermochemical Equations:

A thermochemical equation is a balanced stoichiometric chemical equation that includes the enthalpy change (ΔH). The following conventions are adopted in thermochemical equations:

(i) The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

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(ii) The enthalpy change of the reaction ΔH_r has to be specified with appropriate sign and unit.

(iii) When the chemical reaction is reversed, the value of ΔH is reversed in sign with the same magnitude.

(iv) The physical states (gas, liquid, aqueous, solid in brackets) of all species are important and must be specified in a thermochemical reaction, since ΔH depends on the physical state of reactants and products.

(v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also multiplied by the same number.

(vi) The negative sign of ΔH_r indicates that the reaction is exothermic and the positive sign of ΔH_r indicates an endothermic reaction.

For example, consider the following reaction,

$$2\ H_2(g)+O_2(g)\rightarrow 2\ H_2O(g)$$

$$\Delta H_r^0 = -\ 967.4\ kJ$$

$$2\ H_2O\ (g) \rightarrow 2\ H_2(g) + O_2(g)$$

$$\Delta H_r^0 = +\ 967.4\ kJ$$

Standard enthalpy of reaction (ΔH_r^0) from standard enthalpy of formation (ΔH_f^0)

The standard enthalpy of a reaction is the enthalpy change for a reaction when all the reactants and products are present in their standard states. Standard conditions are denoted by adding the superscript 0 to the symbol (ΔH^0)

We can calculate the enthalpy of a reaction under standard conditions from the values of standard enthalpies of formation of various reactants and products. The standard enthalpy of reaction is equal to the difference between standard enthalpy of formation of products and the standard enthalpies of formation of reactants.

$$\Delta H_r^{0} = \Sigma\ \Delta H_r^{0}{}_{(products)} - \Sigma\ \Delta H_r^{0}{}_{(reactants)}$$

For a general reaction

$$aA + bB \rightarrow cC + dD$$

$$\Delta H_f^0 = \Sigma\ \Delta H_f^0{}_{(products)} - \Sigma\ \Delta H_f^0{}_{(reactants)}$$

$$\Delta H_f^0 = \{c\ \Delta H_f^0\ (C) + d\ \Delta H_f^0\ (D)\} - \{a\ \Delta H_f^0(A) + b\ \Delta H_f^0(B)\}$$

Problem : 7.2

The standard enthalpies of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are - 277, -393.5 and -285.5 kJ mol^{-1} respectively. Calculate the standard enthalpy change for the reaction

$$C_2H_5OH(l)+3O_2(g)\rightarrow 2CO_2(g)+ 3\ H_2O(l)$$

The enthalpy of formation of $O_2(g)$ in the standard state is Zero, by definition

Solution:

For example, the standard enthalpy change for the combustion of ethanol can be calculated from the standard enthalpies of formation of $C_2H_5OH(l)$, $CO_2(g)$

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and $H_2O(l)$. The enthalpies of formation are –277, – 393.5 and –285.5 kJ mol^{-1} respectively.

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H_r^0 = \left\{\left(\Delta H_f^0\right)_{products} - \left(\Delta H_f^0\right)_{reactants}\right\}$$

$$\Delta H_r^0 = \left[2\left(\Delta H_f^0\right)_{CO_2} + 3\left(\Delta H_f^0\right)_{H_2O}\right] - \left[1\left(\Delta H_f^0\right)_{C_2H_5OH} + 3\left(\Delta H_f^0\right)_{O_2}\right]$$

$$\Delta H_r^0 = \begin{bmatrix} 2mol\,(-393.5)\,kJ\,mol^{-1} \\ +\,3mol\,(-285.5)\,kJ\,mol^{-1} \end{bmatrix} - \begin{bmatrix} 1mol\,(-277)\,kJ\,mol^{-1} \\ +\,3mol\,(0)kJ\,mol^{-1} \end{bmatrix}$$

$$= [-787 - 856.5] - [-277]$$

$$= -1643.5 + 277$$

$$\Delta H_r^0 = -1366.5\ KJ$$

Evaluate Yourself - 1

Calculate ΔH_f^0 for the reaction

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

given that ΔH_f^0 for CO_2 (g), CO (g) and H_2O(g) are – 393.5, – 111.31 and – 242 kJ mol^{-1} respectively.

Heat of combustion

The heat of combustion of a substance is defined as "The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen". It is denoted by ΔH_C. For example, the heat of combustion of methane is – 87.78 kJ mol^{-1}

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

ΔH_C = – 87.78 kJ mol^{-1}

For the combustion of carbon,

$C(s) + O_2(g) \rightarrow CO_2(g)$

ΔH_C = – 394.55 kJ mol^{-1}

Combustion reactions are always exothermic. Hence the enthalpy change is always negative.

Molar heat capacities

When heat (q) is supplied to a system, the molecules in the system absorb the heat and hence their kinetic energy increases, which in turn raises the temperature of the system from T_1 to T_2. This increase $(T_2 - T_1)$ in temperature is directly proportional to the amount of heat absorbed and inversely proportional to mass of the substance. In other words,

$q \alpha m\Delta T$

$q = c\ m\ \Delta T$

$c = q/m\ \Delta T$

The constant c is called heat capacity.

$$c = \left(\frac{q}{m\,(T_2 - T_1)}\right) \quad -------(7.18)$$

when m=1 kg and $(T_2 - T_1)$ = 1 K then the heat capacity is referred as specific heat capacity. The equation 7.18 becomes

$c = q$

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Thus specific heat capacity of a system is defined as "The heat absorbed by one kilogram of a substance to raise its temperature by one Kelvin at a specified temperature".

The heat capacity for 1 mole of substance, is called molar heat capacity (c_m). It is defined as "The amount of heat absorbed by one mole of the substance to raise its temperature by 1 kelvin".

Units of Heat Capacity:

The SI unit of molar heat capacity is $JK^{-1}mol^{-1}$

The molar heat capacities can be expressed either at constant volume (C_v) or at constant pressure (C_p).

According to the first law of thermodynamics

$U = q + w$ or $U = q - PdV$

$q = U + PdV$ ----------(7.19)

Differentiate (7.19) with respect to temperature at constant volume i.e dV=0,

$$\left(\frac{\partial q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad -------7.20$$

Thus the heat capacity at constant volume (C_V) is defined as the rate of change of internal energy with respect to temperature at constant volume.

Similarly the molar heat capacity at constant pressure (C_P) can be defined as the rate of change of enthalpy with respect to temperature at constant pressure.

$$c_P = \left(\frac{\partial H}{\partial T}\right)_P \quad -------(7.21)$$

Relation between Cp and Cv for an ideal gas.

From the definition of enthalpy

$H=U+PV$ ------(7.8)

for 1 mole of an ideal gas

$PV = nRT$ -----(7.22)

By substituting (7.22) in (7.8)

$H = U + nRT$ ---- (7.23)

Differentiating the above equation with respect to T,

$$\frac{\partial H}{\partial T} = \frac{\partial U}{\partial T} + nR\frac{\partial T}{\partial T}$$

$C_p = C_v + nR$ (1)

$C_p - C_v = nR$ .....(7.24) $\left[\because \left(\frac{\partial H}{\partial T}\right)_P = C_P \text{ and } \left(\frac{\partial U}{\partial T}\right)_V = C_V\right]$

At constant pressure processes, a system has to do work against the surroundings. Hence, the system would require more heat to effect a given temperature rise than at constant volume, so C_p is always greater than C_v

Calculation of ΔU and ΔH

For one mole of an ideal gas, we have

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$$C_V = \frac{dU}{dT}$$

$dU = C_V\, dT$

For a finite change, we have

$\Delta U = C_V\, \Delta T$

$$\Delta U = C_V\, (T_2 - T_1)$$

and for n moles of an ideal gas we get

$\Delta U = n\, C_v (T_2 - T_1)$ ---------- (7.25)

Similarly for *n* moles of an ideal gas we get

$\Delta H = n\, C_P\, (T_2 - T_1)$------ (7.26)

Problem 7.3

Calculate the value of ΔU and ΔH on heating 128.0 g of oxygen from 0° C to 100^0 C. C_V and C_P on an average are 21 and 29 J mol^{-1} K^{-1}. (The difference is 8Jmol^{-1} K^{-1} which is approximately equal to R)

Solution.

We know

$\Delta U = n\, C_v\, (T_2 - T_1)$

$\Delta H = n\, C_P\, (T_2 - T_1)$

Here $n = \frac{128}{32} = 4$ moles ;

$T_2 = 100^0$ C =373K; $T_1 = 0^0$ C = 273K

$\Delta U = n\, C_v\, (T_2 - T_1)$

$\Delta U = 4 \times 21 \times (373 - 273)$

$\Delta U = 8400$ J

$\Delta U = 8.4$ kJ

$\Delta H = n\, Cp\, (T_2 - T_1)$

$\Delta H = 4 \times 29 \times (373 - 273)$

$\Delta H = 11600$ J

$\Delta H = 11.6$ kJ

Evaluate Yourself -2

Calculate the amount of heat necessary to raise 180 g of water from 25^0 C to 100^0 C. Molar heat capacity of water is 75.3 J mol^{-1} K^{-1}

7.7 Measurement of ΔU and ΔH using Calorimetry.

Calorimeter is used for measuring the amount of heat change in a chemical or physical change. In calorimetry, the temperature change in the process is measured which is inversely proportional to the heat change. By using the expression $C = q/m\Delta T$, we can calculate the amount of heat change in the process. Calorimetric measurements are made under two different conditions

i) At constant volume (q_V)

ii) At constant pressure (q_p)

(A) ΔU Measurements

For chemical reactions, heat evolved at constant volume, is measured in a *bomb calorimeter*.

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The inner vessel (the bomb) and its cover are made of strong steel. The cover is fitted tightly to the vessel by means of metal lid and screws.

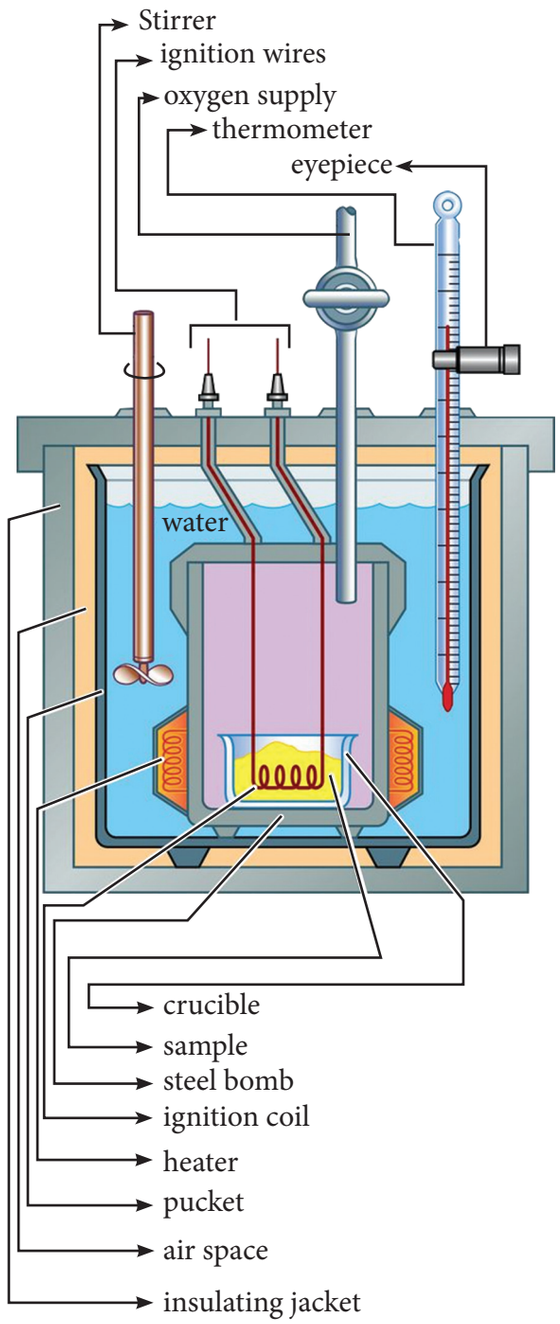

Figure 7.6 Bomb calorimeter

A weighed amount of the substance is taken in a platinum cup connected with electrical wires for striking an arc instantly to kindle combustion. The bomb is then tightly closed and pressurized with excess oxygen. The bomb is immersed in water, in the inner volume of the calorimeter. A stirrer is placed in the space between the wall of the calorimeter and the bomb, so that water can be stirred, uniformly. The reaction is started by striking the substance through electrical heating.

A known amount of combustible substance is burnt in oxygen in the bomb. Heat evolved during the reaction is absorbed by the calorimeter as well as the water in which the bomb is immersed. The change in temperature is measured using a Beckman thermometer. Since the bomb is sealed its volume does not change and hence the heat measurements is equal to the heat of combustion at a constant volume (ΔU_c^0).

The amount of heat produced in the reaction (ΔU_c^0) is equal to the sum of the heat abosrbed by the calorimeter and water.

Heat absorbed by the calorimeter

$$q_1 = k.\Delta T$$

where k is a calorimeter constant equal to m_c C_c (m_c is mass of the calorimeter and C_c is heat capacity of calorimeter)

Heat absorbed by the water

$$q_2 = m_w C_w \Delta T$$

where m_w is molar mass of water

C_w is molar heat capacity of water (75.29 J K^{-1} mol^{-1})

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Therefore $\Delta U_c = q_1 + q_2$

$= k.\Delta T + m_w C_w \Delta T$

$= (k+m_w C_w)\Delta T$

Calorimeter constant can be determined by burning a known mass of standard sample (benzoic acid) for which the heat of combustion is known (-3227 $kJmol^{-1}$)

The enthalpy of combustion at constant pressure of the substance is calculated from the equation (7.17)

$$\Delta H_C^0{}_{(pressure)} = \Delta U_C^0{}_{(Vol)} + \Delta n_g RT$$

Applications of bomb calorimeter:

1. Bomb calorimeter is used to determine the amount of heat released in combustion reaction.

2. It is used to determine the calorific value of food.

3. Bomb calorimeter is used in many industries such as metabolic study, food processing, explosive testing etc.

(b) ΔH Measurements

Heat change at constant pressure (at atmospheric pressure) can be measured using a coffee cup calorimeter. A schematic representation of a coffee cup calorimeter is given in Figure 7.7. Instead of bomb, a styrofoam cup is used in this calorimeter. It acts as good adiabatic wall and doesn't allow transfer of heat produced during the reaction to its surrounding. This entire heat energy is absorbed by the water inside the cup. This method can be used for the reactions where there is no appreciable change in volume. The change in the temperature of water is measured and used to calculate the amount of heat that has been absorbed or evolved in the reaction using the following expression.

$$q = m_w C_w \Delta T$$

where m_w is the molar mass of water and C_w is the molar heat capacity of water (75.29 $J\ K^{-1}\ mol^{-1}$)

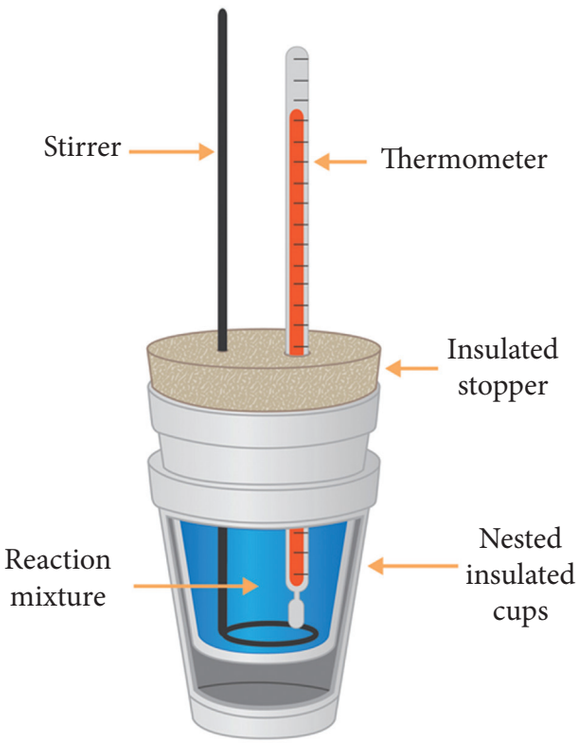

Figure 7.7 Coffee cup Calorimeter

Problem 7. 4

Calculate the enthalpy of combustion of ethylene at 300 K at constant pressure, if its heat of combustion at constant volume (ΔU) is −1406 kJ .

The complete ethylene combustion reaction can be written as,

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$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$

$\Delta U = -1406$ kJ

$\Delta n = n_{p(g)} - n_{r(g)}$

$\Delta n = 2 - 4 = -2$

$\Delta H = \Delta U + RT\Delta n_g$

$\Delta H = -1406 + (8.314 \times 10^{-3} \times 300 \times (-2)$

$\Delta H = -1410.9$ kJ

Evaluate Yourself - 3

From the following data at constant volume for combustion of benzene, calculate the heat of this reaction at constant pressure condition.

$C_6H_6(l) + 7½\ O_2(g) \rightarrow$

$6CO_2(g) + 3\ H_2O(l)$

ΔU at 25^0 C = -3268.12 kJ

Applications of the heat of combustion:

(1) Calculation of heat of formation: Since the heat of combustion of organic compounds can be determined with considerable ease, they are employed to calculate the heat of formation of other compounds.

For example let us calculate the standard enthalpy of formation ΔH_f^0 of CH_4 from the values of enthalpy of combustion for H_2, C(graphite) and CH_4 which are - 285.8, - 393.5, and -890.4 kJ mol^{-1} respectively.

Let us interpret the information about enthalpy of formation by writing out the equations. It is important to note that the standard enthalpy of formation of pure elemental gases and elements is assumed to be zero under standard conditions. Thermochemical equation for the formation of methane from its constituent elements is,

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$

$\Delta H_f^0 = X$ kJ mol^{-1}--- (i)

Thermo chemical equations for the combustion of given substances are,

$H_2(g) + \frac{1}{2} O_2 \rightarrow H_2O(l)$

$\Delta H^0 = -285.8$ kJ mol^{-1}--- (ii)

$C_{(graphite)} + O_2 \rightarrow CO_2$

$\Delta H^0 = -393.5$ kJ mol^{-1}--- (iii)

$CH_4(g) + 2\ O_2 \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H^0 = -890.4$ kJ mol^{-1}--- (iv)

Since methane is in the product side of the required equation (i), we have to reverse the equation (iv)

$CO_2(g) + 2\ H_2O(l) \rightarrow CH_4(g) + 2\ O_2$

$\Delta H^0 = +890.4$ kJ mol^{-1}--- (v)

In order to get equation (i) from the remaining,

(i) = [(ii) × 2] + (iii) + (v)

$X = [(-285.8) \times 2] + [-393.5] + [+890.4]$

$= -74.7$ kJ

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Hence, the amount of energy required for the formation of 1 mole of methane is -74.7 kJ

The heat of formation methane = -74.7 kJ mol^{-1}

(2) Calculation of calorific value of food and fuels: The calorific value is defined as the amount of heat produced in calories (or joules) when one gram of the substance is completely burnt. The SI unit of calorific value is J kg^{-1}. However, it is usually expressed in cal g^{-1}.

Heat of solution:

Heat changes are usually observed when a substance is dissolved in a solvent. The heat of solution is defined as the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

Heat of neutralisation:

The heat of neutralisation is defined as "The change in enthalpy when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base or vice versa in dilute solution".

$HCl(aq)+NaOH(aq) \rightarrow NaCl\,(aq)+ H_2O(l)$

$\Delta H = -57.32$ kJ

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

$\Delta H = -57.32$ kJ

The heat of neutralisation of a strong acid and strong base is around –57.32 kJ, irrespective of nature of acid or base used which is evident from the below mentioned examples.

$HCl\,(aq) + KOH(aq) \rightarrow KCl\,(aq) + H_2O(l)$

$\Delta H = -57.32$ kJ

$HNO_3(aq)+KOH(aq) \rightarrow KNO_3(aq)+ H_2O(l)$

$\Delta H = -57.32$ kJ

$H_2SO_4(aq) + 2KOH(aq) \rightarrow$

$K_2SO_4(aq) + 2\,H_2O(l)$

$\Delta H = -57.32$ kJ x 2

The reason for this can be explained on the basis of Arrhenius theory of acids and bases which states that strong acids and strong bases completely ionise in aqueous solution to produce H^+ and OH^- ions respectively. Therefore in all the above mentioned reactions the neutralisation can be expressed as follows.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

$\Delta H = -57.32$ kJ

Molar heat of fusion

The molar heat of fusion is defined as "the change in enthalpy when one mole of a solid substance is converted into the liquid state at its melting point".

For example, the heat of fusion of ice can be represented as

$H_2O(s) \xrightarrow{273K} H_2O(l)\ \Delta H_{fusion} = +5.98$kJ

Molar heat of vapourisation

The molar heat of vaporisation is defined as "the change in enthalpy when

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one mole of liquid is converted into vapour state at its boiling point".

For example, heat of vaporisation of water can be represented as

$$H_2O(l) \xrightarrow{373K} H_2O(v) \quad \Delta H_{vap} = +40.626 \text{ kJ}$$

Molar heat of sublimation

Sublimation is a process when a solid changes directly into its vapour state without changing into liquid state. Molar heat of sublimation is defined as "the change in enthalpy when one mole of a solid is directly converted into the vapour state at its sublimation temperature". For example, the heat of sublimation of iodine is represented as

$$I_2(s) \xrightarrow{373K} I_2(v) \quad \Delta H_{sub} = +62.42 \text{ kJ}$$

Another example of sublimation process is solid CO_2 to gas at atmospheric pressure at very low temperatures.

Heat of transition

The heat of transition is defined as "The change in enthalpy when one mole of an element changes from one of its allotropic form to another. For example, the transition of diamond into graphite may be represented as

$$C_{(diamond)} \longrightarrow C_{(graphite)}$$

$$\Delta H_{trans} = +13.81 \text{ kJ}$$

Similarly the allotropic transitions in sulphur and phsphorous can be represented as follows,

$$S_{(monoclinic)} \longrightarrow S_{(rhombic)}$$

$$\Delta H_{trans} = -0.067 \text{ kJ}$$

$$P_{(white)} \longrightarrow P_{(red)}$$

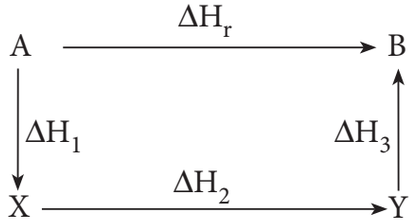
$$\Delta H_{trans} = -4.301 \text{ kJ}$$

7.8 Hess's law of constant heat summation

We have already seen that the heat changes in chemical reactions are equal to the difference in internal energy (ΔU) or heat content (ΔH) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since ΔU and ΔH are functions of the state of the system, the heat evolved or absorbed in a given reaction depends only on the initial state and final state of the system and not on the path or the steps by which the change takes place.

This generalisation is known as **Hess's law** and stated as:

The enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps provided the initial and final states are same.



$$\Delta H_r = \Delta H_1 + \Delta H_2 + \Delta H_3$$

Application of Hess's Law: Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure. For example, it is very difficult to measure the heat of combustion of graphite to give pure CO.

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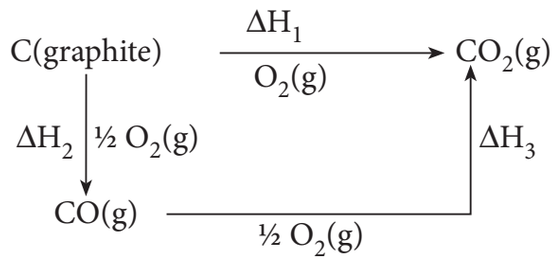
However, enthalpy for the oxidation of graphite to CO_2 and CO to CO_2 can easily be measured. For these conversions, the heat of combustion values are –393.5 kJ and – 283.5 kJ respectively.

From these data the enthalpy of combustion of graphite to CO can be calculated by applying Hess's law.

