University School of Automation and Robotics
GURU GOBIND SINGH INDRAPRASTHA UNIVERSITY
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Engineering Chemistry-1 (BS109)

Atomic Structure

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		L	T/P	C
PaperCode: BS109	Paper: Engineering Chemistry - I			
PaperID: 99109		3	-	3

Marking Scheme:

1. Teachers Continuous Evaluation: 25 marks
2. Term end Theory Examinations: 75 marks

Instruction for paper