The reactions involved in this process can be expressed as follows



According to Hess law,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

$$-393.5 \text{ kJ} = X - 283.5 \text{ kJ}$$

$$X = -110.5 \text{ kJ}$$

7.9 Lattice energy ($\Delta H_{lattice}$)

Lattice energy is defined as the amount of energy required to completely remove the constituent ions from its crystal lattice to an infinite distance from one mole of crystal. It is also referred as lattice enthalpy.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$$

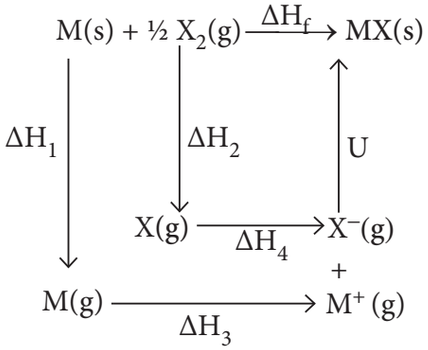
$$\Delta H_{lattice} = + 788 \text{ kJ mol}^{-1}$$

From the above equation it is clear that 788 kJ of energy is required to separate Na^+ and Cl^- ions from 1 mole of NaCl.

Born - Haber cycle

The Born–Haber cycle is an approach to analyse reaction energies. It was named after two German scientists Max Born and Fritz Haber who developed this cycle. The cycle is concerned with the formation of an ionic compound from the reaction of a metal with a halogen or other non-metallic element such as oxygen.

Born–Haber cycle is primarily used in calculating lattice energy, which cannot be measured directly. The Born–Haber cycle applies Hess's law to calculate the lattice enthalpy. For example consider the formation of a simple ionic solid such as an alkali metal halide MX, the following steps are considered.



ΔH_1 - enthalpy change for the sublimation M(s) to M(g)

ΔH_2- enthalpy change for the dissociation of $\frac{1}{2} X_2$ (g) to X(g)

ΔH_3- Ionisation energy for M(g) to M^+(g)

ΔH_4 - electron affinity for the conversion of X(g) to X^-(g)

U - the lattice enthalpy for the formation of solid MX

ΔH_f - enthalpy change for the formation of solid MX directly form elements

According to Hess's law of heat summation

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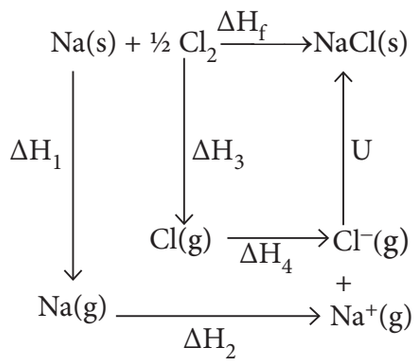
$$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + U$$

Let us use the Born - Haber cycle for determining the lattice enthalpy of NaCl as follows:

Since the reaction is carried out with reactants in elemental forms and products in their standard states, at 1 bar, the overall enthalpy change of the reaction is also the enthalpy of formation for NaCl. Also, the formation of NaCl can be considered in 5 steps. The sum of the enthalpy changes of these steps is equal to the enthalpy change for the overall reaction from which the lattice enthalpy of NaCl is calculated.

Let us calculate the lattice energy of sodium chloride using Born-Haber cycle



ΔH_f = heat of formation of sodium chloride = – 411.3 kJ mol^{-1}

ΔH_1 = heat of sublimation of Na(g) = 108.7 kJ mol^{-1}

ΔH_2 = ionisation energy of Na(g) = 495.0 kJ mol^{-1}

ΔH_3 = dissociation energy of Cl_2(g) = 244 kJ mol^{-1}

ΔH_4 = Electron affinity of Cl(S)= – 349.0 kJ mol^{-1}

U = lattice energy of NaCl

$$\Delta H_f = \Delta H_1 + \Delta H_2 + \tfrac{1}{2}\Delta H_3 + \Delta H_4 + U$$

$$\therefore U = \left(\Delta H_f\right) - \left(\Delta H_1 + \Delta H_2 + \tfrac{1}{2}\Delta H_3 + \Delta H_4\right)$$

$\Rightarrow$ U = (–411.3) – (108.7 + 495.0 + 122 – 349)

U = (–411.3) – (376.7)

$\therefore$ U = – 788 kJ mol^{-1}

This negative sign in lattice energy indicates that the energy is released when sodium is formed from its constituent gaseous ions Na^+ and Cl^-

Evaluate Yourself - 4

When a mole of magnesium bromide is prepared from 1 mole of magnesium and 1 mole of liquid bromine, 524 kJ of energy is released.The heat of sublimation of Mg metal is 148 kJ mol^{-1}. The heat of dissociation of bromine gas into atoms is 193 kJ mol^{-1}. The heat of vapourisation of liquid bromine is 31 kJ mol^{-1}. The firat and second ionisation energies of magnesium are IE_1=737.5 kJ mol^{-1} and IE_2=1450.5 kJ mol^{-1} and the electron affinity of bromine is – 324.5 kJ mol^{-1}. Calculate the lattice energy of magnesium bromide.

7.10. Second Law of thermodynamics:

Need for the second law of thermodynamics:

We know from the first law of thermodynamics, the energy of the universe is conserved. Let us consider the following processes:

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1. A glass of hot water over time loses heat energy to the surrounding and becomes cold.
2. When you mix hydrochloric acid with sodium hydroxide, it forms sodium chloride and water with evolution of heat.

In both these processes, the total energy is conserved and are consistent with the first law of thermodynamics. However, the reverse process i.e. cold water becoming hot water by absorbing heat from surrounding on its own does not occur spontaneously even though the energy change involved in this process is also consistent with the first law. However, if the heat energy is supplied to cold water, then it will become hot. i.e. the change that does not occur spontaneously and an be driven by supplying energy.

Similarly, a solution of sodium chloride does not absorb heat energy on its own, to form hydrochloric acid and sodium hydroxide. But, this process can not be driven even by supplying energy. From these kinds of our natural experiences, we have come to know that certain processes are spontaneous while the others are not, and some processes have a preferred direction. In order to explain the feasibility of a process, we need the second law of thermodynamics.

7.10.1 Various statements of the second law of thermodynamics

Entropy

The second law of thermodynamics introduces another state function called entropy. Entropy is a measure of the molecular disorder (randomness) of a system. But thermodynamic definition of entropy is concerned with the change in entropy that occurs as a result of a process.

It is defined as, $dS = dq_{rev} / T$

Entropy statement:

The second law of thermodynamics can be expressed in terms of entropy. i.e "the entropy of an isolated system increases during a spontaneous process".

For an irreversible process such as spontaneous expansion of a gas,

$\Delta S_{total} > 0$

$\Delta S_{total} > \Delta S_{system} + \Delta S_{surrounding}$

i.e. $\Delta S_{total} > \Delta S_{system} + \Delta S_{surrounding}$

For a reversible process such as melting of ice,

$\Delta S_{system} = - \Delta S_{surrounding}$

$\Delta S_{total} = 0$

Kelvin-Planck statement:

It is impossible to construct a machine that absorbs heat from a hot source and converts it completely into work by a cyclic process without transferring a part of heat to a cold sink. The second law of thermodynamics explains why even an ideal, frictionless engine cannot convert 100% of its input heat into work. Carnot on his analysis of heat engines, found that the maximum efficiency of a heat engine which operates reversibly, depends only on the two temperatures between which it is operated.

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Efficiency = work performed / heat absorbed

$$\eta = \frac{|q_h| - |q_c|}{|q_h|}$$

q_h - heat absorbed from the hot reservoir

q_c - heat transferred to cold reservoir

$$\eta = 1 - \frac{|q_c|}{|q_h|} \quad ---(7.27)$$

For a reversible cyclic process

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0$

$$\Delta S_{system} = - \Delta S_{surroundings}$$

$$\frac{q_h}{T_h} = \frac{-q_c}{T_c}$$

$$\frac{T_c}{T_h} = \frac{-q_c}{q_h}$$

$$\frac{T_c}{T_h} = \frac{|q_c|}{|q_h|} ----7.28$$

Sustituting 7.28 in 7.27

$$\Rightarrow \eta = 1 - \frac{T_c}{T_h} -------7.29$$

$T_h >> T_c$

Hence, $\eta < 1$

efficiency in percentage can be expressed as

$$\text{Efficiency in percentage} = \left[1 - \frac{T_c}{T_h}\right] x\,100$$

Clausius statement:

It is impossible to transfer heat from a cold reservoir to a hot reservoir without doing some work.

Problem: 7.10

If an automobile engine burns petrol at a temperature of 816° C and if the surrounding temperature is 21° C, calculate its maximum possible efficiency.

Solution:

$$\% \text{ Efficiency} = \left[\frac{T_h - T_c}{T_h}\right] \times 100$$

Here

T_h = 816+273= 1089 K;

T_c= 21+273= 294K

$$\% \text{ Efficiency} = \left(\frac{1089 - 294}{1089}\right) \times 100$$

% Efficiency=73%

Evaluate Yourself - 5

An engine operating between 127^0 C and 47^0 C takes some specified amount of heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the percentage efficiency of an engine.

Unit of entropy:

The entropy (S) is equal to heat energy exchanged (q) divided by the temperature (T) at which the exchange takes place. Therefore, The SI unit of entropy is JK^{-1}.

Spontaneity and Randomness

Careful examination shows that in each of the processes viz., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice

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are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer in the liquid phase and even more free in the vapour phase. In other words, we can say that the randomness of the water molecules increases, as ice melts into water or water evaporates. Both are spontaneous processes which result in a increase in randomness (entropy).

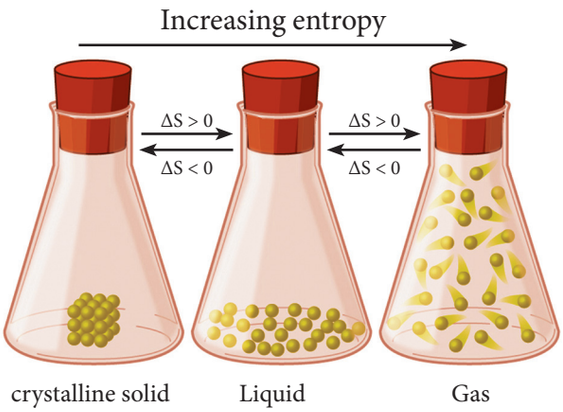

Figure 7.8 Illustration showing an increase in disorder.

Standard Entropy Change(ΔS^0):

It is possible to calculate the actual entropy of a substance at any temperature above 0 K. The absolute entropy of a substance at 298 K and one bar pressure is called the standard entropy S^o. The third law of thermodynamics states, according to Nernst, that the absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. Once we know the entropies of different substances, we can calculate the standard entropy change (ΔS_r^0) for chemical reactions.

$$\Delta S_r^0 = \sum S^0_{products} - \sum S^0_{reactants} \quad \text{------- (7.30)}$$

Standard Entropy of Formation:

Standard entropy of formation is defined as "the entropy of formation of 1 mole of a compound from the elements under standard conditions". It is denoted as ΔS_f^0. We can calculate the value of entropy of a given compound from the values of S^0 of elements.

Problem: 7.6

Calculate the standard entropy change for the following reaction(ΔS_f^0), given the standard entropies of $CO_2(g)$, $C(s)$,$O_2(g)$ as 213.6 , 5.740 and 205 JK^{-1} respectively.

$$C(g) + O_2(g) \longrightarrow CO_2(g)$$

$$\Delta S_r^0 = \sum S^0_{products} - \sum S^0_{reactants}$$

$$\Delta S_r^0 = \{S^0_{CO_2}\} - \{S^0_C + S^0_{O_2}\}$$

$$\Delta S_r^0 = 213.6 - [5.74 + 205]$$

$$\Delta S_r^0 = 213.6 - [210.74]$$

$$\Delta S_r^0 = 2.86\ JK^{-1}$$

Evaluate Yourself- 6

Urea on hydrolysis produces ammonia and carbon dioxide. The standard entropies of urea, H_2O, CO_2, NH_3 are 173.8, 70, 213.5 and 192.5J $mole^{-1}K^{-1}$ respectively. Calculate the entropy change for this reaction.

Entropy change accompanying change of phase

When there is a change of state from solid to liquid (melting), liquid to

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vapour (evaporation) or solid to vapour (sublimation) there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{rev}}{T} \quad -------(7.31)$$

Entropy of fusion:

The heat absorbed, when one mole of a solid melts at its melting point reversibly, is called molar heat of fusion. The entropy change for this process is given by

$$\Delta S_{rev} = \frac{dq_{rev}}{T}$$

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \quad -------(7.32)$$

where ΔH_{fusion} is Molar heat of fusion. T_f is the melting point.

Entropy of vapourisation:

The heat absorbed, when one mole of liquid is boiled at its boiling point reversibly, is called molar heat of vapourisation. The entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b} \quad -------(7.33)$$

where ΔH_v is Molar heat of vaporisation. T_b is the boiling point.

Entropy of transition:

The heat change, when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature is called enthalpy of transition. The entropy change is given

$$\Delta S_t = \frac{\Delta H_t}{T_t} \quad -------(7.34)$$

where ΔH_t is the molar heat of transition, T_t is the transition temperature.

Problem: 7.7

Calculate the entropy change during the melting of one mole of ice into water at 0^0 C and 1 atm pressure. Enthalpy of fusion of ice is 6008 J mol^{-1}

Given:

$\Delta H_{fusion} = 6008\ Jmol^{-1}$

$T_f = 0^0\ C = 273\ K$

$H_2O(S) \xrightarrow{273\ K} H_2O\ (l)$

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$$

$$\Delta S_{fusion} = \frac{6008}{273}$$

$\Delta S_{fusion} = 22.007\ J\ K^{-1}\ mole^{-1}$

Evaluate Yourself - 7

Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol^{-1}

7.11 Gibbs free energy (G)

One of the important applications of the second law of thermodynamics is to predict the spontaneity of a reaction under a specific set of conditions. A reaction that occurs under the given set of conditions without any external driving force is called a spontaneous reaction. Otherwise, it is said to be non-spontaneous. In our day today life, we observe many spontaneous physical and chemical processes, which includes the following examples.

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1. A waterfall runs downhill, but never uphill, spontaneously.

2. A lump of sugar dissolves spontaneously in a cup of coffee, but never reappears in its original form spontaneously.

3. Heat flows from hotter object to a colder one, but never flows from colder to hotter object spontaneously.

4. The expansion of a gas into an evacuated bulb is a spontaneous process, the reverse process that is gathering of all molecules into one bulb is not. spontaneous.

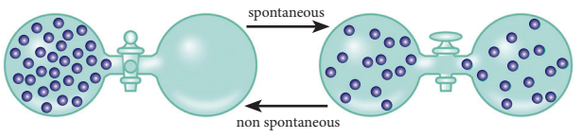

Figure 7.9 Spontaneous process illustration

These examples show that the processes that occur spontaneously in one direction, cannot take place in opposite direction spontaneously.

Similarly a large number of exothermic reactions are spontaneous. An example is combustion of methane.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2\,H_2O$$

$$\Delta H^o = -890.4 \text{ kJ mol}^{-1}$$

Another example is acid-base neutralization reaction:

$$H^+ + OH^- \longrightarrow H_2O$$

$$\Delta H^o = -57.32 \text{ kJ mol}^{-1}$$

However, some endothermic processes are also spontaneous. For example ammonium nitrate dissolves in water spontaneously though this dissolution is endothermic.

$$NH_4NO_3 \xrightarrow{H_2O} NH_4^+ + NO_3^-$$

$$\Delta H^o = +25 \text{ kJ mol}^{-1}$$

From the above examples we can come to the conclusion that exothermicity favors the spontaneity but does not guarantee it. We cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system. We know from second law of thermodynamics that in a spontaneous process, the entropy increases. But not all the processes which are accompanied by an increase in entropy are spontaneous. In order to predict the spontaneity of a reaction, we need some other thermodynamic function.

The second law of thermodynamics introduces another thermodynamic function called Gibbs free energy which finds useful in predicting the spontaneity of a reaction. The Gibbs free energy (G) was developed in the 1870's by Josiah Willard Gibbs. He originally termed this energy as the "available energy" to do work in a system. This quantity is the energy associated with a chemical reaction that can be used to do work.

Gibbs free energy is defined as below

$$G = H - TS \text{ ---------- (7.35)}$$

Gibbs free energy (G) is an extensive property and it is a single valued state function.

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Let us consider a system which undergoes a change of state from state (1) to state (2) at constant temperature.

$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$

$\Delta G = \Delta H - T\,\Delta S$ ------(7.36)

Now let us consider how ΔG is related to reaction spontaneity.

We know that

$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$

For a reversible process (equilibrium), the change in entropy of universe is zero. $\Delta S_{total} = 0$ [$\because \Delta S_{sys} = -\Delta S_{surr}$]

Similarly, for an equilibrium process ΔG=0

For spontaneous process, $\Delta S_{total} > 0$

$\Delta S_{sys} + \Delta S_{surr} > 0$

$\Delta S_{sys} + \frac{dq_{surr}}{T} > 0$

$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$

$T\Delta S_{sys} - \Delta H_{sys} > 0$

$-(\Delta H_{sys} - T\Delta S_{sys}) > 0$

$-\Delta G > 0$

hence for a spontaneous process,

$\Delta G < 0$

i.e. $\Delta H - T\,\Delta S < 0$ ------(7.37)

ΔH_{sys} is the enthalpy change of a reaction, $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction. For non spontaneous process, ΔG > 0

Gibbs free energy and the net work done by the system:

For any system at constant pressure and temperature

$\Delta G = \Delta H - T\,\Delta S$ ---- (7.36)

We know that,

$\Delta H = \Delta U + P\Delta V$

$\therefore\ \Delta G = \Delta U + P\Delta V - T\Delta S$

from first law of thermodynamics

if work is done by the system

$\Delta U = q - w$

from second law of thermodynamics

$\Delta S = \frac{q}{T}$

$\Delta G = q - w + P\Delta V - T\left(\frac{q}{T}\right)$

$\Delta G = -w + P\Delta V$

$-\Delta G = w - P\Delta V$ .....(7.38)

Here, $-P\Delta V$ represents the work done due to expansion against a constant external pressure. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion.

7.11.1 Criteria for spontaneity of a process

The spontaneity of any process depends on three different factors.

- If the enthalpy change of a process is negative, then the process is exothermic and may be spontaneous. (ΔH is negative)
- If the entropy change of a process is positive, then the process may occur spontaneously. (ΔS is positive)

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- The gibbs free energy which is the combination of the above two ($\Delta H - T\Delta S$) should be negative for a reaction to occur spontaneously, i.e. the necessary condition for a reaction to be spontaneous is $\Delta H - T\Delta S < 0$

Table 7.5 Effect of Temperature on Spontaneity of Reactions:

ΔH_r	ΔS_r	$\Delta G_r = \Delta H_r - T\Delta S_r$	Description	Example
–	+	– (at all T)	Spontaneous at all temperature	$2O_3(g) \rightarrow 3O_2(g)$
–	–	– (at low T)	spontaneous at low temperature	Adsorption of gases
		+ (at high T)	non-spontaneous at high temperature	
+	+	+ (at low T)	non-spontaneous at low temperature	Melting of a solid
		– (at high T)	spontaneous at high temperature	
+	–	+ (at all T)	non spontaneous at all temperatures	$2H_2O(g) + O_2(g) \rightarrow 2H_2O_2(l)$

The Table assumes ΔH and ΔS will remain the way indicated for all temperatures. It may not be necessary that way. The spontaneity of a chemical reaction is only the potential for the reaction to proceed as written. The rate of such processes is determined by kinetic factors, outside of thermodynamical prediction.

Problem: 7. 8

Show that the reaction $CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$ at 300K is spontaneous. The standard Gibbs free energies of formation of CO_2 and CO are –394.4 and –137.2 kJ mole^{-1} respectively.

$$CO + \left(\frac{1}{2}\right)O_2 \rightarrow CO_2$$

$$\Delta G^0_{(reaction)} = \sum G^0_{f\,(products)} - \sum G^0_{f\,(reactants)}$$

$$\Delta G^0_{(reaction)} = \left[G^0_{CO_2}\right] - \left[G^0_{CO} + \frac{1}{2}G^0_{O_2}\right]$$

$$\Delta G^0_{(reaction)} = -394.4 + [137.2 + 0]$$

$$\Delta G^0_{(reaction)} = -257.2 \text{ kJ mol}^{-1}$$

$\Delta G_{(reaction)}$ of a reaction at a given temperature is negative hence the reaction is spontaneous.

Evaluate Yourself - 8

For a chemical reaction the values of ΔH and ΔS at 300K are – 10 kJ mole^{-1} and –20 J deg^{-1} mole^{-1} respectively. What is the value of ΔG of the reaction? Calculate the ΔG of a reaction at 600 K assuming ΔH and ΔS values are constant. Predict the nature of the reaction.

7.11.2 Relationship between standard free energy change (ΔG^0) and equilibrium constant (K_{eq}):

In a reversible process, the system is in perfect equilibrium with its surroundings at all times. A reversible chemical reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. This means that the reactions in both the directions should proceed with decrease in free energy, which is impossible. It is possible only if at equilibrium, the free energy of a system is minimum. Lets consider a general equilibrium reaction

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$$A+B \rightleftharpoons C + D$$

The free energy change of the above reaction in any state (ΔG) is related to the standard free energy change of the reaction (ΔG^0) according to the following equation.

$$\Delta G = \Delta G^0 + RT \ln Q \text{ ------(7.39)}$$

where Q is reaction quotient and is defined as the ratio of concentration of the products to the concentrations of the reactants under non equilibrium condition.

When equilibrium is attained, there is no further free energy change i.e. $\Delta G = 0$ and Q becomes equal to equilibrium constant. Hence the above equation becomes.

$$\Delta G^0 = -RT \ln K_{eq}$$

This equation is known as Van't Hoff equation.

$$\Delta G^0 = -2.303\ RT \log K_{eq} \text{ ----------(7.40)}$$

We also know that

$$\Delta G^0 = \Delta H^0 - T\ \Delta S^0 = -\ RT \ln K_{eq}$$

Problem: 7.9

Calculate ΔG^0 for conversion of oxygen to ozone $3/2\ O_2 \rightleftharpoons O_{3(g)}$ at 298 K, if K_p for this conversion is 2.47×10^{-29} in standard pressure units.

Solution:

$$\Delta G^0 = -\ 2.303\ RT \log K_p$$

Where

$R = 8.314\ JK^{-1}mol^{-1}$

$K_p = 2.47 \times 10^{-29}$

$T = 298K$

$\Delta G^0 = -2.303(8.314)(298)\log(2.47\times10^{-29})$

$\Delta G^0 = 163229\ Jmol^{-1}$

$\Delta G^0 = 163.229\ KJ\ mol^{-1}$

7.12 Third law of Thermodynamics

The entropy of a substance varies directly with temperature. Lower the temperature, lower is the entropy. For example, water above 100^0 C at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid. The water molecules in liquid phase still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water freezes to form ice crystal. The water molecules in the ice crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy.

At absolute zero {0 K (or) -273^0C}, theoretically all modes of motion stop.

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Absolute zero is a temperature that an object can get arbitrarily close to but absolute zero will remain unattainable.

Thus the third law of thermodynamics states that the entropy of pure crystalline substance at absolute zero is zero. Otherwise it can be stated as it is impossible to lower the temperature of an object to absolute zero in a finite number of steps. Mathematically,

$\lim_{T \to 0} S = 0$ for a perfectly ordered crystalline state.

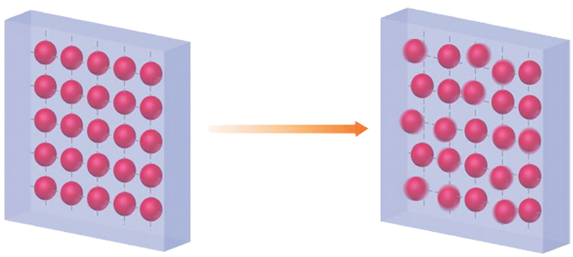

Figure 7.10 Third law of Thermodynamics

Crystals with defects (imperfection) at absolute zero, have entropy greater than zero. Absolute entropy of a substance can never be negative.

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SUMMARY

The branch of science which deals the relation between energy, heat and work is called Thermodynamics. The main aim of the study of chemical thermodynamics is to learn (i) transformation of energy from one form into another form (ii) Utilization of various forms of energies.

System: A system is defined as any part of universe under consideration. There are three types of thermodynamic systems. They are (i) isolated system (ii) closed system and (iii) open system.

Surrounding: Everything in the universe that is not the part of the system is called surrounding.

Boundary: Anything which separates the system from its surrounding is called boundary.

Thermodynamic Properties: Any quantity that depends only on the state of system is called thermodynamic property of a system. There are two kinds of thermodynamic properties called (1) intensive - independent of the quantity of material and (2) extensive - directly proportional to the quantity of material. There are five basic thermodynamic properties. (U,H,S and G)

Thermodynamic Processes:

Adiabatic process in which no heat transfer takes place (q = 0)

Isothermal process in which temperature remains constant (dT =0).

Isobaric process in which pressure remains constant(dP =0).

Isochoric process in which volume remains constant(dV =0).

Cyclic process in which the system returns to its original state after completing a series of changes.

Internal energy (U): Internal energy of a system is equal to the energy possessed by all its constituents namely atoms, ions and molecules. The energy of a system of molecules is equal to the sum of its translational energy, vibrational energy, rotational energy, bond energy, electronic energy and energy due to molecular interactions.

Heat: Heat is regarded as the energy in transit across the boundary separating a system from its surrounding. Heat is a path function. The SI unit of heat is joule (J)

Work : Work is defined as the force (F) multiplied by the displacement -w=F.x, work is measured in Joules, i.e the SI unit of work is Joule. During expansion or compression of a gas the work done is calculated by the relation w= -PΔV.

The sign conventions for heat and work are as follows:

If heat is absorbed by the system : +q

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If heat is evolved by the system : -q

If work is done by the system : -w

If work is done on the system : +w

Laws of Thermodynamics:

Zeroth law : When two systems are separately in equilibrium with a third system, they are in equilibrium with each other.

First law: "Energy can neither be created nor destroyed, but may be converted from one form to another".

$\Delta U = q + w$.

Enthalpy is a thermodynamic property of a system. Enthalpy H is defined as the sum of the internal energy and pressure volume work.

$H=U+PV$. Enthalpy change, $\Delta H = \Delta U + \Delta n_g RT$.

Hess's law: It states that "the enthalpy change of a reaction either at constant volume or constant pressure is the same whether it takes place in a single or multiple steps". Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure.

Heat capacities: [C_p and C_v]

Heat capacity is defined as the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions. It can be measured under two different conditions, namely,

(a) constant pressure $C_p = (dH/dT)_p$

(b) constant volume $C_v = (dU/dT)_v$

Second law of thermodynamics:

The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tells the direction of the flow of heat.

To predict spontaneity of a process, a new thermodynamic quantity namely entropy (S) was introduced. Entropy is a measure of the randomness or disorderliness of the system.

Entropy statement: "whenever a spontaneous process takes place, it is accompanied by an increase in the total entropy of the universe".

Kelvin-Planck statement: It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of that heat to a colder reservoir.

Clausius statement: This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to spend some work.

Gibbs Free Energy (G):

G is expressed as $G=H-TS$, free energy change of a process is given by the relation $\Delta G= \Delta H-T\Delta S$.

Standard free energy change and equilibrium constants are related by the equation $\Delta G^0 = -RT\ln K_{eq}$

Third law:

The entropy of a perfectly crystalline material at absolute zero is zero.

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EVALUATION

I. Choose the best answer

1. The amount of heat exchanged with the surrounding at constant pressure is given by the quantity

   a) ΔE b) ΔH c) ΔS d) ΔG

2. All the naturally occurring processes proceed spontaneously in a direction which leads to

   a) decrease in entropy b) increase in enthalpy

   c) increase in free energy d) decrease in free energy

3. In an adiabatic process, which of the following is true ?

   a) $q = w$ b) $q = 0$ c) $\Delta E = q$ d) $P \Delta V = 0$

4. In a reversible process, the change in entropy of the universe is

   a) > 0 b) ≥ 0 c) < 0 d) $= 0$

5. In an adiabatic expansion of an ideal gas

   a) $w = -\Delta u$ b) $w = \Delta u + \Delta H$ c) $\Delta u = 0$ d) $w = 0$

6. The intensive property among the quantities below is

   a) mass b) volume c) enthalpy d) $\frac{\text{mass}}{\text{volume}}$

7. An ideal gas expands from the volume of 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure at 1×10^5 Nm^{-2}. The work done is

   a) – 900 J b) 900 kJ c) 270 kJ d) – 900 kJ

8. Heat of combustion is always

   a) positive b) negative c) zero d) either positive or negative

9. The heat of formation of CO and CO_2 are – 26.4 kCal and – 94 kCal, respectively. Heat of combustion of carbon monoxide will be

   a) + 26.4 kcal b) – 67.6 kcal c) – 120.6 kcal d) + 52.8 kcal

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10. C(diamond) → C(graphite), ΔH = –ve, this indicates that

a) graphite is more stable than diamond

b) graphite has more energy than diamond

c) both are equally stable

d) stability cannot be predicted

11. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are – 1596 kJ and – 1134 kJ, respectively.

ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

a) – 1365 kJ b) 2730 kJ c) – 2730 kJ d) – 462 kJ

12. Which of the following is not a thermodynamic function ?

a) internal energy b) enthalpy c) entropy d) frictional energy

13. If one mole of ammonia and one mole of hydrogen chloride are mixed in a closed container to form ammonium chloride gas, then

a) $\Delta H > \Delta U$ b) $\Delta H - \Delta U = 0$ c) $\Delta H + \Delta U = 0$ d) $\Delta H < \Delta U$

14. Change in internal energy, when 4 kJ of work is done on the system and 1 kJ of heat is given out by the system is

a) +1 kJ b) – 5 kJ c) +3 kJ d) – 3 kJ

15. The work done by the liberated gas when 55.85 g of iron (molar mass 55.85 g mol^{-1}) reacts with hydrochloric acid in an open beaker at 25^0 C

a) – 2.48 kJ b) – 2.22 kJ c) + 2.22 kJ d) + 2.48 kJ

16. The value of ΔH for cooling 2 moles of an ideal monatomic gas from 125^0 C to 25^0 C at constant pressure will be $\left[\text{given } C_P = \frac{5}{2} R\right]$

a) – 250 R b) – 500 R c) 500 R d) + 250 R

17. Given that $C(g) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^0 = -$ a kJ; $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^0 = -$b kJ; Calculate the ΔH^0 for the reaction $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

a) $\frac{b+2a}{2}$ b) $2a-b$ c) $\frac{2a-b}{2}$ d) $\frac{b-2a}{2}$

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18. When 15.68 litres of a gas mixture of methane and propane are fully combusted at 0^0 C and 1 atmosphere, 32 litres of oxygen at the same temperature and pressure are consumed. The amount of heat of released from this combustion in kJ is (ΔH_C (CH_4) = – 890 kJ mol^{-1} and ΔH_C (C_3H_8) = – 2220 kJ mol^{-1})

a) – 889 kJ b) – 1390 kJ c) – 3180 kJ d) – 632.68 kJ

19. The bond dissociation energy of methane and ethane are 360 kJ mol^{-1} and 620 kJ mol^{-1} respectively. Then, the bond dissociation energy of C-C bond is

a) 170 kJ mol^{-1} b) 50 kJ mol^{-1} c) 80 kJ mol^{-1} d) 220 kJ mol^{-1}

20. The correct thermodynamic conditions for the spontaneous reaction at all temperature is (NEET Phase - I)

a) $\Delta H < 0$ and $\Delta S > 0$

b) $\Delta H < 0$ and $\Delta S < 0$

c) $\Delta H > 0$ and $\Delta S = 0$

d) $\Delta H > 0$ and $\Delta S > 0$

21. The temperature of the system, decreases in an _____

a) Isothermal expansion b) Isothermal Compression c) adiabatic expansion

d) adiabatic compression

22. In an isothermal reversible compression of an ideal gas the sign of q, ΔS and w are respectively

a) +, –, – b) –, +, – c) +, –, + d) –, –, +

23. Molar heat of vapourisation of a liquid is 4.8 kJ mol^{-1}. If the entropy change is 16 J mol^{-1} K^{-1}, the boiling point of the liquid is

a) 323 K b) 27^0 C c) 164 K d) 0.3 K

24. ΔS is expected to be maximum for the reaction

a) $Ca(S) + ½\ O_2(g) \rightarrow CaO(S)$

b) $C(S) + O_2(g) \rightarrow CO_2(g)$

c) $N_2(g) + O_2(g) \rightarrow 2NO(g)$

d) $CaCO_3(S) \rightarrow CaO(S) + CO_2(g)$

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25. The values of ΔH and ΔS for a reaction are respectively 30 kJ mol^{-1} and 100 JK^{-1} mol^{-1}. Then the temperature above which the reaction will become spontaneous is

a) 300 K b) 30 K c) 100 K d) 20^0 C

II. Write brief answer to the following questions:

26. State the first law of thermodynamics.

27. Define Hess's law of constant heat summation.

28. Explain intensive properties with two examples

29. Define the following terms:

a. isothermal process b. adiabatic process

c. isobaric process d. isochoric process

30. What is the usual definition of entropy? What is the unit of entropy?

31. Predict the feasibility of a reaction when

i) both ΔH and ΔS positive ii) both ΔH and ΔS negative

iii) ΔH decreases but ΔS increases

32. Define is Gibb's free energy.

33. Define enthalpy of combustion.

34. Define molar heat capacity. Give its unit.

35. Define the calorific value of food. What is the unit of calorific value?

36. Define enthalpy of neutralization.

37. What is lattice energy?

38. What are state and path functions? Give two examples.

39. Give Kelvin statement of second law of thermodynamics.

40. The equilibrium constant of a reaction is 10, what will be the sign of ΔG? Will this reaction be spontaneous?

41. Enthalpy of neutralization is always a constant when a strong acid is neutralized by a strong base: account for the statement.

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42. State the third law of thermodynamics.

43. Write down the Born-Haber cycle for the formation of $CaCl_2$

44. Identify the state and path functions out of the following: a)Enthalpy b)Entropy c) Heat d) Temperature e) Work f)Free energy.

45. State the various statements of second law of thermodynamics.

46. What are spontaneous reactions? What are the conditions for the spontaneity of a process?

47. List the characteristics of internal energy.

48. Explain how heat absorbed at constant volume is measured using bomb calorimeter with a neat diagram.

49. Calculate the work involved in expansion and compression process.

50. Derive the relation between ΔH and ΔU for an ideal gas. Explain each term involved in the equation.

51. Suggest and explain an indirect method to calculate lattice enthalpy of sodium chloride crystal.

52. List the characteristics of Gibbs free energy.

53. Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500 ml to a volume of 2 L at 25°C and normal pressure.

54. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298 K. The temperature of the calorimeter was found to increase from 298 K to 298.45 K due to the combustion process. Given that the calorimeter constant is 2.5 kJ K^{-1}. Calculate the enthalpy of combustion of the gas in kJ mol^{-1}.

55. Calculate the entropy change in the system, and surroundings, and the total entropy change in the universe during a process in which 245 J of heat flow out of the system at 77°C to the surrounding at 33°C.

56. 1 mole of an ideal gas, maintained at 4.1 atm and at a certain temperature, absorbs heat 3710J and expands to 2 litres. Calculate the entropy change in expansion process.

57. 30.4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 JK^{-1} mol^{-1}. Calculate the melting point of sodium chloride.

58. Calculate the standard heat of formation of propane, if its heat of combustion is −2220.2 kJ mol^{-1}. the heats of formation of $CO_2(g)$ and $H_2O(l)$ are −393.5 and −285.8 kJ mol^{-1} respectively.

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59. You are given normal boiling points and standard enthalpies of vapourisation. Calculate the entropy of vapourisation of liquids listed below.

S. No	Liquid	Boiling points (^{0}C)	ΔH (kJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

60. For the reaction $Ag_2O(s) \rightarrow 2Ag(s) + \frac{1}{2} O_2(g)$: ΔH = 30.56 kJ mol^{-1} and ΔS=6.66JK^{-1}mol^{-1}(at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction (i) at this temperature and (ii) below this temperature.

61. What is the equilibrium constant Keq for the following reaction at 400K.

$2NOCl\ (g) \rightleftharpoons 2NO(g) + Cl_2(g)$,

given that $\Delta H^0 = 77.2$kJ mol^{-1} ;

and ΔS^0=122JK^{-1}mol^{-1}.

62. Cyanamide (NH_2CN) is completely burnt in excess oxygen in a bomb calorimeter, ΔU was found to be −742.4 kJ mol−1, calculate the enthalpy change of the reaction at 298K. $NH_2CN(s) + \frac{3}{2} O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$ ΔH= ?

63. Calculate the enthalpy of hydrogenation of ethylene from the following data. Bond energies of C – H, C – C , C = C and H – H are 414, 347, 618 and 435 kJ mol^{-1}.

64. Calculate the lattice energy of $CaCl_2$ from the given data

$Ca(s) + Cl_2(g) \rightarrow CaCl_2(s)$ ΔH_f^0 = – 795 kJ mol^{-1}

Sublimation : $Ca(s) \rightarrow Ca(g)$ ΔH_1^0 = + 121 kJ mol^{-1}

Ionisation : $Ca(g) \rightarrow Ca^{2+}(g) + 2e^-$ ΔH_2^0 = + 2422 kJ mol^{-1}

Dissociation : $Cl_2(g) \rightarrow 2Cl(g)$ ΔH_3^0 = + 242.8 kJ mol^{-1}

Electron affinity : $Cl(g) + e^- \rightarrow Cl^-(g)$ ΔH_4^0 = –355 kJ mol^{-1}

65. Calculate the enthalpy change for the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ from the following data.

$2Fe + \frac{3}{2} O_2 \rightarrow Fe_2O_3$; ΔH = –741 kJ

$C + \frac{1}{2} O_2 \rightarrow CO$; ΔH = –137 kJ

$C + O_2 \rightarrow CO_2$; ΔH = – 394.5 kJ

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66. When 1-pentyne (A) is treated with 4N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne(A) , 95.2% 2-pentyne(B) and 3.5% of 1,2 pentadiene (C) the equilibrium was maintained at 175°C, calculate ΔG^0 for the following equilibria.

$B \rightleftharpoons A \qquad \Delta G_1^0 = ?$

$B \rightleftharpoons C \qquad \Delta G_2^0 = ?$

67. At 33K, N_2O_4 is fifty percent dissociated. Calculate the standard free energy change at this temperature and at one atmosphere.

68. The standard enthalpies of formation of SO_2 and SO_3 are –297 kJ mol^{-1} and –396 kJ mol^{-1} respectively. Calculate the standard enthalpy of reaction for the reaction: $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$

69. For the reaction at 298 K : 2A +B → C

ΔH=400 KJ mol^{-1} ; ΔS = 0.2 KJK^{-1} mol^{-1} Determine the temperature at which the reaction would be spontaneous.

70. Find out the value of equilibrium constant for the following reaction at 298K, 2 $NH_3(g) + CO_2(g) \rightleftharpoons NH_2CONH_2$ (aq) + H_2O (l) Standard Gibbs energy change, ΔG_r^0 at the given temperature is –13.6 kJ mol–1.

71. A gas mixture of 3.67 lit of ethylene and methane on complete combustion at 25°C and at 1 atm pressure produce 6.11 lit of carbondioxide. Find out the amount of heat evolved in kJ, during this combustion. ($\Delta H_C(CH_4)$= – 890 kJ mol^{-1} and ($\Delta H_C(C_2H_4)$= –1423 kJ mol^{-1}

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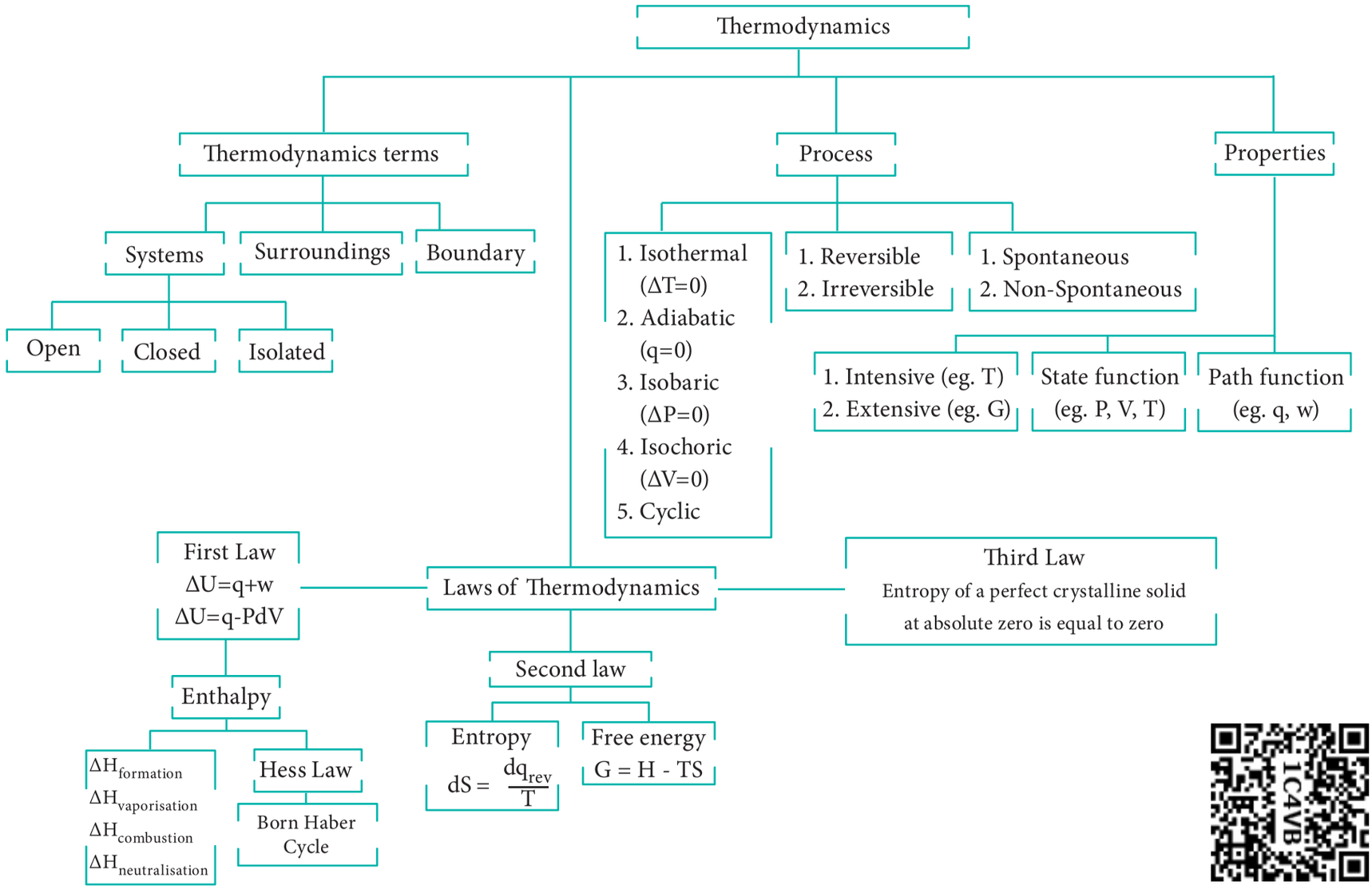
CONCEPT MAP



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Fundamental constants

Avogadro number	N	6.022×10^{23}
Atomic mass unit (or) Unified atomic mass	amu (or) u	1.660×10^{-27} kg
Speed of light	c	2.997×10^{8} m s^{-1}
Elementary charge (or) Charge of an electron	e	1.602×10^{-19} C
Planck's constant	h	6.626×10^{-34} Js
Mass of electron	m_e	9.109×10^{-31} kg
Mass of proton	m_p	1.672×10^{-27} kg
Mass of neutron	m_n	1.674×10^{-27} kg
Bohr's radius	a_0	0.529 Å
Rydberg constant	R_∞	1.097×10^{5} cm^{-1}
Universal gas constant	R	8.314 J K^{-1} mol^{-1} 0.082 L atm K^{-1} mol^{-1} 1.987 cal K^{-1} mol^{-1} 62.36 L mmHg K^{-1} mol^{-1} 83.14 L mbar K^{-1} mol^{-1}

Commonly used SI Prefixes

femto	pico	nano	micro	milli	centi	deci	kilo	mega	giga
f	p	n	μ	m	c	d	k	M	G
10^{-15}	10^{-12}	10^{-9}	10^{-6}	10^{-3}	10^{-2}	10^{-1}	10^{3}	10^{6}	10^{9}

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Inter - Conversion of Units

1 Å	=	10^{-10} m		
1 atm	=	101.325 kPa	=	1.01325 x 10^5 N m^{-2}
1 atm	=	1.01325 x 10^5 J m^{-3}	=	760 Torr (mmHg)
1 eV	=	1.60219 x 10^{-19} J		
1 N	=	1 J m^{-1}	=	10^5 dyne
1 J	=	10^7 erg	=	1 Kg m^2 s^{-2}
1 cal	=	4.184 J		

Critical constants of selected gases

Gas	Critical Pressure, P_c (atm)	Critical Volume, V_c (cm^3 mol^{-1})	Critical Temperature, T_c (K)
He	2.26	57.76	5.21
Ne	26.86	41.74	44.44
Ar	48.00	75.25	150.72
Kr	54.27	92.24	209.39
Xe	58.0	118.8	289.75
H_2	12.8	64.99	33.23
N_2	33.54	90.10	126.3
O_2	50.14	78.0	154.8
Cl_2	76.1	124	417.2
Br_2	102	135	584
HCl	81.5	81.0	324.7
CO_2	72.85	94.0	304.2
H_2O	218.3	55.3	647.4
NH_3	111.3	72.5	405.5
CH_4	45.6	98.7	190.6
C_2H_4	50.50	124	283.1
C_2H_6	48.20	148	305.4
C_6H_6	48.6	260	562.7

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Van der waals constants for select gases

Name	a (L^2 bar mol^{-2})	b (L mol^{-1})
Ammonia	4.225	0.0371
Benzene	18.24	0.1154
Carbon dioxide	3.64	0.04267
Carbon monoxide	1.505	0.03985
Chlorine	6.579	0.05622
Helium	0.0346	0.0238
Hexane	24.71	0.1735
Hydrogen	0.2476	0.02661
Hydrogen bromide	4.51	0.04431
Hydrogen chloride	3.716	0.04081
Hydrogen sulfide	4.49	0.04287
Mercury	8.2	0.01696
Methane	2.283	0.04278
Nitric oxide	1.358	0.02789
Nitrogen	1.37	0.0387
Nitrogen dioxide	5.354	0.04424
Nitrous oxide	3.832	0.04415
Oxygen	1.382	0.03186
Sulfur dioxide	6.803	0.05636
Water	5.536	0.03049

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Molar heat capacities of select compounds:

	$C_{v,m}$ ($J\ K^{-1}\ mol^{-1}$)	$C_{p,m}$ ($J\ K^{-1}\ mol^{-1}$)
Gases		
Inert gases	12.48	20.79
H_2	20.44	28.82
N_2	20.74	29.12
O_2	20.95	29.36
CO_2	28.46	37.11
Liquids		
H_2O	-	75.29
CH_3OH	-	81.6
C_2H_5OH	-	111.5
C_6H_6	-	136.1
Solids		
C (diamond)	-	6.11
Cu	-	244.4
Fe	-	25.1
SiO_2	-	44.4

Standard heat of combustion (ΔH_f^0 , kJ mol^{-1})

Methane(g)	=	- 890	Ethanol(l)	=	- 1368
Ethane(g)	=	- 1560	Acetic acid (l)	=	- 875
Propane(g)	=	- 2220	Benzoic acid (s)	=	- 3227
Butane(g)	=	- 2878	Glucose (s)	=	- 2808
Benzene(l)	=	- 3268	Sucrose (s)	=	- 5645
Methanol(l)	=	- 726			

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Thermodynamic data for select compounds

	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})	S^0 (J K^{-1} mol^{-1})
C (s , graphite)	0	0	5.740
$H_2(g)$	0	0	130.684
$N_2(g)$	0	0	191.61
$O_2(g)$	0	0	205.138
$Cl_2(g)$	0	0	223.07
Ag(s)	0	0	42.55
Cu(s)	0	0	33.150
Au(s)	0	0	47.40
Fe(s)	0	0	27.28
Zinc(s)	0	0	41.63
C(s, diamond)	1.895	2.900	2.377
CO(g)	-110.53	-137.17	197.67
$CO_2(g)$	-393.51	-394.36	213.74
HCl(g)	-92.31	-95.30	186.91
$H_2O(l)$	-285.83	-237.13	69.91
$H_2O(g)$	-241.82	-228.57	188.83
$NH_3(g)$	-46.11	-16.45	192.45
Methane(g)	-74.81	-50.72	186.26
Ethane(g)	-84.68	-32.82	229.60
Propane(g)	-103.85	-23.49	269.91
Butane(g)	-126.15	-17.03	310.23
Benzene(l)	49.0	124.3	173.3
Methanol(l)	-238.66	-166.27	126.8
Ethanol(l)	-277.69	-174.78	160.7

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Lattice Enthalpies of alkali metal halides ($-\Delta H^0$ Lattice, kJ mol^{-1})

	F	Cl	Br	I
Li	1022	846	800	744
Na	902	771	733	684
K	801	701	670	629
Rb	767	675	647	609
Cs	716	645	619	585

C_P and C_V for Mono, di and tri atomic gases

	C_V Value	C_P Value ($C_P = R+C_V$)
Monatomic gas	$\frac{3}{2}R$	$\frac{5}{2}R$
Diatomic gas	$\frac{5}{2}R$	$\frac{7}{2}R$
Triatomic	$\frac{6}{2}R$	$\frac{8}{2}R$

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Evaluate yourself :

1. (i) **Element** - Copper wire, Silver plate

(ii) **Compound** - Sugar, distilled water, carbon dioxide, Table salt, Naphthalene balls

(iii) **Mixture** - Sea water

2. (i) C_2H_5OH : (2 x 12) + (5 x 1) + (1 x 16) + (1 x 1) = **46 g**

(ii) $KMnO_4$: (1 x 39) + (1 x 55) + (4 x 16) = **158 g**

(iii) $K_2Cr_2O_7$: (2 x 39) + (2 x 52) + (7 x 16) = **294 g**

(iv) $C_{12}H_{22}O_{11}$: (12 x 12) + (22 x 1) + (11 x 16) = **342 g**

3. (a) Molar mass of ethane, C_2H_6 = (2 x 12)+ (6 x 1) = 30 g mol^{-1}

n = mass / molar mass = 9 g / 30 g mol^{-1} = **0.3 mole**

(b) At 273 K and 1 atm pressure 1 mole of a gas occupies a volume of 22.4 L

Therefore,

number of moles of oxygen, that occupies a volume of 224 ml at 273 K and 3 atm pressure

$$= \frac{1\,\text{mole}}{273\,\text{K} \times 1\,\text{atm} \times 22.4\,\text{L}} \times 0.224\,\text{L} \times 273\,\text{K} \times 3\,\text{atm}$$

$$= 0.03\,\text{mole}$$

1 mole of oxygen contains 6.022 x 10^{23} molecules

0.03 mole of oxygen contains = 6.022 x 10^{23} x 0.03

= **1.807 x 10^{22} molecules of oxygen**

4. (a) Mass of the metal = 0.456 g

Mass of the metal chloride = 0.606 g

0.456 g of the metal combines with 0.15 g of chlorine.

Mass of the metal that combines with 35.5 g of chlorine is $\frac{0.456}{0.15} \times 35.5$

= 107.92 g eq^{-1}.

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(b) Equivalent mass of a oxidising agent $= \dfrac{\text{molar mass}}{\text{number of moles of electrons gained by one mole of the reducing agent}}$

$= \dfrac{294.2 \text{ g mol}^{-1}}{6 \text{ eq mol}^{-1}}$

$= \mathbf{49.0 \text{ g eq}^{-1}}$

5.

Element	**Percentage Composition**	**Atomic mass**	**Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$**	**Simple ratio**
C	54.55 %	12	54.55/12 = 4.55	4.55 / 2.27 = 2
H	9.09 %	1	9.09 / 1 = 9.09	9.09 / 2.27 = 4
O	36.36 %	16	36.36/16 = 2.27	2.27/2.27 = 1
Empirical formula (C_2H_4O)				

6.

Element	**Percentage Composition**	**Relative no. of atoms = $\frac{\text{Percentage}}{\text{Atomic mass}}$**	**Atomic mass= $\frac{\text{Percentage}}{\text{Relative no. of atoms}}$**	**Simple ratio**
X	32 %	2	16	4
Y	24 %	1	24	2
Z	44 %	0.5	88	1
Empirical formula ($X_4 Y_2 Z$)				

Calculated empirical formula mass $= (16 \times 4) + (24 \times 2) + 88$

$= 64 + 48 + 88 = 200$

$n = \dfrac{\text{molar mass}}{\text{calculated empirical formula mass}}$

$\therefore n = \dfrac{400}{200}$

$= 2$

$\therefore$ **Molecular formula $(X_4Y_2Z)_2$** $= \mathbf{X_8Y_4Z_2}$

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7.

Content	Reactant		Products	
	x	y	*l*	m
Stoichiometric coefficient	2	3	4	1
No. of moles allowed to react	8	15	–	–
No. of moles of reactant reacted and product formed	8	12	16	4
No. of moles of un-reacted reactants and the product formed	–	3	16	4

Limiting reagent **: x**

Product formed **: 16 moles of *l* & 4 moles of m**

Amount of excess reactant **: 3 moles of y**

8.

$$\overset{+3}{As_2}\ \overset{-2}{S_3} + H\overset{+5}{N}O_3 \rightarrow H_3\overset{+5}{As}O_4 + H_2\overset{+6}{S}O_4 + \overset{+2}{N}O$$

$2\times2e^-$ $3\times8e^-$ $3e^-$

$4e^- + 24e^-$

$28e^-$

Equate the total no. of electrons in the reactant side by cross multiplying,

$\Rightarrow$ $3\ As_2S_3 + 28\ HNO_3 \rightarrow H_3AsO_4 + H_2SO_4 + NO$

Based on reactant side, balance the products

$\Rightarrow$ $3\ As_2S_3 + 28\ HNO_3 \rightarrow 6\ H_3AsO_4 + 9\ H_2SO_4 + 28\ NO$

Product side :36 hydrogen atoms & 88 oxygen atoms

Reactant side :28 hydrogen atoms & 84 oxygen atoms

Difference is 8 hydrogen atoms & 4 oxygen atoms

$\therefore$ Add 4 H_2O molecule on the reactant side.

Balanced equation is,

$3\ As_2S_3 + 28\ HNO_3 + 4\ H_2O \rightarrow 6\ H_3AsO_4 + 9\ H_2SO_4 + 28\ NO$

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EVALUATION

I Choose the best answer

1. (a) 40 ml of CO_2 gas
2. (d) 200 u
3. (c) assertion is true but reason is false
4. (b) oxygen
5. (a) 102 g
6. (c) 6.022×10^{20}
7. (c) 16 %
8. (c) 0.075
9. (d) 1 mole of HCl
10. (c) $BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ HCl$
11. (b) $P_4 + 3\ NaOH + 3\ H_2O \rightarrow PH_3 + 3\ NaH_2PO_2$
12. (b) 52.7
13. (d) 6.022×10^{24} molecules of water
14. (a) NO
15. (a) 6.022×10^{23}
16. (c) $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-} < SO_4^{2-}$
17. (c) molar mass of ferrous oxalate / 3
18. (d) the mass of one mole of carbon
19. (c) the ratio between the number of molecules in A to number of molecules in B is 2:1
20. (a) 3.59 g
21. (b) 44 g mol^{-1}
22. (c) both (a) & (b)
23. (a) propene
24. (a) relative atomic mass is 12 u
25. (a) ${}_6C^{12}$

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Key to the multiple choice questions

1. $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2\,H_2O(l)$

Content	CH_4	O_2	CO_2
Stoichiometric coefficient	1	2	1
Volume of reactants allowed to react	40 mL	80 mL	
Volume of reactant reacted and product formed	40 mL	80 mL	40 mL
Volume of gas after cooling to the room temperature	-	-	40 mL

Since the product was cooled to room temperature, water exists mostly as liquid. Hence, option (a) is correct

2.

$$= \frac{(200\times 90)+(199\times 8)+(202\times 2)}{100} = 199.96$$
$$\simeq 200\ \text{u}$$

3. Correct reason: Total number of entities present in one mole of any substance is equal to 6.022×10^{23}.

4. Reaction 1 : $2\,C + O_2 \rightarrow 2\,CO$

2×12 g carbon combines with 32 g of oxygen. Hence,

Equivalent mass of carbon $= \frac{2\times 12}{32}\times 8 = 6$

Reaction 2 : $C + O_2 \rightarrow CO_2$

12 g carbon combines with 32 g of oxygen. Hence,

Equivalent mass of carbon $= \frac{12}{32}\times 8 = 3$

5. Let the trivalent metal be M^{3+}

Equivalent mass = mass of the metal / valance factor

$9\ g\ eq^{-1}$ = mass of the metal / 3 eq

Mass of the metal = 27 g

Oxide formed M_2O_3;

Mass of the oxide = (2 x 27) + (3 x 16)

= **102 g**

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6. Weight of the water drop = 0.018 g

No. of moles of water in the drop = Mass of water / molar mass

= 0.018 / 18 = 10^{-3} mole

No of water molecules present in 1 mole of water = 6.022×10^{23}

No. water molecules in one drop of water (10^{-3} mole) = $6.022 \times 10^{23} \times 10^{-3}$

= **6.022×10^{20}**

7. $MgCO_3 \rightarrow MgO + CO_2 \uparrow$

$MgCO_3$: (1 x 24) + (1 x 12) + (3 x 16) = 84 g

CO_2 : (1 x 12) + (2 x 16) = 44 g

100 % pure 84 g $MgCO_3$ on heating gives 44 g CO_2

Given that 1 g of $MgCO_3$ on heating gives 0.44 g CO_2

Therefore, 84 g $MgCO_3$ sample on heating gives 36.96 g CO_2

$$\text{Percentage of purity of the sample} = \frac{100\,\%}{44\ \text{g}\ CO_2} \times 36.96\ \text{g}\ CO_2$$
$$= 84\,\%$$

Percentage of impurity = **16 %**

8. $NaHCO_3 + CH_3COOH \rightarrow \underbrace{CH_3COONa + H_2O}\ + CO_2 \uparrow$

6.3 g + 30 g → 33 g + x

The amount of CO_2 released, x = 3.3 g

No. of moles of CO_2 released = 3.3 / 44 = 0.075 mol

9 $H_2(g) + Cl_2(g) \rightarrow 2\ HCl\ (g)$

Content	**$H_2(g)$**	**$Cl_2(g)$**	**HCl (g)**
Stoichiometric coefficient	1	1	2
No. of moles of reactants allowed to react at 273 K and 1 atm pressure	22.4 L (1 mol)	11.2 L (0.5 mol)	-
No. of moles of reactant reacted and product formed	0.5	0.5	1
Amount of HCl formed = 1 mol			

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10. $\overset{+2}{Ba}\overset{-1}{Cl_2} + \overset{+1}{H_2}\overset{+6}{S}\overset{-2}{O_4} \rightarrow \overset{+2}{Ba}\overset{+6}{S}\overset{-2}{O_4} + 2\ \overset{+1}{H}\overset{-1}{Cl}$

11. $\overset{0}{P_4} + 3\,NaOH + 3\,H_2O \rightarrow \overset{-3}{P}H_3 + 3\,NaH_2\overset{+1}{P}O_2$

12. The reduction reaction of the oxidising agent(MnO_4^-) involves gain of 3 electrons. Hence the equivalent mass = (Molar mass of $KMnO_4$)/3 = 158.1/3 = 52.7

13. No. of moles of water present in 180 g

= Mass of water / Molar mass of water

= 180 g / 18 g mol^{-1} = 10 moles

One mole of water contains

= 6.022 x 10^{23} water molecules

10 mole of water contains = 6.022 x 10^{23} x 10 = 6.022 x 10^{24} water molecules

14. 7.5 g of gas occupies a volume of 5.6 liters at 273 K and 1 atm pressure Therefore, the mass of gas that occupies a volume of 22.4 liters

$$= \frac{7.5\,g}{5.6\,L} \times 22.4\,L = 30\,g$$

Molar mass of NO (14+16) = 30 g

15. No. of electrons present in one ammonia (NH_3) molecule (7 + 3) = 10

$$\text{No. of moles of ammonia} = \frac{\text{Mass}}{\text{Molar mass}}$$

$$= \frac{1.7\,g}{17\,gmol^{-1}}$$

$$= 0.1\,mol$$

No. of molecules present in 0.1 mol of ammonia

$$= 0.1 \times 6.022 \times 10^{23} = 6.022 \times 10^{22}$$

No. of electrons present in 0.1 mol of ammonia

$$= 10 \times 6.022 \times 10^{22} = 6.022 \times 10^{23}$$

16. $\overset{+3}{S_2}O_4^{2-} < \overset{+4}{S}O_3^{2-} < \overset{+5}{S_2}O_6^{2-} < \overset{+6}{S}O_4^{2-}$

17. $\overset{2+}{Fe}\,\overset{3+}{C_2}O_4 \xrightarrow{\text{Oxidising agent}} \overset{3+}{Fe} + \overset{+4}{C}O_2$

$n = 1 + 2(1) = 3$

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18. The mass of one mole of carbon

19. No, of moles of oxygen = 8 g/32 g
= 0.25 moles of oxygen

No. of moles of sulphur dioxide = 8 g / 64 g
= 0.125 moles of sulphur dioxide

Ratio between the no. of molecules = 0.25: 0.125
= 2:1

20. $AgNO_3 + KCl \rightarrow KNO_3 + AgCl$

50 mL of 8.5 % solution contains 4.25 g of $AgNO_3$

No. of moles of AgNO3 present in 50 mL of 8.5 % $AgNO_3$ solution

= Mass / Molar mass

= 4.25 / 170

= 0.025 moles

Similarly, No of moles of KCl present in 100 mL of 1.865 % KCl solution

= 1.865 / 74.5

= 0.025 moles

So total amount of AgCl formed is 0.025 moles (based on the stoichiometry)

Amount of AgCl present in 0.025 moles of AgCl

= no. of moles x molar mass

= **0.025 x 143.5 = 3.59 g**

21. No. of moles of a gas that occupies a volume of 612.5 mL at room temperature and pressure (25 ^{0}C and 1 atm pressure)

= 612.5×10^{-3} L / 24.5 $Lmol^{-1}$

= 0.025 moles

We know that,

Molar mass = Mass / no. of moles

= **1.1 g /0.025 mol = 44 g mol^{-1}**

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22. No. of moles of carbon present in 6 g of C-12 = Mass / Molar mass

= 6/12 = 0.5 moles = 0.5 × 6.022 × 10^{23} carbon atoms.

No. of moles in 8 g of methane = 8 / 16 = 0.5 moles

= 0.5 × 6.022 × 10^{23} carbon atoms.

No. of moles in 7.5 g of ethane = 7.5 / 30 = 0.25 moles

= 2 × 0.25 × 6.022 × 10^{23} carbon atoms.

23. Percentage of carbon in ethylene $(C_2H_4) = \frac{\text{mass of carbon}}{\text{Molar mass}} \times 100$

$= \frac{24}{28} \times 100 = 85.71\%$

Percentage of carbon in propene $(C_3H_6) = \frac{36}{42} \times 100 = 85.71\%$

24. (a) relative atomic mass of C-12 is 12 u

25. ${}_6C^{12}$

II Key to brief answer questions:

32. Given :

The density of CO_2 at 273 K and 1 atm pressure = 1.965 kgm^{-3}

Molar mass of CO_2 = ?

At 273 K and 1 atm pressure, 1 mole of CO_2 occupies a volume of 22.4 L

Mass of 1 mole of $CO_2 = \frac{1.965\ \text{Kg}}{1\text{m}^3} \times 22.4\ \text{L}$

$= \frac{1.965 \times 10^3\ \text{g} \times 22.4 \times 10^{-3}\ \cancel{\text{m}^3}}{1\ \cancel{\text{m}^3}}$

$= 44.01\ \text{g}$

Molar mass of CO_2 = 44 $gmol^{-1}$

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33.

Compound	Given no. of moles	No. of oxygen atoms
Ethanol - C_2H_5OH	1	$1 \times 6.022 \times 10^{23}$
Formic acid - HCOOH	1	$2 \times 6.022 \times 10^{23}$
Water - H_2O	1	$1 \times 6.022 \times 10^{23}$
Answer : Formic acid		

34. Average atomic mass $= \frac{(78.99 \times 23.99) + (10 \times 24.99) + (11.01 \times 25.98)}{100}$

$= \frac{2430.9}{100}$

$= 24.31u$

35. Reaction : $x + y + z_2 \rightarrow xyz_2$

Question	Number of moles of reactants allowed to react			Number of moles of reactants consumed during reaction			Limiting reagent
	x	y	z_2	x	y	z_2	
(a)	200 atoms	200 atoms	50 molecules	50 atoms	50 atoms	50 molecules	z_2
(b)	1 mol	1mol	3 mol	1 mol	1 mol	1 mol	x and y
(c)	50 atom	25 atom	50 molecules	25 atom	25 atom	25 molecules	y
(d)	2.5 mol	5 mol	5 mol	2.5 mol	2.5 mol	2.5 mol	x

36. Given: mass of one atom $= 6.645 \times 10^{-23}$ g

$\therefore$ mass of 1 mole of atom $= 6.645 \times 10^{-23}$ g $\times 6.022 \times 10^{23}$

$= 40$ g

$\therefore$ number of moles of element in 0.320 kg $= \frac{1 \text{ mole}}{40 \text{ g}} \times 0.320 \text{ kg}$

$= \frac{1 \text{ mol} \times 320 \text{ g}}{40 \text{ g}}$

$= 8$ mol.

38.

Compound	Molecular formula	Empirical formula
Fructose	$C_6H_{12}O_6$	CH_2O
Caffeine	$C_8H_{10}N_4O_2$	$C_4H_5N_2O$

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39. Given $2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe$

	Reactants		Products	
	Al	**Fe_2O_3**	**Al_2O_3**	**Fe**
Amount of reactant allowed to react	324 g	1.12 kg	-	-
Number of moles allowed to react	$\frac{324}{27} = 12$ mol	$\frac{1.12 \times 10^3}{160} = 7$ mol	-	-
Stoichiometric Co-efficient	2	1	1	2
Number of moles consumed during reaction	12 mol	6 mol	-	-
Number of moles of reactant unreacted and number of moles of product formed	-	1 mol	6 mol	12 mol

Molar mass of Al_2O_3 formed

$$= 6 \text{ mol} \times 102 \text{ g mol}^{-1} \left[\begin{array}{l} Al_2O_3 \\ (2 \times 27) + 3 (\times 16) \\ 54 + 48 = 102 \end{array} \right] \quad = 612 \text{ g}$$

Excess reagent = Fe_2O_3

Amount of excess reagent left at the end of the reaction = 1 mol × 160 g mol^{-1}

$$= 160 \text{ g} \left[\begin{array}{l} Fe_2O_3 \\ (2 \times 56) + (3 \times 16) \\ 112 + 48 = 160 \end{array} \right] \quad = 160 \text{ g}$$

40. Balanced equation for the combustion of ethane

$$C_2H_6 + \tfrac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O$$

$$\Rightarrow \quad 2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6\ H_2O$$

To produce 4 moles of CO_2, 2 moles of ethane is required

$\therefore$ To produce 1 mole (44 g) of CO_2 required

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number of moles of ethane $= \frac{2 \text{ mol ethane}}{4 \text{ mol } CO_2} \times 1 \text{ mol } CO_2$

$= \frac{1}{2}$ mole of ethane

= 0.5 mole of ethane

41.

$$\overset{-1}{H_2O_2} + Fe^{2+} \longrightarrow Fe^{3+} + \overset{-2}{H_2O}$$

$(1e^- \times 2)$ $1e^-$

$1\ H_2O_2 + 2Fe^{2+} \rightarrow Fe^{3+} + H_2O$

$\Rightarrow \quad H_2O_2 + 2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$

42.

Element	Percentage	Atomic mass	Relative number of atoms	Simple ratio	Whole no.
C	76.6	12	$\frac{76.6}{12} = 6.38$	$\frac{6.38}{1.06} = 6$	6
H	6.38	1	$\frac{6.38}{1} = 6.38$	$\frac{6.38}{1.06} = 6$	6
O	17.02	16	$\frac{17.02}{16} = 1.06$	$\frac{1.06}{1.06} = 1$	1

Empirical formula = C_6H_6O

$$n = \frac{\text{Molar mass}}{\text{Calculated empirical formula mass}}$$

$$= \frac{2 \times \text{vapour density}}{94} = \frac{2 \times 47}{94} = 1$$

$\therefore$ **molecular formula $(C_6H_6O) \times 1 = C_6H_6O$**

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43.

Element	%	Relative no. of atoms	Simple ratio
Na	14.31	$\frac{14.31}{23} = 0.62$	$\frac{0.62}{0.31} = 2$
S	9.97	$\frac{9.97}{32} = 0.31$	$\frac{0.31}{0.31} = 1$
H	6.22	$\frac{6.22}{1} = 6.22$	$\frac{6.22}{0.31} = 20$
O	69.5	$\frac{69.5}{16} = 4.34$	$\frac{4.34}{0.31} = 14$

$\therefore$ Empirical formula = $Na_2\ S\ H_{20}\ O_{14}$

$$n = \frac{\text{molar mass}}{\text{calculated empirical formula mass}} = \frac{322}{322} = 1$$

$$\begin{aligned} & Na_2\ S\ H_{20}\ O_{14} \\ &= (2\times 23) + (1\times 32) + (20\times 1) + 14\,(16) \\ &= 46 + 32 + 20 + 224 \\ &= 322 \end{aligned}$$

Molecular formula = $Na_2\ S\ H_{20}\ O_{14}$

Since all the hydrogen in the compound present as water

$\therefore$ Molecular formula is $Na_2\ SO_4\ .\ 10H_2O$

44. (i)

$$K_2\overset{+6}{Cr_2}O_7 + K\overset{-1}{I} + H_2SO_4 \rightarrow K_2SO_4 + \overset{+3}{Cr_2}(SO_4)_3 + \overset{0}{I_2} + H_2O$$

$2 \times 3e^-$ $\quad$ $1e^-$

$$\mathbf{K_2Cr_2O_7} + \mathbf{6KI} + H_2SO_4 \rightarrow K_2SO_4 + Cr_2\,(SO_4)_3 + I_2 + H_2O$$

$$K_2Cr_2O_7 + 6KI + H_2SO_4 \rightarrow K_2SO_4 + \mathbf{Cr_2(SO_4)_3} + \mathbf{3I_2} + H_2O$$

$$K_2Cr_2O_7 + 6KI + \mathbf{7H_2SO_4} \rightarrow \mathbf{4K_2SO_4} + Cr_2\,(SO_4)_3 + 3I_2 + \mathbf{7H_2O}$$

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(ii)

$$\overset{+7}{K}\overset{+7}{M}nO_4 + Na_2\overset{+4}{S}O_3 \longrightarrow \overset{+4}{M}nO_2 + Na_2\overset{+6}{S}O_4 + KOH$$

$3e^-$ $2e^-$

$\Rightarrow$ $\mathbf{2KMnO_4 + 3Na_2SO_3} \longrightarrow MnO_2 + Na_2SO_4 + KOH$

$\Rightarrow$ $2KMnO_4 + 3Na_2SO_3 \longrightarrow \mathbf{2MnO_2 + 3Na_2SO_4} + KOH$

$\Rightarrow$ $2KMnO_4 + 3Na_2SO_3 + \mathbf{H_2O} \longrightarrow 2MnO_2 + 3Na_2SO_4 + \mathbf{2KOH}$

(iii)

$$\overset{0}{C}u + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{C}u(NO_3)_2 + \overset{+4}{N}o_2 + H_2O$$

$2e^-$ $1e^-$

$\mathbf{Cu + 2HNO_3} \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$

$Cu + 2HNO_3 + \mathbf{2HNO_3} \longrightarrow Cu(NO_3)_2 + \mathbf{2NO_2} + 2H_2O$

$Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

(iv)

$$\overset{+7}{K}\overset{+7}{M}nO_4 + H_2\overset{+3}{C}_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \overset{+2}{M}nSO_4 + \overset{+4}{C}O_2 + H_2O$$

$5e^-$ $1e^- \times 2$

$\mathbf{2KMnO_4 + 5H_2C_2O_4} + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + CO_2 + H_2O$

$2KMnO_4 + 5H_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + \mathbf{2MnSO_4 + 10CO_2} + H_2O$

$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

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45. (i) Half reaction are

$$\overset{+7}{M}nO_4^- \longrightarrow Mn^{2+} \quad \text{..... (1)}$$

and $\quad Sn^{2+} \longrightarrow Sn^{4+} \quad \text{..... (2)}$

(1) $\Rightarrow$ $\quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

(2) $\Rightarrow$ $\quad Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

(1) $\times$ 2 $\Rightarrow$ $\quad 2MnO_4^- + 16H^+ + \cancel{10e^-} \longrightarrow 2Mn^{2+} + 8H_2O$

(2) $\times$ 5 $\Rightarrow$ $\quad 5\,Sn^{2+} \longrightarrow 5Sn^{4+} + \cancel{10e^-}$

$$\Rightarrow \quad 2MnO_4^- + 5Sn^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(ii)

$$\overset{+3}{C}_2O_4^{2-} \longrightarrow \overset{+4}{C}O_2 \quad \text{..... (1)}$$

$$\overset{+6}{Cr}_2O_7^{2-} \longrightarrow Cr^{3+} \quad \text{..... (2)}$$

(1) $\Rightarrow$ $\quad C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^- \quad \text{..... (3)}$

$$Cr_2O_7^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad \text{..... (4)}$$

(3) $\times$ 3 $\Rightarrow$ $\quad 3\,C_2O_4^{2-} \longrightarrow 6\,CO_2 + \cancel{6\,e^-} \quad \text{..... (5)}$

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H^2O \quad \text{..... (4)}$$

$$Cr_2O_7^{2-} + 3\,C_2O_4^{2-} + 14\,H^+ \longrightarrow 2\,Cr^{3+} + 6\,CO_2 + 7\,H_2O$$

(iii)

half reaction $\Rightarrow$ $\quad S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{..... (1)}$

$$I_2 \longrightarrow I^- \quad \text{..... (2)}$$

(1) $\Rightarrow$ $\quad 2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + \cancel{2e^-} \quad \text{..... (3)}$

(2) $\Rightarrow$ $\quad I_2 + \cancel{2e^-} \longrightarrow 2I^- \quad \text{..... (4)}$

(3) + (4) $\Rightarrow$ $\quad 2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

(iv) Half reactions are

$$\overset{0}{Z}n \longrightarrow Zn^{2+} \quad \text{..... (1)}$$

$$\overset{+5}{N}O_3^- \longrightarrow \overset{+2}{N}O \quad \text{..... (2)}$$

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(1) $\Rightarrow$ $Zn \longrightarrow Zn^{2+} + 2e^-$ ..... (3)

(2) $\Rightarrow$ $NO_3^- + 3e^- + 4H^+ \longrightarrow NO + 2H_2O$ ..... (4)

(3) $\times 3$ $\Rightarrow$ $3Zn \longrightarrow 3Zn^{2+} + \cancel{6e^-}$ ..... (5)

(4) $\times 2$ $\Rightarrow$ $2NO_3^- + \cancel{6e^-} + 8H^+ \longrightarrow 2NO + 4H_2O$ ..... (6)

$$3Zn + 2NO_3^- + 8H^+ \longrightarrow 3Zn^{2+} + 2NO + 4H_2O$$

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Unit - 2
Quantum Mechanical Model of Atom

Evaluate yourself:

1) Given: accelerated potential = 1 keV

The kinetic energy of the electron =

the energy due to accelerating potential.

$$\frac{1}{2}mv^2 = eV$$

$$mv^2 = 2eV$$

$$m^2v^2 = 2meV \Rightarrow (mv)^2 = 2meV$$

$$\Rightarrow mv = \sqrt{2meV}$$

de Broglie wavelength $\lambda = \frac{h}{mv}$

$$\Rightarrow \lambda = \frac{h}{\sqrt{2meV}}$$

m = mass of the electron = 9.1×10^{-31} kg

h = Planck constant = 6.626×10^{-34} Js

1 eV = 1.6×10^{-19} J

$$\lambda = \frac{6.626\times10^{-34}\,Js}{\sqrt{2\times9.1\times10^{-31}\,kg\times1keV}}$$

$$\lambda = \frac{6.626\times10^{-34}\,JS}{\sqrt{2\times9.1\times10^{-31}\times1\times10^{3}\times1.6\times10^{-19}\,kgJ}}$$

$$\lambda = 3.88\times10^{-11}\,m$$

$$\left[\because \frac{Js}{\sqrt{J\,kg}} = J^{1/2}kg^{-1/2}.s\right.$$

$$= (kgm^2s^{-2})^{1/2}.kg^{-1/2}s$$

$$\left. = m\right]$$

2. Given

$\Delta v = 5.7 \times 10^5 ms^{-1}$ Δx = ?

According to Heisenberg's uncertainty principle, $\Delta x \,.\, \Delta p \geq \frac{h}{4\pi}$

$$\frac{h}{4\pi} = \frac{6.626\times10^{-34}}{4\times3.14}\,kgm^2s^{-1}$$

$$\frac{h}{4\pi} = 5.28\times10^{-35}$$

$$\Delta x \,.\, \Delta p \geq 5.28\times10^{-35}$$

$$\Delta x \,.\, m.\Delta v \geq 5.28\times10^{-35}$$

$$\Rightarrow \Delta x \geq \frac{5.28\times10^{-35}\,kgm^2s^{-1}}{9.1\times10^{-31}\,kg\times5.7\times10^{5}\,ms^{-1}}$$

$$\Rightarrow \Delta x \geq 1.017\times10^{-10}\,m$$

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3. n = 4

l = 0, 1, 2, 3

$\therefore$ 4 sub shells s, p, d & f.

$l = 0$ $m_l = 0 \Rightarrow$ one 4s orbital.

$l = 1$ $m_l = -1, 0, +1 \Rightarrow$ three 4p orbitals.

$l = 2$ $m_l = -2, -1, 0, +1, +2 \Rightarrow$ five 4d orbitals.

$l = 3$ $m_l = -3, -2, -1, 0, +1, +2, +3 \Rightarrow$ seven 4f orbitals.

Over all 16 orbitals are possible.

4.

Orbital	**n**	***l***	**Radial node n – *l* – 1**	**Angular node *l***	**Total node n – 1**
3d	3	2	0	2	2
4f	4	3	0	3	3

5. $E_n = \frac{-13.6}{n^2} eV$

Second excited state

$n = 3 \quad \therefore E_3 = \frac{-13.6}{9} eV$

$E_3 = -1.51 eV$

6. Electronic configuration of Fe^{3+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

Five unpaired electrons.

1	1	1	1	1

$3d^5$

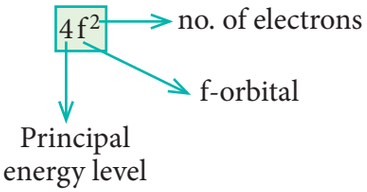
Electronic configuration of Mn^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

$\therefore$ **Five unpaired electrons.**

Electronic configuration of Ar: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

no unpaired electrons.

7.



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n = 4 ; f orbital $l = 3 \Rightarrow m_l = -3, -2, -1, 0, +1, +2, +3$

Out of two electrons, one electron occupies 4f orbital with $m_l = -3$ and another electron occupies 4f orbital with $m_l = -2$.

$\therefore$ All the four quantum numbers for the two electrons are

Electron	n	l	m_l	m_s
$1e^-$	4	3	–3	+1/2
$2e^-$	4	3	–2	+1/2

8.

Electronic configuration of Fe^{3+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^5$

Electronic configuration of Ni^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^0\ 3d^8$

Fe^{3+} has stable $3d^5$ half filled configuration.

EVALUATION

I Choose the best answer:

1. (c) 30
2. (c) 4.42×10^{-18} J
3. (b) $\lambda_1 = 2\lambda_2$
4. (d) Stark effect
5. (b)
6. (d) n=6 to n=5
7. (a)
8. (c) d_{z^2}, $d_{x^2-y^2}$
9. (b) Spin quantum number
10. (b) $[Xe]4f^7\ 6s^2$; $[Xe]4f^7\ 5d^1\ 6s^2$; $[Xe]4f^9\ 6s^2$
11. (c) 4l+2
12. (d) $\sqrt{6}\ h/2\pi$
13. (c) 2
14. (c)
15. (a) 9
16. (a) ns→(n-2)f→(n-1)d→np
17. (b) (ii),(iv) & (v)
18. (b) 17
19. (a) Zero
20. (c) $1/2m\ \sqrt{h}/\pi$
21. (c) 6.6×10^{-31} cm
22. (d) 0.4
23. (d) -9E
24. (a) $\hat{H}\psi = E\psi$
25. (d) $\Delta E.\Delta X \geq h/4\pi$

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Key to multiple choice questions:

1.

M^{2+} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$

M : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^8$

Atomic number = 26

Mass number =56

No. of neutrons = 56 -26 = 30

2. $E = h\nu = hc/\lambda$

$$= \frac{6.626\times10^{-34}\ \text{J s}\times3\times10^{8}\ \text{m s}^{-1}}{45\times10^{-9}\ \text{m}}$$

$$= 4.42\times10^{-18}\ \text{J}$$

3.

$$\frac{E1}{E2} = \frac{25\ \text{eV}}{50\ \text{eV}} = \frac{1}{2}$$

$$\frac{hc}{\lambda_1}\times\frac{\lambda_2}{hc} = \frac{1}{2}$$

$$2\lambda_2 = \lambda_1$$

4. Spliting of spectral lines in magnetic field is called Zeeman effect and spliting of spectral lines in electric field, is called Stark effect.

5. **Correct statement:** For n=1, the electron has more negative energy than it does for n=6 which means that the electron is **strongly** bound in the smallest allowed orbit.

6. n = 6 to n=5

$E_6 = -13.6 / 6^2$; $E_5 = -13.6 / 5^2$

$E_6 - E_5 = (-13.6/6^2) - (-13.6/5^2)$

$= 0.166$ eV atom^{-1}

$E_5 - E_4 = (-13.6/5^2) - (-13.6/4^2)$

$= 0.306$ eV atom^{-1}

9. Spin quantum number

For the first electron $m_s = +½$

For the second electron $m_s = -½$

10. Eu : [Xe] $4f^7, 5d^0, 6s^2$

Gd : [Xe] $4f^7, 5d^1, 6s^2$

Tb: [Xe] $4f^9, 5d^0, 6s^2$

11 $2(2l+1) = 4l+2$

12. Orbital angular momentum = $\sqrt{(l(l+1)}\ h/2\pi$ For d orbital = $\sqrt{(2 \times 3)}\ h/2\pi = \sqrt{6}\ h/2\pi$

13 n = 3; l=1; m = -1

either $3p_x$ or $3p_y$

i.e., Maximum two electrons can be accomodated either in $3p_x$ or in $3p_y$

14 No. of radial node = n-l-1

No. of angular node = l

for 3p orbital

No. of angular node = l = 1

No. of radial node = n-l-1 = 3-1-1 = 1

15. n = 3; l = 0; m_l = 0 - one s orbital

n = 3; l = 1; m_l = -1, 0, 1 - three p orbitals

n = 3; l = 2; m_l = -2, -1, 0, 1, 2 - five d Orbitals

Overall nine orbitals are possible.

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16. n = 6

According Aufbau principle,

6s →4f →5d →6p

ns → (n-2)f →(n-1)d → np

17 (ii) l can have the values from 0 to n-1

n=2; possible 'l' values are 0, 1 hence l = 2 is not possible.

(iv) for l=0; m=-1 not possible

(v) for n=3 l = 4 and m = 3 not possible

18. n+l = 8

Electronic configuration of atom with atomic number 105 is [Rn] $5f^{14}$ $6d^3$ $7s^2$

Orbital	(n+l)	No. of electrons
5f	5+3 = 8	14
6d	6+2 = 8	3
7s	7+0 = 7	2
No of electrons = 14 + 3 = 17		

19. Option (a) - Zero **(Refer to Figure 2.9)**

20.

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

$$\Delta p.\Delta p \geq \frac{h}{4\pi}$$

$$\Delta p^2 \geq \frac{h}{4\pi}$$

$$m^2(\Delta v)^2 \geq \frac{h}{4\pi}$$

$$(\Delta v) \geq \sqrt{\frac{h}{4\pi m^2}}$$

$$\Delta v \geq \frac{1}{2m}\sqrt{\frac{h}{\pi}}$$

21.

m = 100 g = 100 x 10^{-3} kg

v = 100 cm s^{-1} = 100 x 10^{-2} m s^{-1}

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.626\times10^{34}\,Js^{-1}}{100\times10^{-3}\,kg\times100\times10^{-2}\,ms^{-1}}$$

$$= 6.626\times10^{-33}\,ms^{-1}$$

$$= 6.626\times10^{-31}\,cms^{-1}$$

23.

$$E_n = \frac{-13.6}{n^2}\,eV\ atom^{-1}$$

$$E_1 = \frac{-13.6}{(1)^2} = -13.6$$

$$E_3 = \frac{-13.6}{(3)^2} = -\frac{13.6}{9}$$

Givethat

$$E_3 = -E$$

$$-\frac{13.6}{9} = -E$$

$$-13.6 = -9E$$

$$\Rightarrow E_1 = -9E$$

II Key to brief answer question:

27. n = 4 l = 0, 1, 2, 3

four sub-shells ⇒ s, p, d, f

l = 0 m_l = 0; one 4s orbital.

l = 1 m_l = −1, 0, +1 ; three 4p orbitals.

l = 2 m_l = −2, −1, 0, +1, +2 ; five 4d orbitals.

l = 3 m_l = -3, −2, −1, 0, +1, +2 , +3; seven 4f orbitals

Over all Sixteen orbitals.

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28.

Orbital	n	l	Radial node $n - l - 1$	Angular node l
2s	2	0	1	0
4p	4	1	2	1
5d	5	2	2	2
4f	4	3	0	3

30. i) ground state

1	1	1	1	1

ii) maximum exchange energy

1	1	1	1	1

32.

Orbital	n	l
$3p_x$	3	1
$4d_{x^2-y^2}$	4	2

34.

$$\Delta x.\ \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x.\ \Delta p \geq 5.28 \times 10^{-35}\ Kgm^2s^{-1}$$

$$\Delta x.\ (m\Delta v) \geq 5.28 \times 10^{-35}\ Kgm^2s^{-1}$$

Given $\Delta v = 0.1\%$

$v = 2.2 \times 10^6\ ms^{-1}$

$m = 9.1 \times 10^{-31}\ Kg$

$$\Delta v = \frac{0.1}{100} \times 2.2 \times 10^6\ ms^{-1}$$

$$= 2.2 \times 10^3\ ms^{-1}$$

$$\therefore \Delta x \geq \frac{5.28 \times 10^{-35}\ Kgm^2s^{-1}}{9.1 \times 10^{-31}\ Kg \times 2.2 \times 10^3\ ms^{-1}}$$

$$\Delta x \geq 2.64 \times 10^{-8}\ m$$

35. Electronic configuration of oxygen

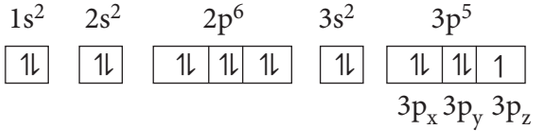
$= 1s^2\ \ 2s^2\ \ 2p^4$



$\therefore$ 8th electron present in $2p_x$ orbital and the quantum numbers are

$n = 2, l = 1, m_l =$ either +1 or -1 and $s = -1/2$

Electronic configuration of chlorine =



15th electron present in $3P_Z$ orbital and the quantum numbers are n = 3, l = 1, m_l =either +1 or -1 and $m_s = +1/2$

36.

$$E_n = \frac{-13.6}{n^2} eV\ \ atom^{-1}$$

$$n = 3\ \ E_3 = \frac{-13.6}{3^2} = \frac{-13.6}{9} = -1.51\ eV\ atom^{-1}$$

$$n = 4\ \ E_4 = \frac{-13.6}{4^2} = \frac{-13.6}{16} = -0.85\ eV\ atom^{-1}$$

$\Delta E = (E_4 - E_3) = (-0.85) - (-1.51)$ eV atom^{-1}

$= (-0.85 + 1.51)$

$= \mathbf{0.66\ eV\ atom^{-1}}$

$(1eV = 1.6 \times 10^{-19}\ J)$

$\Delta E = 0.66 \times 1.6 \times 10^{-19}\ J$

$\Delta E = 1.06 \times 10^{-19}\ J$

$hv = 1.06 \times 10^{-19}\ J$

$$\frac{hc}{\lambda} = 1.06 \times 10^{-19} J$$

$$\therefore \lambda = \frac{hc}{1.06 \times 10^{-19} J}$$

$$= \frac{6.626 \times 10^{-34} JS \times 3 \times 10^8\ ms^{-1}}{1.06 \times 10^{-19} J}$$

$$\lambda = 1.875 \times 10^{-6}\ m$$

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37. Given : de Broglie wavelength of the tennis ball equal to 5400 Å.

m = 54 g

v = ?

$$\lambda = \frac{h}{mV}$$

$$V = \frac{h}{m\lambda}$$

$$V = \frac{6.626 \times 10^{-34}\,JS}{54 \times 10^{-3}\,Kg \times 5400 \times 10^{-10}\,m}$$

$$V = 2.27 \times 10^{-26}\,ms^{-1}$$

38.

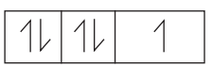
n	l	Sub Enery levels	m_l values	Number of orbitals
4	2	4d	–2, –1, 0, +1, +2	five 4d orbitals
5	3	5f	–3, –2, –1, 0, +1, +2, +3	seven 5f orbitals
7	0	7s	0	one 7s orbitals

41. no. of electrons : 35 (given)

no. of protons : 35

Electronic configuration

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$



$4P_x$ $4P_y$ $4P_z$

last electron present in $4P_y$ orbital

n = 4 l = 1 m_l = either +1 or -1 and s = –1/2

43. $He^+ \rightarrow He^{2+} + e^-$

$$E_n = \frac{-13.6z^2}{n^2}$$

$$E_1 = \frac{-13.6\,(2)^2}{(1)^2} = -54.4$$

$$E_\infty = \frac{-13.6(2)^2}{(\infty)^2} = 0$$

∴ Required Energy for the given process = $E_\infty - E_1 = 0 - (-54.4) = 54.4$ ev

44.

	Atom	Uni-negative ion
number of electron	x – 1	x
number of protons	x – 1	x –1
number of neutrons	y	y

Given that, y = x + 11.1% of x

$$= \left(x + \frac{11.1}{100}x\right) = x + 0.111x$$

$$y = 1.111x$$

mass number = 37

number of protons + number of neutrons = 37

(x – 1) + 1.111x = 37

x + 1.111x = 38

2.111x = 38

$$x = \frac{38}{2.11}$$

x = 18.009 x = 18 (whole number)

∴ Atomic number = x – 1

= 18 –1 = 17

Mass number = 37

Symbol of the ion $^{37}_{17}Cl^-$

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45)

$r_n = \frac{(0.529)n^2}{z}$ Å $\quad E_n = \frac{-13.6\,(z^2)}{n^2}$ ev atom^{-1}

for Li^{2+} z = 3

Bohr raduis for the third orbit (r_3)

$= \frac{(0.529)\,(3)^2}{3}$

$= 0.529 \times 3$

$= 1.587$ Å

Energy of an electron in the fourth orbit (E_4) $= \frac{-13.6\,(3)^2}{(4)^2}$

= – 7.65 eV atom^{-1}

46) Given

$v = 2.85 \times 10^8$ ms^{-1}

$m_p = 1.673 \times 10^{-27}$ Kg

$\lambda = \frac{h}{mv}$

$= \frac{6.626\times10^{-34}\,kgm^2s^{-1}}{1.673\times10^{-27}\,kg\times2.85\times10^{8}\,ms^{-1}}$

$\lambda = 1.389\times10^{-15} \Rightarrow \lambda = 1.389\times10^{-5}$ Å

$[\because 1\text{Å} = 10^{-10}\,m]$

47) m = 160 g = 160×10^{-3} kg

v = 140 km hr^{-1} = $\frac{140\times10^3}{60\times60}$ ms^{-1}

v = 38.88 ms^{-1}

$\lambda = \frac{h}{mv}$

$\lambda = \frac{6.626\times10^{-34}\,Kgm^2s^{-1}}{160\times10^{-3}\,Kg\times38.88\ ms^{-1}}$

$\lambda = 1.065\times10^{-34}\,m$

48) $\Delta x = 0.6$ Å $= 0.6 \times 10^{-10}$ m

Δp = ?

$\Delta x\,.\,\Delta p \geq \frac{h}{4\pi}$

$\Delta x\,.\,\Delta p \geq 5.28\times10^{-35}\,kgm^2s^{-1}$

$(0.6\times10^{-10})\Delta p \geq 5.28\times10^{-35}$

$\Rightarrow \Delta p \geq \frac{5.28\times10^{-35}\,kgm^2s^{-1}}{0.6\times10^{-10}\,m}$

$\Delta p \geq 8.8\times10^{-25}$ kgms^{-1}

49)

$\Delta x\,.\,\Delta p \geq \frac{h}{4\pi}$

$\lambda.(m\Delta v) \geq \frac{h}{4\pi}$

$\Delta v \geq \frac{h}{4\pi(m\lambda)}$

$\Delta v \geq \frac{h}{4\pi\times m\times\frac{h}{mv}} \qquad \left[\because \lambda = \frac{h}{mv}\right]$

$\Delta v \geq \frac{v}{4\pi}$

Therefore,

minimum uncertainity in velocity $= \frac{v}{4\pi}$

50) Potential difference = 100V

$= 100 \times 1.6 \times 10^{-19}$J

$\lambda = \frac{h}{\sqrt{2mev}}$

$= \frac{6.626\times10^{-34}\,Kgm^2s^{-1}}{\sqrt{2\times9.1\times10^{-31}\,Kg\times100\times1.6\times10^{-19}\,J}}$

$\lambda = 1.22\times10^{-10}\,m$

51)

n	l	m_l	sub energy level
4	**2**	0	4d
3	1	0	**3p**
5	**1**	**any one value –1, 0, +1**	5p
3	**2**	–2	3d

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Evaluate yourself

2. Atomic number : 120

IUPAC temporary symbol : Unbinilium

IUPAC temporary symbol : Ubn

Possible electronic configuration :[Og] $8s^2$

3. Electronic Configuration : $(n-1)d^2 ns^2$

for n = 5, the electronic configuration is,

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 4d^2\ 5s^2$ Atomic number : 40

4th group 5th period (d block element) = Zirconium

4. Electronic Configuration of Aluminium

$_{13}Al\ \underbrace{1s^2}_{(n-2)}\ \underbrace{2s^2\ 2p^6}_{(n-1)}\ \underbrace{3s^2\ 3p^1}_{n}$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	2	0.35	0.70
(n – 1)	8	0.85	6.80
(n – 2)	2	1	2.00
			9.50

∴ Effective nuclear charge = Z – S

= 13 – 9.5

$(Z_{eff})_{Al}$ = 3.5

Electronic Configuration of chlorine

$\underbrace{1s^2}_{n-2}\ \underbrace{2s^2\ 2p^6}_{n-1}\ \underbrace{3s^2\ 3p^5}_{n}$

Group	no. of electrons	Contribution of each electron to 'S' value	Contribution of a particular group
n	6	0.35	2.1
(n – 1)	8	0.85	6.8
(n –2)	2	1	2
		S =	10.9

∴ Effective nuclear charge = Z – S

= 17 – 10.9

$(Z_{eff})_{cl}$ = 6.1

$(Z_{eff})_{cl} > (Z_{eff})_{Al}$ and. Hence $r_{cl} < r_{Al}$.

5.

X^{3+}, Y^{2+}, Z^- are isoelectronic.

∴ Effective nuclear charge is in the order $(Z_{eff})_{Z^-} < (Z_{eff})_{Y^{2+}} < (Z_{eff})_{X^{3+}}$ and

Hence, ionic radii should be in the order

$r_{Z^-} > r_{Y^{2+}} > r_{X^{3+}}$

∴ The correct values are,

Species	Ionic radii
Z^-	136
Y^{2+}	64
X^{3+}	49

6. **Noble gases :** Ioniation energy ranging from 2372 $KJmol^{-1}$ to 1037 kJ mol^{-1}.

For element X, the IE_1, value is in the

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range of noble gas, moreover for this element both IE_1 and IE_2 are higher and hence X is the noble gas.

For Y, the first ionisation energy is low and second ionisation energy is very high and hence Y is most reactive metal.

For Z, both IE_1 and IE_2 are higher and hence it is least reactive.

7. $Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta H = 348$ kJ mol^{-1}

For one mole (35.5g) 348 kJ is released.

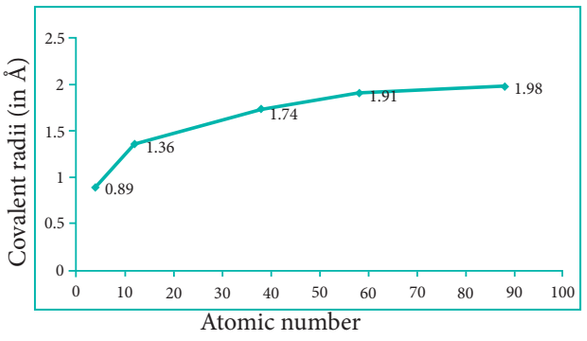
$\therefore$ For 17.75g chlorine, $\frac{348 \text{ kJ}}{35.5 \cancel{g}} \times 17.75 \cancel{g}$ energy leased.

$\therefore$ The amount of energy released $= \frac{348}{2}$

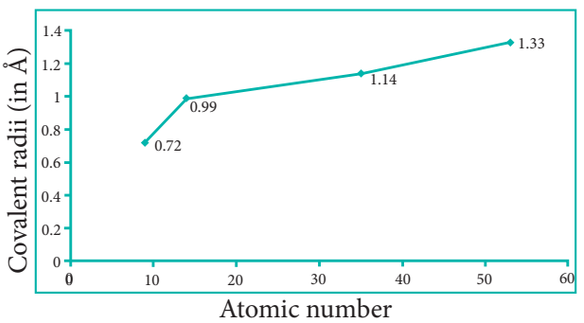
$= 174$ kJ

Activitiy : 3.1

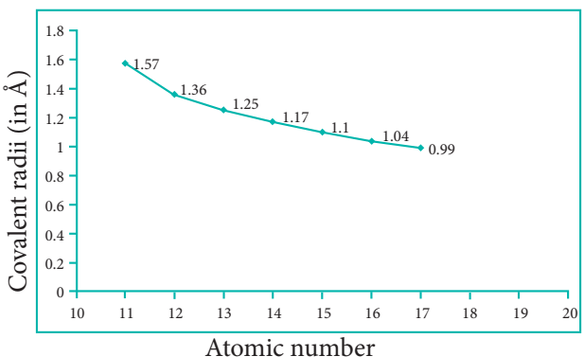
Covalent radii - 2nd group elements



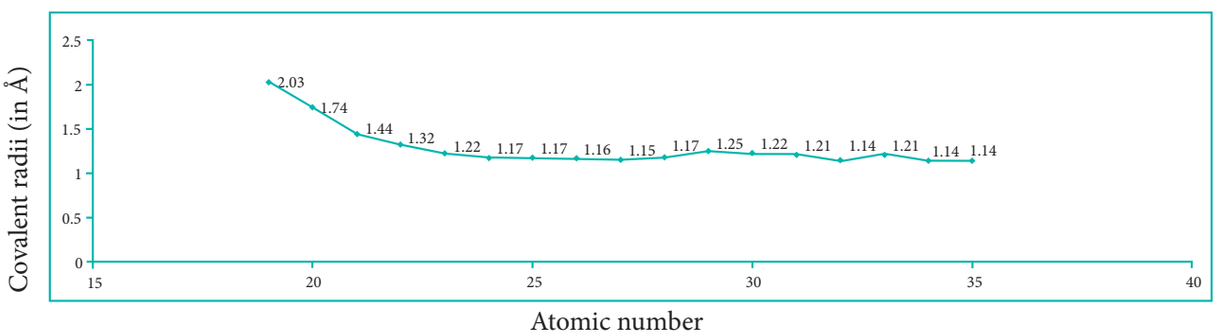
Covalent radii - 17th group elements



Covalent radii - 3rd period elements



Covalent radii - 4th period elements



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EVALUATION

I Choose the best answer:

1. (d) bibibium
2. (b) AB_2
3. (d) f-block elements
4. (a) I < Br < Cl < F (increasing electron gain enthalpy)
5. (d) fluorine
6. (c) Aluminium
7. (b) Na < Al < Mg < Si < P
8. (a)
9. (d) Ca < Al < C < O < F
10. (c) Cl > F > Br > I
11. (d) Hydrogen
12. (c) Argon
13. (a) Y > Z > X > A
14. (c)
15. (a) $1s^2$, $2s^2$, $2p^6$, $3s^1$
16. (c) Oxygen
17. (c) +527 kcal mol^{-1}
18. (a) s > p > d > f
19. (d) None of these
20. (b) 575 kJ mol^{-1}
21. (a)
22. (a) Generally increases
23. (d) Be and Al

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Unit - 4
Hydrogen

EVALUATION

I Choose the best answer:

1. (c)
2. (c) $CO + H_2$
3. (b)
4. (d) group one elements
5. (c) 1p+2n
6. (a) Palladium, Vanadium
7. (a)
8. (a) 1.2 g
9. (d) EDTA
10. (c) $CaCl_2$
11. (a) sodium aluminium silicate
12. (a)
13. (c) $CrO(O_2)_2$
14. (c) 5/2
15. (d) 8.4
16. (d) sp^3 and sp^3
17. (c) monobasic acid
18. (a) tetrahedrally by 4-H atoms
19. (b) intra-molecular hydrogen bonding and inter molecular hydrogen bonding
20. (c) both (a) & (b)
21) (c) amphoteric oxide

Key for multiple choice questions:

1) Option (c)

Correct statement : Hydrogen has three isotopes of which **protium** is the most common.

2) Option (c)

$CO + H_2$ - Water gas

3) Option (b)

Correct statement : Ortho isomer - one nuclear spin

Para isomer - zero nuclear spin

4) Option (d)

eg : Sodium hydride ($Na^+ H^-$)

5) Option (c)

$_1T^3$ ($1e^-$, 1p, 2n)

7) Option (a)

$Ca^{2+} + Na_2CO_3 \rightarrow CaCO_3 \downarrow + 2Na^+$

8) mass of deuterium = 2 × mass of protium

If all the 1.2 g hydrogen is replaced with deuterium, the weight will become 2.4g. Hence the increase in body weight is (2.4 – 1.2 = 1.2 g)

Option (a)

9) EDTA (option (d))

10) Permanent hardness if water is due to the presence of the chlorides, nitrates and sulphates of Ca^{2+} and Mg^{2+} ions.

Option (c) $CaCl_2$

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11) Zeolite is sodium aluminium silicate.

$(NaAlSi_2O_6 . H_2O)$

Option (a)

12) (a) 1 mL of H_2O_2 will give 100ml O_2 at STP.

13) $Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \rightarrow 2CrO(O_2)_2 + 5H_2O$

Option (c)

14) $2MnO_4^- + 5H_2O_2(aq) + 6H^+ \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$

Option (c) 5/2 moles

15) Volume strength of hydrogen peroxide = Normality of hydrogen peroxide × 5.6

$= 1.5 \times 5.6$

$= 8.4$

Option (d)

$$\underset{(2\times 34g)}{2H_2O_2} \rightarrow 2H_2O + \underset{(22.4 \text{ litres})}{O_2}\uparrow$$

Volume strength of Hydrogen peroxide

$$= \frac{\text{Normality} \times \text{Equivalent weight of } H_2O_2 \times 22.4}{68}$$

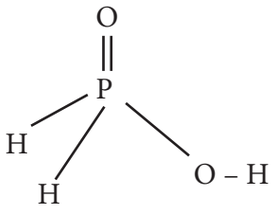
$$= \text{Normality} \times \left(\frac{17\times 22.4}{68}\right)$$

Volume strength of hydrogen peroxide
= Normality × 5.6

16) sp^3 and sp^3

Option (d)

17) Hypophosphorus acid on reaction with D_2O, only one hydrogen is replaced by deuterium and hence it is mono basic

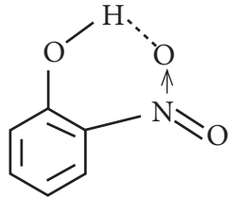


Option (c) monobasic acid

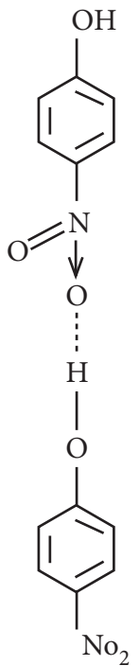
18) (a) tetrahedrally surrounded by 4 hydrogen atoms (refer 4.6 (a) Structure of ice)

19)

o-nitro phenol



p - nitro phenol



Option (b)

20) Heavy water is used as moderator as well as coolant in nuclear reactions.

Option (c)

21) Water is a amphoteric oxide.

Option (c)

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Unit - 5
Alkali and Alkaline Earth Metals

EVALUATION

I Choose the best answer.

1. (c) Density: Li < K < Na < Rb < C
2. (a) Li^+ has minimum degree of hydration among alkali metal cations
3. (d) none of these
4. (b) Li
5. (c) kerosene
6. (a) superoxide and paramagnetic
7. (c) Potassium carbonate can be prepared by solvay process
8. (b) Magnesium
9. (b) MI < MBr < MCl < MF
10. (a) Castners process
11. (c) $Ca(CN)_2$
12. (a) $MgCl_2$
13. (a) p-2, q-1, r-4, s-5, t-6, u-3
14. (d) both assertion and reason are false
15. (a)
16. (b) $MgCO_3$ > $CaCO_3$ > $SrCO_3$ > $BaCO_3$
17. (c) Its salts are rarely hydrolysed
18. (c) milk of lime
19. (b) $NaHCO_3$
20. (b) $Ca(OH)_2$
21. (a) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
22. (b) CaF_2
23. (a) $CaSO_4.2H_2O$
24. (b) CaNCN
25. (d) Li_2CO_3

Keys to multiple choice questions:

1) Option (c)

Potassium is lighter than sodium

(Refer table 5.3)

The correct order of density is

Li < K < Na < Rb < Cs

0.54 < 0.86 < 0.97< 1.53< 1.90(in g cm^{-3})

2) Option (a)

Li^+ has maximum degree of hydration among alkali metal cations.

$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

3) All these compounds reacts with alkali metals to evolve hydrogen gas.

(d) none of these.

4) hydration energy of Li^+ is more and hence Li^+ is stabilized in aqueous medium.

(b) Li

5) (c) Kerosene

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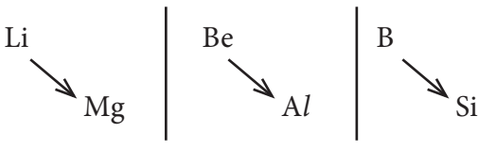
6) RbO_2 is a super oxide which contains Rb+ and O_2^- ions. O_2^- contains one unpaired electron and hence it is paramagnetic.

Option (a)

7) Potassium carbonate cannot be prepared by solvay process. Potassium bicarbonate is fairly soluble in water and does not precipitate out.

Option (c)

8) 

Option (b)

9) ionic character (difference in electronegativity)

MI < MBr < MCl < MF

Option (b)

10) Castner's process

$NaOH \rightleftharpoons Na^+ + OH^-$

Cathode : $Na^+ + e^- \rightarrow Na$

Anode : $2OH^- \rightarrow H_2O + 1/2O_2 + 2e^-$

Option (a)

11) $CaC_2 + N_2 \xrightarrow{300-350^oC} \underset{\text{Calciumcyanide}}{Ca(CN)_2}$

Option (c)

12) (a) $MgCl_2$

The order of hydration energy of alkaline earth metal is

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$

13. (p) sodium –yellow (2)

(q) Calcium – Brick red (1)

(r) Barium – apple green (4)

(s) Strontium – Crimson red (5)

(t) Cesium – blue (6)

(u) Potassium – Violet (3)

Option (a)

14. (d)

Among alkali and alkaline earth metals,

K, Rb and Cs alone forms superoxides.

Superoxide O_2^- has 3 electron bond.

15. (a)

both are true and reason is the correct explanation of assertion.

16. Solubility of carbonates decreases down the group and hence the correct order of solubility is,

(b) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$

17) **Correct Statement:** Beryllium salts are easily hydrolysed

option (c)

18) Slaked lime $Ca(OH)_2$

The suspension is called milk of lime and the clear solution is called lime water.

Option (c)

19)

$$2NaHCO_3 \xrightarrow{\Delta} \underset{\text{(Soluble in water)}}{Na_2CO_3} + H_2O + CO_2 \uparrow$$

$$\downarrow 2HCl$$

$$2\,NaCl + H_2O + CO_2 \uparrow$$

Correct option (b)

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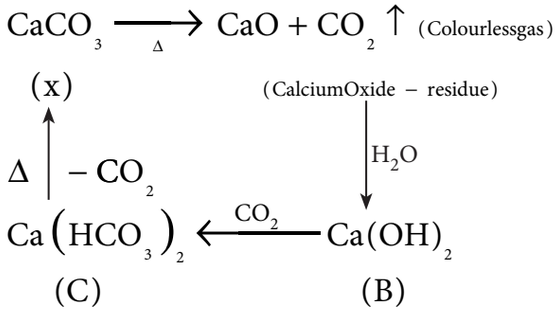
20)



Option (b)

21) Ca^{2+} ion plays an important role in maintaining regular heart beat.

Option (a)

22) 'Blue john' – CaF_2

(A variety of fluorite)

∴ Option (b)

23) $CaSO_4 . 2H_2O$ ∴ Option (a)

24) $CaC_2 + N_2 \xrightarrow[1\ atm]{} CaNCN$

nitrolium
(or)
Calcium cyanamide

∴ Option (b)

25) Li_2CO_3 is least stable.

Option (d)

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Unit - 6
Gaseous State

Evaluate yourself:

1. Volume of freon (V_1) = 1.5 dm^3

   Pressure (P_1) = 0.3 atm

   'T' isconstant

   P_2 = 1.2 atm

   V_2 = ?

   $\therefore P_1V_1 = P_2V_2$

   $$\Rightarrow V_2 = \frac{P_1V_1}{P_2}$$

   $$= \frac{0.3\ \cancel{atm} \times 1.5\ dm^3}{1.2\ \cancel{atm}}$$

   $$= 0.375\ dm^3$$

   $\therefore$ Volume decreased from 1.5 dm^3 to 0.375 dm^3

2. V_1 = 0.375 dm^3 V_2 = 0.125

   P_1 = 1.05 atm P_2 = ?

   'T' - Constant

   $P_1V_1 = P_2V_2$

   $$\therefore P_2 = \frac{P_1V_1}{V_2} = \frac{1.05 \times 0.375}{0.125}$$

   $$= 3.15\ atm$$

3. V_1 = 3.8 dm^3 $T_2 = 0^0C = 273$ K

   T_1 = ? V_2 = 2.27 dm^3

   $$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad T_1 = \left(\frac{T_2}{V_2}\right) \times V_1$$

   $$= \frac{273\ K}{2.27\ \cancel{dm^3}} \times 3.8\ \cancel{dm^3}$$

   $$T_1 = 457\ K$$

4. V_1 = 7.05 dm^3 V_2 = 2.35 dm^3

   η_1 = 0.312 mol η_2 = ?

   'P' and 'T' are constant

   $$\therefore \frac{V_1}{n_1} = \frac{V_2}{n_2}$$

   $$\Rightarrow n_2 = \left(\frac{n_1}{V_1}\right) \times V_2$$

   $$n_2 = \frac{0.312\ mol}{7.05\ \cancel{dm^3}} \times 2.35\ \cancel{dm^3}$$

   $$n_2 = 0.104\ mol$$

   Number of moles exhaled =

   0.312 - 0.104 = 0.208 moles

5) $T_1 = 8\ ^0C = 8 + 273 = 281$ K

   P_1 = 6.4 atm V_1 = 2.1 ml

   $T_2 = 25^0$ C = 25 + 273 = 298 K

   P_2 = 1 atm V_2 = ?

   $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

   $$\Rightarrow V_2 = \left(\frac{P_1V_1}{T_1}\right) \times \frac{T_2}{P_2}$$

   $$= \frac{6.4\ \cancel{atm} \times 2.1\ ml}{281\ \cancel{K}} \times \frac{298\ \cancel{K}}{1\ \cancel{atm}}$$

   $$V_2 = 14.25\ ml$$

6(a)

Vo_2 = 12 dm^3 P = 1 atm

V_{He} = 46 dm^3

V_{total} = 5 dm^3

$$P_{O_2} = x_{O_2} \times P_{total} \qquad n_{O_2} = \frac{1\ mol}{22.4\ \cancel{L}} \times 12\ \cancel{L}$$

$$x_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{He}} \qquad n_{O_2} = 0.54\ mol$$

$$= \frac{0.54}{0.54 + 2.05} \qquad n_{H_e} = \frac{1\ mol}{22.4\ \cancel{L}} \times 46\ \cancel{L}$$

$$= \frac{0.54}{2.59} = 0.21 \qquad n_{H_e} = 2.05\ mol$$

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$P_{total} \times V_{total} = 1 \text{ atm} \times 22.4\ l$

$\therefore P_{total} = \dfrac{1 \text{ atm} \times 22.4\ \cancel{l}}{5\ \cancel{l}}$

$P_{total} = 4.48 \text{ atm}$

$\therefore P_{O_2} = 0.21 \times 4.48 \text{ atm}$

$= 0.94 \text{ atm}$

$P_{He} = x_{He} \times P_{total}$

$x_{He} = \dfrac{n_{He}}{n_{O_2} + n_{He}}$

$= \dfrac{2.05}{0.54 + 2.05}$

$x_{He} = \dfrac{2.05}{2.59} = 0.79$

$\therefore P_{He} = 0.79 \times 4.48 \text{ atm}$

$P_{He} = 3.54 \text{ atm}$

6 (b) $2KClO_{3\,(s)} \longrightarrow 2KCl_{(s)} + 3O_{2\,(g)}$

$P_{total} = 772 \text{ mm Hg}$

$P_{H_2O} = 26.7 \text{ mm Hg}$

$P_{total} = P_{O_2} + P_{H_2O}$

$\therefore P_{O_2} = P_{total} - P_{H_2O}$

$P_1 = 26.7 \text{ mm Hg}$ $\quad T_2 = 295 \text{ K}$

$T_1 = 300 \text{ K}$ $\quad P_2 = ?$

$\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$

$\Rightarrow P_2 = \left(\dfrac{P_1}{T_1}\right) T_2 = \dfrac{26.7 \text{ mm Hg}}{300\ \cancel{K}} \times 295\ \cancel{K}$

$P_2 = 26.26 \text{ mm Hg}$

$\therefore P_{O_2} = 772 - 26.26$

$= 745.74 \text{ mm Hg}$

7) $t_1 = 1.5$ minutes $\quad (gas)_{\text{hydro carbon}}$

$t_2 = 4.73$ minutes $\quad (gas)_{\text{Bromine}}$

$\dfrac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \dfrac{t_{\text{Bromine}}}{t_{\text{Hydrocarbon}}}$

($\because$ Volume is constant)

$= \dfrac{4.73 \text{ minutes}}{1.5 \text{ minutes}}$

$= 3.15$

$\dfrac{\gamma_{\text{Hydrocarbon}}}{\gamma_{\text{Bromine}}} = \sqrt{\dfrac{M_{\text{Bromine}}}{M_{\text{hydrocarbon}}}}$

$3.15 = \sqrt{\dfrac{159.8 \text{ gmol}^{-1}}{M_{\text{hydro carbon}}}}$

Squaring on both sides and rearranging,

$M_{\text{hydro carbon}} = \dfrac{159.8 \text{ g mol}^{-1}}{(3.15)^2}$

$M_{\text{hydro carbon}} = 16.1 \text{ g mol}^{-1}$

$n(12) + (2n+2)\ 1 = 16$ $\quad \left[\because \text{general formula for hydrocarbon } C_nH_{2n+2} \text{ (alkane)}\right]$

$12n + 2n + 2 = 16$

$14n = 16 - 2$

$14n = 14$

$n = 1$

$\therefore$ The hydro carbon is $C_1H_{2(1)+2} = CH_4$

8) Critical temperature of a gas is defined as the temperature above which it cannot be liquified even at high pressures.

$\therefore$ When cooling starts from 700 K, H_2O will liquify first, then followed by ammonia and finally carbondioxide will liquify.

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EVALUATION

I Choose the correct answer:

1. (d) at high pressure the intermolecular interactions become significant
2. (d) inversely proportional to the square root of its molecular weight
3. (c) $\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT$
4. (b) exert no attractive forces on each other
5. (a) 1/3
6. (b) Boyle temperature
7. (c) diffusion
8. (b) near the hydrogen chloride bottle
9. (d) units of pressure and volume
10. (c) 8.3 J mol^{-1} K^{-1}
11. (a) Boyle's Law
12. (c) NH_3
13. (d) I, II and III
14. (c) 0.41 dm^3
15. (c) P
16. (b) 4
17. (c) 1/8
18. (b) 1/T
19. (a) P
20. (b) NH_3
21. (c) mol^{-1} L and L^2 atm mol^{-2}
22. (d) both assertion and reasons are false
23. (c) 3.41 g L^{-1}
24. (c)
25. (d) HI

Keys to multiple choice questions:

5. mass of methane
   = mass of oxygen = a

   number of moles of methane = $\frac{a}{16}$

   number of moles of Oxygen = $\frac{a}{32}$

   mole fraction of Oxygen = $\frac{\frac{a}{32}}{\frac{a}{16}+\frac{a}{32}}$

   $=\frac{\frac{a}{32}}{\frac{3a}{32}}$

   $=\frac{1}{3}$

   Partial pressure of oxygen
   = mole fraction × Total Pressure

   $=\frac{1}{3}P$

6. The temperature at which real gases obey the ideal gas laws over a wide range of pressure is called Boyle temperature

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8. Rate of diffusion $\alpha\ 1/\sqrt{M}$

$M_{NH_3} = 17$; $M_{HCl} = 36.5$

$\gamma_{NH_3} > \gamma_{HCl}$

Hence white fumes first formed near hydrogen chloride

12. Higher the value of 'a', greater the intermolecular force of attraction, easier the liquefaction.

option (c) is correct

14.

$$\text{Compressibility factor (z)} = \frac{PV}{nRT}$$

$$V = \frac{z \times nRT}{P}$$

$$= \frac{\begin{matrix}0.8697 \times 1 \times 8.314 \\ \times 10^{-2}\ \text{bar dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \\ \times 400\ \text{K}\end{matrix}}{71\ \text{bar}}$$

$$V = 0.41\ \text{dm}^3$$

Option (c)

15. T_1 $T_2 = 2T_1$

V_1 $V_2 = 2V_1$

P_1 $P_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2} = \frac{P_1V_1}{T_1} \times \frac{2T_1}{2V_1}$$

$$P_2 = P_1$$

Option (c)

16.

$$\frac{\gamma_{H_2}}{\gamma_{C_nH_{2n+2}}} = \sqrt{\frac{M_{C_nH_{2n+2}}}{M_{H_2}}}$$

$$3\sqrt{3} = \sqrt{\frac{M_{C_nH_{2n+2}}}{2}}$$

Squaring on both sides and rearranging

$27 \times 2 = M_{C_nH_{2n-2}}$

$54 = n(12) + (2n-2)(1)$

$54 = 12n + 2n - 2$

$54 = 14n - 2$

$n = (54+2)/14 = 56/14 = 4$

Option (b)

17.

$$\frac{\gamma_{O_2}}{\gamma_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}} = \sqrt{\frac{2}{32}} = \frac{1}{4}$$

$$\gamma_{O_2} = \frac{1}{4}\gamma_{H_2}$$

The fraction of oxygen that escapes in the time required for one half of the hydrogen to escape is 1/8

Option (c)

18.

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad [\text{For an ideal gas } PV = nRT]$$

$$= \frac{1}{V}\left(\frac{\partial\left(\frac{nRT}{P}\right)}{\partial T}\right)_P$$

$$= \frac{nR}{PV}\left(\frac{\partial T}{\partial T}\right) = \frac{nR}{nRT} = \frac{1}{T}$$

Option (b)

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19. Greater the 'a' value, easier the liquefaction

21. $an^2/V^2 = atm$

$a = atm\ L^2/mol^2 = L^2\ mol^{-2}\ atm$

$nb = L$

$b = L/mol = L\ mol^{-1}$

Option (c)

22. **Correct Statement:** Critical temperature of CO_2 is 304 K. It means that CO_2 cannot be liquefied above 304 K, whatever the pressure may applied.

Pressure is inversely proportional to volume

Option (d)

23.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$= \frac{m}{\left(\frac{nRT}{P}\right)} = \left(\frac{m}{n}\right)\frac{P}{RT}$$

$$= \text{Molar mass} \times \frac{P}{RT}$$

$$= \frac{28\ g\ mol^{-1} \times 5\ atm}{0.082\ L\ atm\ K^{-1}\ mol^{-1} \times 500\ K}$$

$$= 3.41 g\ L^{-1}$$

Option (c)

24. For a fixed mass of an ideal gas $V \alpha T$

$P \alpha 1/V$

and $PV = Constant$

Option (c)

25. At a given temperature and pressure

Volume α no. of moles

Volume α Mass / Molar mass

Volume α 28 / Molar mass

i.e. if molar mass is more, volume is less. Hence HI has the least volume

Option (d)

II Key to short answer questions:

44. $T_1 = 15^0\ C + 273$ $T_2 = 38 + 273$

$T_1 = 288\ K$ $T_2 = 311\ K$

$V_1 = 2.58\ dm^3$ $V_2 = ?$

(P = 1 atom constant)

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \left(\frac{V_1}{T_1}\right) \times T_2$$

$$= \frac{2.58\ dm^3}{288\ \cancel{K}} \times 311\ \cancel{K}$$

$V_2 = 2.78\ dm^3$ i.e. volume increased from $2.58\ dm^3$ to $2.78\ dm^3$

45. $V_1 = 8.5\ dm^3$ $V_2 = 6.37\ dm^3$

$T_1 = ?$ $T_2 = 0^0\ C = 273\ K$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 \times \left(\frac{T_2}{V_2}\right) = T_1$$

$$T_1 = 8.5\ \cancel{dm^3} \times \frac{273\ K}{6.37\ \cancel{dm^3}}$$

$T_1 = 364.28 K$

46. $n_A = 1.5\ mol$ $n_B = ?$

$V_A = 37.6\ dm^3$ $V_B = 16.5\ dm^3$

(T = 298 K constant)

$$\frac{V_A}{n_A} = \frac{V_B}{n_B}$$

$$n_A = \left(\frac{n_A}{V_A}\right) V_B$$

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$$= \frac{1.5 \text{ mol}}{37.6 \cancel{\text{dm}^3}} \times 16.5 \cancel{\text{dm}^3}$$

$$= 0.66 \text{ mol}$$

47. n = 1.82 mole

$V = 5.43 \text{ dm}^3$

$T = 69.5 + 273 = 342.5$

P = ?

PV = nRT

$$P = \frac{nRT}{V}$$

$$P = \frac{1.82 \text{ mol} \times 0.0821 \cancel{\text{dm}^3} \text{ atm mol}^{-1} \text{ K}^{-1} \times 342.5 \text{ K}}{5.43 \cancel{\text{dm}^3}}$$

$$P = 9.425 \text{ atm}$$

48.

$P_1 = 1.2$ atm

$T_1 = 18^0$ C + 273 = 291 K

$T_2 = 85^0$ C + 273 = 358 K

P_2 = ?

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \left(\frac{P_1}{T_1}\right) \times T_2$$

$$= \frac{1.2 \text{ atm}}{291 \cancel{K}} \times 358 \cancel{K}$$

$$P_2 = 1.48 \text{ atm}$$

49. $T_1 = 6\ ^0$C + 273 = 279 K

$P_1 = 4$ atm $\quad V_1 = 1.5$ ml

$T_2 = 25^0$ C + 273 = 298 K

$P_2 = 1$ atm $\quad V_2 = ?$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{P_2}$$

$$= \frac{4 \cancel{\text{atm}} \times 1.5 \text{ ml} \times 298 \cancel{K}}{279 \cancel{K} \times 1 \cancel{\text{atm}}}$$

$V_2 = 6.41$ ml

50. Given,

$V = 154.4 \times 10^{-3} \text{ dm}^3$,

P = 742 mm of Hg

T = 298 K $\quad$ m = ?

$$n = \frac{PV}{RT} = \frac{742 \text{ mm Hg} \times 154.4 \times 10^{-3} \text{ L}}{62 \text{ mm Hg L K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}$$

$$= 0.006 \text{ mol}$$

$$n = \frac{\text{Mass}}{\text{Molar mass}}$$

$$\text{Mass} = n \times \text{Molar mass}$$

$$= 0.006 \times 2.016$$

$$= 0.0121 \text{ g} = 12.1 \text{ mg}$$

51.

$$\frac{\gamma_{unknown}}{\gamma_{N_2}} = \frac{t_{N_2}}{t_{unknown}} = \sqrt{\frac{M_{N_2}}{M_{unknown}}}$$

$$\frac{84 \text{ sec}}{192 \text{ sec}} = \sqrt{\frac{28 \text{ g mol}^{-1}}{M_{unknown}}}$$

On squaring both sides and rearranging

$$\left(\frac{84 \text{ sec}}{192 \text{ sec}}\right)^2 = \frac{28 \text{ g mol}^{-1}}{M_{unknown}}$$

$$M_{unknown} = 28 \text{ g mol}^{-1} \times \left(\frac{192 \text{ sec}}{84 \text{ sec}}\right)^2$$

$$M_{unknown} = 146.28 \text{ g mol}^{-1}$$

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52. $m_{O_2} = 52.5\ g$ $P_{O_2} = ?$

$m_{CO_2} = 65.1\ g$ $P_{CO_2} = ?$

$T = 300\ K$ $P = 9.21\ atm$

$P_{O_2} = X_{O_2}$ x Total Pressure

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}}$$

$$n_{O_2} = \frac{\text{Mass of } O_2}{\text{Molar mass of } O_2}$$

$$= \frac{52.5\ g}{32\ g\ mol^{-1}} = 1.64\ mol$$

$$n_{CO_2} = \frac{\text{Mass of } CO_2}{\text{Molar mass of } CO_2}$$

$$= \frac{65.1\ g}{44\ g\ mol^{-1}} = 1.48\ mol$$

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{CO_2}} = \frac{1.64}{3.12} = 0.53$$

$$X_{CO_2} = \frac{n_{CO_2}}{n_{O_2} + n_{CO_2}} = \frac{1.48}{3.12} = 0.47$$

$$P_{O_2} = X_{O_2} \times \text{Total pressure}$$

$$= 0.53 \times 9.21\ atm = 4.88\ atm$$

$$P_{CO_2} = X_{CO_2} \times \text{Total pressure}$$

$$= 0.47 \times 9.21\ atm = 4.33\ atm$$

53. Pressure of the gas in the tank at its melting point

$T_1 = 298\ K; P_1 = 2.98\ atom; T_2 = 1100\ K; P_2 = ?$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\Rightarrow \quad P_2 = \frac{P_1}{T_1} \times T_2$$

$$= \frac{2.98\ atm}{298\ K} \times 1100\ K = 11\ atm$$

At 1100 K the pressure of the gas inside the tank will become 11 atm. Given that tank can withstand a maximum pressure of 12 atm, the tank will start melting first.

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Unit - 7
Thermodynamics

Evaluation Yourself

1.

Solution :

Given

$\Delta H_f^0\ CO_2 = -393.5\ kJ\ mol^{-1}$

$\Delta H_f^0\ CO = -111.31\ kJ\ mol^{-1}$

$\Delta H_f^0\ (H_2O) = -242\ kJ\ mol^{-1}$

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$

$\Delta H_r^0 = ?$

$\Delta H_r^0 = \Sigma\ (\Delta H_f^0)_{products} - \Sigma\ (\Delta H_f^0)_{reactants}$

$\Delta H_r^0 = [\Delta H_f^0\ (CO) + \Delta H_f^0\ (H_2O)] - [\Delta H_f^0\ (CO_2) + \Delta H_f^0\ (H_2)]$

$\Delta H_r^0 = [-111.31 + (-242)] - [-393.5 + (0)]$

$\Delta H_r^0 = [-353.31] + 393.5$

$\Delta H_r^0 = 40.19$

$\Delta H_r^0 = +40.19\ kJ\ mol^{-1}$

2.

Solution :

Given :

number of moles of water n

$= \frac{180\ g}{18\ g\ mol^{-1}} = 10\ mol$

molar heat capacity of water

$C_P = 75.3\ J\ K^{-1}\ mol^{-1}$

$T_2 = 100^0\ C = 373\ K$

$T_1 = 25^0\ C = 298\ K$

$\Delta H = ?$

$\Delta H = nC_P\ (T_2 - T_1)$

$\Delta H = 10\ mol \times 75.3\ J\ mol^{-1}\ K^{-1} \times (373 - 298)\ K$

$\Delta H = 56475\ J$

$\Delta H = 56.475\ kJ$

3.

$$C_6H_6\ (l) + \frac{7}{2} O_2(g) \rightarrow 6\ CO_2\ (g) + 3\ H_2O\ (l)$$

ΔU at $25^0\ C = -3268.12\ kJ$

Solution :

Given

$T = 25^0\ C = 298\ K$;

$\Delta U = -3268.12\ kJ\ mol^{-1}$

$\Delta H = ?$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = \Delta U + (n_p - n_r)\ RT$

$$\Delta H = -3268.12 + \left(6 - \frac{15}{2}\right) \times 8.314 \times 10^{-3}\ x\ 298$$

$\Delta H = -3268.12 - (1.5 \times 8.314 \times 10^{-3} \times 298)$

$\Delta H = -3268.12 - 3.72$

$\Delta H = -3271.84\ kJ\ mol^{-1}$

4.

Solution :

Given :

$Mg(S) + Br_2(1) \rightarrow$

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$MgBr_2(S)\ \Delta H_f^0 = -524\ KJ\ mol^{-1}$

Sublimation :

$Mg(S) \rightarrow Mg(g)$

$\Delta H_1^0 = +148\ KJ\ mol^{-1}$

Ionisation :

$Mg(g) \rightarrow Mg^{2+}(g) + 2e^-$

$\Delta H_2^0 = 2188\ KJ\ mol^{-1}$

Vapourisation :

$Br_2(1) \rightarrow Br_2(g)$

$\Delta H_3^0 = +31\ KJ\ mol^{-1}$

Dissociation :

$Br_2(g) \rightarrow 2Br(g)$

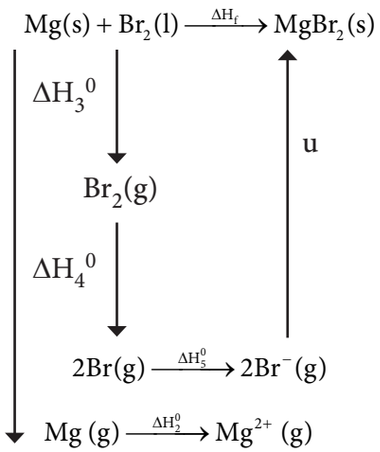
$\Delta H_4^0 = +193\ KJ\ mol^{-1}$

Electron affinity :

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

$\Delta H_5^0 = -324.5\ KJ\ mol^{-1}$

Solution :



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + 2\Delta H_5 + u$

$-524 = 148 + 2188 + 31 + 193 + (2 \times -324.5) + u$

$-524 = 1911 + u$

$u = -524 - 1911$

$u = -2435\ kJ\ mol^{-1}$

5.

Solution:

Given

$T_h = 127^0\ C = 127 + 273 = 400\ K$

$T_C = 47^0\ C = 47 + 273 = 320\ K$

% efficiency η = ?

$$\eta = \left[\frac{T_h - T_C}{T_h}\right] \times 100$$

$$\eta = \left[\frac{400 - 320}{400}\right] \times 100$$

$$\eta = \left[\frac{80}{400}\right] \times 100$$

$\eta = 20\%$

6.

Solution:

Given:

$S^0\ (urea) = 173.8\ J\ mol^{-1}\ K^{-1}$

$S^0\ (H_2O) = 70\ J\ mol^{-1}\ K^{-1}$

$S^0\ (CO_2) = 213.5\ J\ mol^{-1}\ K^{-1}$

$S^0\ (NH_3) = 192.5\ J\ mol^{-1}\ K^{-1}$

$NH_2 - CO - NH_2 + H_2O \rightarrow 2NH_3 + CO_2$

$\Delta S_r^0 = \Sigma\ (S^0)_{products} - \Sigma\ (S^0)_{reactants}$

$\Delta S_r^0 = [2\ S^0\ (NH_3) + S^0\ (CO_2)]$

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$- [S^0 (urea) + S^0 (H_2O)]$

$\Delta S_r^0 = [2 \times 192.5 + 213.5]$

$- [173.8 + 70]$

$\Delta S_r^0 = [598.5] - [243.8]$

$\Delta S_r^0 = 354.7 \text{ J mol}^{-1} \text{ K}^{-1}$

7.

Solution:

Given:

$T_b = 351 \text{ K}$

$\Delta H_{vap} = 39840 \text{ J mol}^{-1}$

$\Delta S_v = ?$

$$\Delta S_v = \frac{\Delta H_{vap}}{T_b}$$

$$\Delta S_v = \frac{39840}{351}$$

$$\Delta S_v = 113.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

8.

Solution:

Given:

$\Delta H = -10 \text{ kJ mol}^{-1} = -10000 \text{ J mol}^{-1}$

$\Delta S = -20 \text{ J K}^{-1} \text{ mol}^{-1}$

$T = 300 \text{ K}$

$\Delta G = ?$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = -10 \text{ kJ mol}^{-1} - 300 \text{ K} \times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$

$\Delta G = (-10+6) \text{ kJ mol}^{-1}$

$\Delta G = -4 \text{ kJ mol}^{-1}$

At 600 K

$\Delta G = -10 \text{ kJ mol}^{-1} - 600 \text{ K} \times (-20 \times 10^{-3}) \text{ kJ K}^{-1} \text{ mol}^{-1}$

$\Delta G = (-10 + 12) \text{ kJ mol}^{-1}$

$\Delta G = +2 \text{ kJ mol}^{-1}$

The value of ΔG is negative at 300K and the reaction is spontaneous, but at 600K the value ΔG becomes positive and the reaction is non spontaneous.

EVALUATION

I Choose the best answer:

1. (b) ΔH
2. (d) decrease in free energy
3. (b) $q = 0$
4. (d) = 0
5. (a) $w = -\Delta U$
6. (d) $\frac{\text{mass}}{\text{volume}}$
7. (a) – 900 J
8. (b) negative
9. (b) – 67.6 kcal
10. (a) graphite is more stable than diamond
11. (d) – 462 kJ
12. (d) frictional energy
13. (d) $\Delta H < \Delta U$
14. (c) + 3 kJ
15. (a) – 2.48 kJ
16. (b) – 500 R
17. (d) $\frac{b-2a}{2}$

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18. (d) – 635.66 kJ

19. (c) 80 kJ mol^{-1}

20. (a) $\Delta H < 0$ and $\Delta S > 0$

21. (c) adiabatic expansion

22. (d) (–, –, +)

23. (b) 27 ^{0}C

24. (d) $CaCO_3(S) \rightarrow CaO(S) + CO_2(g)$

25. (a) 300K

Keys to multiple choice questions:

7.

$w = - P \Delta V$

$w = - (1 \times 10^5 \text{ Nm}^{-2})$

$(1 \times 10^{-2} \text{ m}^3 - 1 \times 10^{-3} \text{ m}^3)$

$w = -10^5 (10^{-2} - 10^{-3})$ Nm

$w = - 10^5 (10 - 1) 10^{-3})$ J

$w = - 10^5 (9 \times 10^{-3})$ J

$w = -9 \times 10^2$ J

$w = -900$ J

9.

$$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$$

$\Delta H_C^0 (CO) = \Delta H_f (CO_2) - \Delta H_f(CO) + \Delta H_f (O_2)]$

$\Delta H_C^0 (CO) =$ – 94 KCal – [– 26.4 KCal + 0]

$\Delta H_C^0 (CO) =$ – 94 KCal + 26.4 KCal

$\Delta H_C^0 (CO) =$ – 67.6 KCal

11.

$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$

$\Delta H_r^0 = [2\Delta H_f (Cr) + \Delta H_f (Al_2O_3)]$

$- [2\Delta H_f (Al) + \Delta H_f (Cr_2O_3)]$

$\Delta H_r^0 = [0 + (- 1596 \text{ kJ})]$

$- [0 + (- 1134)]$

$\Delta H_r^0 = - 1596$ kJ + 1134 kJ

$\Delta H_r^0 = - 462$ kJ

14.

$\Delta U = q + w$

$\Delta U = - 1$ kJ + 4 kJ

$\Delta U = + 3$kJ

15.

$Fe + 2HCl \rightarrow FeCl_2 + H_2$

1 mole of Iron liberates 1 mole of Hydrogen gas

55.85 g Iron = 1 mole Iron

$\therefore n = 1$

$T = 25^0$ C = 298 K

$w = - P \Delta V$

$$w = - P \left(\frac{nRT}{P} \right)$$

$w = - nRT$

$w = -1 \times 8.314 \times 298$ J

$w = - 2477.57$ J

$w = - 2.48$ kJ

16.

$T_i = 125^0$ C = 398 K

$T_f = 25^0$ C = 298 K

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$\Delta H = nC_p (T_f - T_i)$

$$\Delta H = 2 \times \frac{5}{2} R (298 - 398)$$

$\Delta H = -500\ R$

17.

$C + O_2 \rightarrow CO_2$ $\quad \Delta H^0 = -a$ KJ ..... (i)

$2CO + O_2\ 2CO_2$ $\quad \Delta H^0 = -b$ kJ ..... (ii)

$$C + \frac{1}{2} O_2 \rightarrow CO\ \Delta H^0 = ?$$

(i) × 2

$2C + 2O_2 \rightarrow 2CO_2$ $\quad \Delta H^0 = -2a$ kJ ..... (iii)

Reverse of equation (ii) will be

$2CO_2 \rightarrow 2CO + O_2$ $\quad \Delta H^0 = +b$ kJ ..... (iv)

(iii) + (iv)

$2C + O_2 \rightarrow 2CO\ \Delta H^0 = b - 2a$ kJ ..... (v)

(v) ÷ 2

$$C + \frac{1}{2} O_2 \rightarrow CO \quad \Delta H^0 = \frac{(b-2a)}{2} \text{ kJ}$$

18.

Given :

$\Delta H_C (CH_4) = -890$ kJ mol^{-1}

$\Delta H_C (C_3H_8) = -2220$ kJ mol^{-1}

Let the mixture contain lit of and lit of propane.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

x $\quad$ 2x

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

(15.68 – x) $\quad$ 5 (15.68 – x)

Volume of oxygen consumed = 2x + 5 (15.68 – x) = 32 lit

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$2x + 78.4 - 5x = 32$ l

$78.4 - 3x = 32$

$3x = 46.4$ l

$x = 15.47$ l

Given mixture contains 15.47 lit of methane and 0.213 lit of propane, hence

$$\Delta H_C = \left[\left(\frac{\Delta H_C\ (CH_4)}{22.4 \text{ lit}}\right) x \text{ lit}\right] + \left[\left(\frac{\Delta H_C\ (C_3H_8)}{22.4 \text{ lit}}\right)(15.68 - x) \text{ lit}\right]$$

$$\Delta H_C = \left[\left(\frac{-890 \text{ kJ mol}^{-1}}{22.4 \text{ lit}}\right) 15.47 \quad \text{lit}\right] + \left[\left(\frac{-2220}{22.4 \text{ lit}}\right) 0.21 \quad \text{lit}\right]$$

$$\Delta H_C = \left[-611.87 \quad \text{kJ mol}^{-1}\right] + \left[-20.81 \quad \text{kJ mol}^{-1}\right]$$

$$\Delta H_C = -632.68 \text{ KJ mol}^{-1}$$

19.

$4E_{C-H} = 360 \text{ kJ mol}^{-1}$

$E_{C-H} = 90 \text{ kJ mol}^{-1}$

$E_{C-C} + 6\ E_{C-H} = 620 \text{ kJ mol}^{-1}$

$E_{C-C} + 6 \times 90 = 620 \text{ kJ mol}^{-1}$

$E_{C-C} + 540 = 620 \text{ kJ mol}^{-1}$

$E_{C-C} = 80 \text{ kJ mol}^{-1}$

22. During compression, energy of the system increases, in isothermal condition, to maintain temperature constant, heat is liberated from the system. Hence q is negative.

During compression entropy decreases.

During compression work is done on the system, hence w is positive

23.

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$T_b = \frac{\Delta H_V}{\Delta S_V} = \frac{4800 \text{ J mol}^{-1}}{16 \text{ J mol}^{-1} \text{ K}^{-1}} = 300 \text{ K} = 27^0 \text{C}$$

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24. In $CaCO_3(S) \rightarrow CaO(S) + CO_2(g)$, entropy change is positive. **in option d, A solid reactant gives a gaseous product. Hence the entropy change is expected to be maximum for this process.**

25.

$\Delta G = \Delta H - T \Delta S$

At 300K

$\Delta G = 30000 \text{ J mol}^{-1} - 300 \text{ K}$

$\times 100 \text{ J K}^{-1} \text{ mol}^{-1}$

$\Delta G = 0$

above 300 K ; ΔG will be negative and reaction becomes spontaneous.

I Keys to the short answer questions:

53.

SOLUTION :

Given :

$n = 2$ moles

$V_i = 500 \text{ ml} = 0.5 \text{ lit}$

$V_f = 2 \text{ lit}$

$T = 25^0C = 298 \text{ K}$

$w = -2.303 \text{ nRTlog} \left(\frac{V_f}{V_i} \right)$

$w = -2.303 \times 2 \times 8.314 \times 298$

$\times \log \left(\frac{2}{0.5} \right)$

$w = -2.303 \times 2 \times 8.314$

$\times 298 \times \log(4)$

$w = -2.303 \times 2 \times 8.314$

$\times 298 \times 0.6021$

$w = -6871 \text{ J}$

$w = -6.871 \text{ kJ}$

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54.

SOLUTION :

Given :

$T_i = 298$ K

$T_f = 298.45$ K

$k = 2.5$ kJ K^{-1}

$m = 3.5g$

$M_m = 28$

heat evolved = $k \Delta T$

$= k (T_f - T_i)$

$= 2.5$ kJ K^{-1} $(298.45-298)K$

$= 1.125$kJ

$\Delta H_c = \frac{1.125}{3.5} \times 28$ kJ mol^{-1}

$\Delta H_c = 9$ kJ mol^{-1}

55.

SOLUTION :

Given :

$T_{sys} = 77^0C = (77 + 273) = 350$ K

$T_{surr} = 33^0$ C $= (33 + 273) = 306$ K

$q = 245$ J

$\Delta S_{sys} = \frac{q}{T_{sys}} = \frac{-245}{350} = -0.7$ JK^{-1}

$\Delta S_{surr} = \frac{q}{T_{sys}} = \frac{+245}{306} = +0.8$ JK^{-1}

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

$\Delta S_{univ} = -0.7$ $JK^{-1} + 0.8$ JK^{-1}

$\Delta S_{univ} = 0.1$ JK^{-1}

56.

SOLUTION :

Given :

$n = 1$mole

$P = 4.1$ atm

$V = 2$ Lit

$T = ?$

$q = 3710$ J

$\Delta S = \frac{q}{T}$

$\Delta S = \frac{q}{\left(\frac{PV}{nR}\right)}$

$\Delta S = \frac{nRq}{PV}$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm } K^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$$\Delta S = \frac{1 \times 0.082 \text{ lit atm } K^{-1} \times 3710 \text{ J}}{4.1 \text{ atm} \times 2 \text{ lit}}$$

$\Delta S = 37.10$ JK^{-1}

57.

SOLUTION:

Given :

$\Delta H_f(NaCl) = 30.4$ kJ $= 30400$ J mol^{-1}

$\Delta S_f(NaCl) = 28.4$ JK^{-1} mol^{-1}

$T_f = ?$

$\Delta S_f = \frac{\Delta H_f}{T_f}$

$T_f = \frac{\Delta H_f}{\Delta S_f}$

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$$T_f = \frac{30400 \text{ J mol}^{-1}}{28.4 \text{ J K}^{-1} \text{ mol}^{-1}}$$

$$T_f = 1070.4 \text{ K}$$

58.

SOLUTION :

Given

$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

$\Delta H_C^0 = -2220.2 \text{ kJ mol}^{-1}$ -----(1)

$C + O_2 \rightarrow CO_2$

$\Delta H_f^0 = -393.5 \text{ kJ mol}^{-1}$ -----(2)

$H_2 + \frac{1}{2} O_2 \rightarrow H_2O$

$\Delta H_f^0 = -285.8 \text{ kJ mol}^{-1}$ ----- (3)

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H_C^0 = ?$

$(2) \times 3 \Rightarrow 3C + 3O_2 \rightarrow 3CO_2$

$\Delta H_f^0 = -1180.5 \text{ kJ}$ -----(4)

$(3) \times 4 \Rightarrow 4H_2 + 2O_2 \rightarrow 4H_2O$

$\Delta H_f^0 = -1143.2 \text{ kJ}$ -----(5)

$(4) + (5) - (1) \Rightarrow 3C + 3O_2 + 4H_2 + 2O_2 + 3CO_2 + 4H_2O \rightarrow 3CO_2 + 4H_2O + C_3H_8 + 5O_2$

$\Delta H_f^0 = -1180.5 - 1143.2 - (-2220.2) \text{ kJ}$

$3C + 4H_2 \rightarrow C_3H_8$

$\Delta H_f^0 = -103.5 \text{ kJ}$

Standard heat of formation of propane is $\Delta H_f^0 (C_3H_8) = -103.5 \text{ kJ}$

59.

S. No	Liquid	Boiling points (^{0}C)	ΔH (kJ mol^{-1})
1.	Ethanol	78.4	+ 42.4
2.	Toluene	110.6	+ 35.2

SOLUTION :

For ethanol :

Given :

$T_b = 78.4^0 \text{ C} = (78.4 + 273)$

$= 351.4 \text{ K}$

$\Delta H_V (\text{ethanol}) = + 42.4 \text{ kJ mol}^{-1}$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 42.4 \text{ kJ mol}^{-1}}{351.4 \text{ K}}$$

$$\Delta S_V = \frac{+ 42400 \text{ J mol}^{-1}}{351.4 \text{ K}}$$

$\Delta S_V = +120.66 \text{ J K}^{-1} \text{ mol}^{-1}$

For Toluene :

Given :

$T_b = 110.6^0 \text{ C} = (110.6+273)$

$= 383.6 \text{ K}$

$\Delta H_V \text{ (toluene)} = + 35.2 \text{ kJ mol}^{-1}$

$$\Delta S_V = \frac{\Delta H_V}{T_b}$$

$$\Delta S_V = \frac{+ 35.2 \text{ kJ mol}^{-1}}{383.6 \text{ K}}$$

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$$\Delta S_V = \frac{+35200\ J\ mol^{-1}}{383.6\ K}$$

$$\Delta S_V = +\ 91.76\ J\ K^{-1}\ mol^{-1}$$

60.

Solution :

Given :

$\Delta H = 30.56\ kJ\ mol^{-1}$

$= 30560\ J\ mol^{-1}$

$\Delta S = 6.66 \times 10^{-3}\ kJK^{-1}mol^{-1}$

T = ? at which $\Delta G = 0$

$\Delta G = \Delta H - T\Delta S$

$0 = \Delta H - T\Delta S$

$$T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30.56 kJ mol^{-1}}{6.66 \times 10^{-3} kJK^{-1} mol^{-1}}$$

T = 4589 K

(i) At 4589K ; $\Delta G = 0$ the reaction is in equilibrium.

(ii) at temperature below 4598 K , $\Delta H > T\Delta S$

$\Delta G = \Delta H - T\Delta S > 0$, the reaction in the forward direction, is non spontaneous. In other words the reaction occurs in the backward direction.

61.

Solution :

Given

$T = 400K ; \Delta H^0 = 77.2\ kJ\ mol^{-1} = 77200$

$J\ mol^{-1} ; \Delta S^0 = 122\ JK^{-1}\ mol^{-1}$

$\Delta G^0 = -2.303\ RT \log K_{eq}$

$$\log K_{eq} = \frac{-\Delta G^0}{2.303\ RT}$$

$$\log K_{eq} = -\frac{\left(\Delta H^0 - T\Delta S^0\right)}{2.303\ RT}$$

$$\log K_{eq} = -\left(\frac{77200 - 400 \times 122}{2.303 \times 8.314 \times 400}\right)$$

$$\log K_{eq} = -\left(\frac{28400}{7659}\right)$$

$\log K_{eq} = -\ 3.7080$

$K_{eq} = \text{antilog}\ (-3.7080)$

$K_{eq} = 1.95 \times 10^{-4}$

62.

Solution :

Given

$T = 298K ; \Delta U = -\ 742.4\ kJ\ mol^{-1}$

$\Delta H = ?$

$\Delta H = \Delta U + \Delta n_g RT$

$\Delta H = \Delta U + (n_p - n_r)\ RT$

$$\Delta H = -\ 742.4 + \left(2 - \frac{3}{2}\right) \times 8.314 \times 10^{-3} \times 298$$

$= -\ 742.4 + (0.5 \times 8.314 \times 10^{-3} \times 298)$

$= -\ 742.4 + 1.24$

$= -\ 741.16\ kJ\ mol^{-1}$

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63.

Solution :

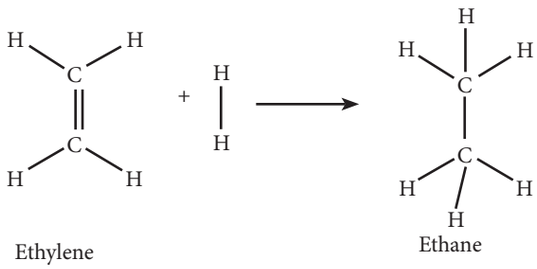
Given :

$E_{C-H} = 414 \text{ kJ mol}^{-1}$

$E_{C-C} = 347 \text{ kJ mol}^{-1}$

$E_{C=C} = 618 \text{ kJ mol}^{-1}$

$E_{H-H} = 435 \text{ kJ mol}^{-1}$



Ethylene Ethane

$\Delta H_r = \Sigma (\text{Bond energy})_r - \Sigma (\text{Bond energy})_p$

$\Delta H_r = (E_{C=C} + 4E_{C-H} + E_{H-H}) - (E_{C-C} + 6E_{C-H})$

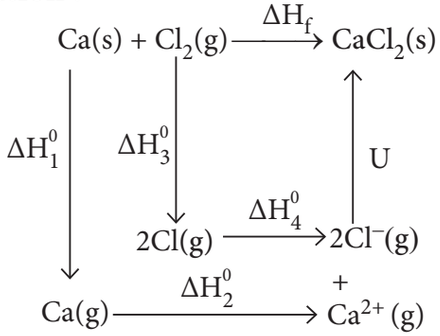
$\Delta H_r = (618 + (4 \times 414) + 435) - (347 + (6 \times 414))$

$\Delta H_r = 2709 - 2831$

$\Delta H_r = -122 \text{ kJ mol}^{-1}$

64.

Solution :



$\Delta H_f = \Delta H_1 + \Delta H_2 + \Delta H_3 + 2\Delta H_4 + u$

$-795 = 121 + 2422 + 242.8 + (2 \times -355) + u$

$-795 = 2785.8 - 710 + u$

$-795 = 2075.8 + u$

$u = -795 - 2075.8$

$u = -2870.8 \text{ kJ mol}^{-1}$

65.

Solution :

Given :

$\Delta H_f (Fe_2O_3) = -741 \text{ kJ mol}^{-1}$

$\Delta H_f (CO) = -137 \text{ kJ mol}^{-1}$

$\Delta H_f (CO_2) = -394.5 \text{ kJ mol}^{-1}$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

$\Delta Hr = ?$

$\Delta Hr = \Sigma(\Delta H_f)_{\text{products}} - \Sigma (\Delta H_f)_{\text{reactants}}$

$\Delta Hr = [2 \Delta H_f (Fe) + 3\Delta H_f (CO_2)] - [\Delta H_f (Fe_2O_3) + 3\Delta H_f (CO)]$

$\Delta Hr = [0 + 3 (-394.5)] - [-741 + 3 (-137)]$

$\Delta Hr = [-1183.5] - [-1152]$

$\Delta Hr = -1183.5 + 1152$

$\Delta Hr = -31.5 \text{ kJ mol}^{-1}$

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66.

Solution:

Given :

$T = 175^0 C = 175 + 273 = 448K$

Concentration of 1-pentyne

[A] = 1.3%

Concentration of 2-pentyne
[B] = 95.2%

Concentration of 1, 2-pentadiene
[C] = 3.5%

At equilibrium

$B \rightleftharpoons A$

95.2% 1.3% $\Rightarrow$

$K_1 = \frac{1.3}{95.2} = 0.0136$

$B \rightleftharpoons C$

95.2% 3.5% $\Rightarrow$

$K_2 = \frac{3.5}{95.2} = 0.0367$

$\Rightarrow \Delta G_1^0 = -2.303\ RT \log K_1$

$\Delta G_1^0 = -2.303 \times 8.314 \times 448 \times \log 0.0136$

$\Delta G_1^0 = +16010\ J$

$\Delta G_1^0 = +16\ kJ$

$\Rightarrow \Delta G_2^0 = -2.303\ RT \log K_2$

$\Delta G_2^0 = -2.303 \times 8.314 \times 448 \times \log 0.0367$

$\Delta G_2^0 = +12312\ J$

$\Delta G_2^0 = +12.312\ kJ$

67.

Solution:

Given :

$T = 33K$

$N_2O_4 \rightleftharpoons 2NO_2$

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial no of moles	100		0
Number of moles dissociated	50		-
No of moles remaining	50		100
Total no of moles	150 moles		

$P_{N_2O_4} = \frac{n_{N_2O_4}}{n_{N_2O_4} + n_{NO_2}} . P$

$P_{N_2O_4} = \frac{50\ mol}{150\ mol} .1\ atm$

$P_{N_2O_4} = 0.333\ atm$

$P_{NO_2} = \frac{n_{NO_2}}{n_{N_2O_4} + n_{NO_2}} . P$

$P_{NO_2} = \frac{100\ mol}{150\ mol} .1\ atm$

$P_{NO_2} = 0.667\ atm$

$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}}$

$K_P = \frac{(0.667)^2\ atm^2}{0.333\ \text{atm}}$

$K_P = 1.336\ atm$

$\Delta G^0 = -2.303\ RT \log K_P$

$\Delta G^0 = -2.303\ X\ 8.314\ X\ 33\ X\ \log 1.336$

$\Delta G^0 = -79.49\ J\ mol^{-1}$

68.

Solution :

Given :

$\Delta H_f^0\ (SO_2) = -297\ kJ\ mol^{-1}$

$\Delta H_f^0\ (SO_3) = -396\ kJ\ mol^{-1}$

$SO_2 + \frac{1}{2} O_2 \rightarrow SO_3 \quad \Delta H_r^0 = ?$

$\Delta H_r^0 = (\Delta H_f^0)_{compound} - \Sigma (\Delta H_f)_{elements}$

$\Delta H_r^0 = \Delta H_f^0\ (SO_3) - \left(\Delta H_f^0\ (SO_2) + \frac{1}{2} \Delta H_f^0\ (O_2) \right)$

$\Delta H_r^0 = -396\ kJ\ mol^{-1} - (-297\ kJ\ mol^{-1} + 0)$

$\Delta H_r^0 = -396\ kJ\ mol^{-1} + 297$

$\Delta H_r^0 = -99\ kJ\ mol^{-1}$

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69.

Solution:

Given :

$T = 298\ K$

$\Delta H = 400\ KJ\ mol^{-1}$

$\Delta S = 0.2\ KJ\ K^{-1}\ mol^{-1}$

$\Delta G = \Delta H - T\Delta S$

if $T = 2000\ K$

$\Delta G = 400 - (0.2 \times 2000) = 0$

$\Delta H = 400\ KJ\ mol^{-1}$ if $T > 2000\ K$

ΔG will be negative.

The reaction would be spontaneous only beyond 2000K

70.

Solution :

Given :

$T = 298K$

$\Delta G_r^0 = -13.6\ kJ\ mol^{-1}$

$= -13600\ J\ mol^{-1}$

$\Delta G^0 = -2.303\ RT \log K_{eq}$

$$\log K_{eq} = \frac{-\Delta G^0}{2.303\ RT} \quad \log K_{eq} = \frac{13.6 kJ\ mol^{-1}}{2.303 \times 8.314 \times 10^{-3} JK^{-1}\ mol^{-1} \times 298\ K}$$

$\log K_{eq} = 2.38$

$K_{eq} = \text{antilog } (2.38)$

$K_{eq} = 239.88$

71.

Solution :

Given :

$\Delta H_C\ (CH_4) = -890\ kJ\ mol^{-1}$

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$\Delta H_C\,(C_2H_4)$ $= -1423\ kJ\ mol^{-1}$

Let the mixture contain x lit of CH_4 and (3.67 – x) lit of ethylene.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

x lit x lit

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

(3.67–x)lit 2 (3.67 – x) lit

Volume of Carbondioxide formed = x + 2 (3.67–x) = 6.11 lit

x + 7.34 – 2x = 6.11

7.34 – x = 6.11

x = 1.23 lit

Given mixture contains 1.23 lit of methane and 2.44 lit of ethylene, hence

$$\Delta H_C = \left[\frac{\Delta H_C\,(CH_4)}{22.4\ lit} \times (x)\ lit\right]$$

$$+\left[\frac{\Delta H_C\,(C_2H_4)}{22.4\ lit} \times (3.67 - x)\ lit\right]$$

$$\Delta H_C = \left[\frac{-890\ kJ\ mol^{-1}}{22.4\ lit} \times 1.23\ lit\right]$$

$$+\left[\frac{-1423}{22.4\ lit} \times (3.67 - 1.23)\ lit\right]$$

$\Delta H_C = [-48.87\ kJ\ mol^{-1}]$

$+ [-155 kJ\ mol^{-1}]$

$\Delta H_C = -203.87\ kJ\ mol^{-1}$

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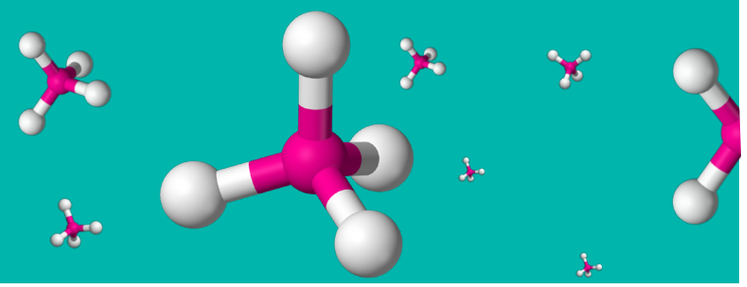
GLOSSARY

A-Z



Absolute zero	தனிச்சுழி
Absorption spectra	உட்கவர் நிறமாலை
Adiabatic process	வெப்பம் மாறாச் செயல்முறை
Alkali metals	கார உலோகங்கள்
Alkaline earth metals	காரமண் உலோகங்கள்
Allotropes	புறவேற்றுமை வடிவங்கள்
Amphoteric	ஈரியல்புள்ள
amu	அணு நிறை அலகு
Anion	எதிர்மின் அயனி
Anode ray	நேர்மின்வாய்க் கதிர்
Anomalous	அசாதாரண
Aqueous solution	நீர்க் கரைசல்
Armor plates	கவச தட்டு
Artificial silk	செயற்கைப் பட்டு
Baking soda	சமையல் சோடா
Boundary	எல்லை
Bunsen flame	புன்சன் சுடர்
Catalyst	வினையூக்கி
Cathode ray	எதிர்மின்வாய்க் கதிர்
Cation	நேர் மின் அயனி
Caustic soda	எரிசோடா
Combustion	எரிதல்
Compression	சுருங்கச் செய்தல்
Concept	கொள்கை
Covalent radius	சகப்பிணைப்பு ஆரம்
Critical constants	நிலைமாறு மாறிலிகள்
Decomposition	சிதைதல்
Diagonal relation	மூலைவிட்டத் தொடர்பு
Diffusion	விரவுதல்
Dipole moment	இருமுனைத் திருப்புத்திறன்

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Direct proportion	நேர்விகிதத் தொடர்பு
Discharge tube	மின்னிறக்க குழாய்
Disproportionation	விகிதச் சிதைவு
Dual behavior	ஈரியல்புத் தன்மை
Efficiency	திறன்
Electron affinity	எலக்ட்ரான் நாட்டம்
Electronegativity	எலக்ட்ரான் கவர்திறன்
Electrostatic attraction	நிலைமின்னியல் கவர்ச்சி
Emission spectra	உமிழ் நிறமாலை
Empirical formula	எளிய விகித வாய்ப்பாடு
Equivalent mass	சமான நிறை
Excited state	கிளர்வு நிலை
Expansion	விரிவடைதல்
Fertilizers	உரங்கள்
Formation	உருவாக்கம்
Gaseous state	வாயு நிலை
Ground state	அடிநிலை (சாதாரண நிலை)
Hard water	கடின நீர்
Hardness	கடினத்தன்மை
Heat capacity	வெப்ப ஏற்புத்திறன்
Heavy water	கன நீர்
Heterogeneous mixture	பலபடித்தான கலவை
Homogeneous mixture	ஒருபடித்தான கலவை
Hydrogen bonding	ஹைட்ரஜன் பிணைப்பு
Ideal gases	நல்லியல்பு வாயுக்கள்
Inter molecular	மூலக்கூறுகளுக்கிடைப்பட்ட
Inner transition metals	உள் இடைநிலைத் தனிமங்கள்
Insoluble	கரையாத்தன்மை
Internal energy	அக ஆற்றல்
Ion exchange	அயனிப் பரிமாற்றம்
Ionic radius	அயனி ஆரம்
Ionisation energy	அயனியாக்கும் ஆற்றல்
Irreversible	மீளாச் செயல்முறை
Isobaric process	அழுத்தம் மாறாச் செயல்முறை
Isochoric process	கனஅளவு மாறாச் செயல்முறை
Isoelectronic species	ஒத்த எலக்ட்ரான் அமைப்பு கொண்ட கூறுகள்
IUPAC	*International Union of Pure and Applied Chemistry*
Lather	நுரை

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Lattice energy	படிகக் கூடு ஆற்றல்
Laundering	சலவை செய்தல்
Lime stone	சுண்ணாம்புக் கல் $CaCO_3$
Linear	நேர்கோட்டு வடிவம்
Lone pair	தனித்த இரட்டை
Matter	பொருண்மை
Milk of lime	சுண்ணப்பால்– $Ca(OH)_2$
Milk of magnesia	மெக்னீஷியா பால்மம் $Mg(OH)_2$
Naphthalene balls	நாஃப்தலீன் உருண்டை (இரசக் கற்பூரம்)
Negligible	புறக்கணிக்கத்தக்க
Neutralisation	நடுநிலையாக்கல்
nm	நேநோ மீட்டர்
Non-spontaneous process	தன்னிச்சையற்ற செயல்முறை
Octahedron	எண்முகி
Octaves	எட்டு எண்ணிக்கை கொண்ட தொகுதி (a group of eight)
Octet rule	எண்ம விதி
Operator	செயலி
Oxidation	ஆக்ஸிஜனேற்றம்
Oxidation number	ஆக்ஸிஜனேற்ற எண்
Path function	வழிச் சார்பு
Periodic table	ஆவர்த்தன அட்டவணை
Photoelectric effect	ஒளிமின் விளைவு
Plaster of Paris	பாரீஸ் சாந்து
pm	பிகோ மீட்டர்
Polarisation	முனைவாக்கல்
Polarisibility	முனைவாக்கும் திறன்
Polyatomic molecule	பல்லணு மூலக்கூறு
Precipitate	வீழ்படிவு
Quantity	பொருளின் அளவு
Quick lime	சுட்ட சுண்ணாம்பு-CaO
Radioactive elements	கதிரியக்கத் தனிமங்கள்
Reagent	வினைக் கரணி
Redox	ஆக்ஸிஜனேற்ற-ஒடுக்கம்
Reduction	ஒடுக்கம்
Relative atomic mass	ஒப்பு அணு நிறை
Reversible process	மீள் செயல்முறை
Saturated solution	நிறைவுற்ற கரைசல்
Scattering	சிதறடித்தல்

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Shielding effect	மறைத்தல் விளைவு
SI unit	*System International* அலகு
Slaked lime - $Ca(OH)_2$	நீர்த்த சுண்ணாம்பு
Soluble	கரையக்கூடிய
Sparingly soluble	பகுதியாக கரையும் தன்மை
Spin	தற்சுழற்சி
Spontaneous process	தன்னிச்சைச் செயல்முறை
State function	நிலைச்சார்பு
Sublimation	பதங்கமாதல்
Surroundings	சுற்றுப்புறம்
Synthesis	தொகுத்தல்
Tetrahedron	நான்முகி
Thermal equilibrium	வெப்பச் சமநிலை
Trans uranium elements	யுரேனியத்தை தொடர்ந்து வரும் தனிமங்கள்
Transition metals	இடைநிலைத் தனிமங்கள்
Triads	மும்மைகள்
Uncertainty	நிச்சயமற்ற தன்மை
Unified mass	வரையறுக்கப்பட்ட நிறை
Universe	அண்டம்
Unsaturated compound	நிறைவுறாச் சேர்மம்
Valence electrons	இணைதிறன் எலக்ட்ரான்கள்
Valency	இணைதிறன்
Vapour pressure	ஆவி அழுத்தம்
Vapourisation	ஆவியாதல்
Viscosity	பாகுநிலைத்தன்மை
Wave function	அலைச் சார்பு

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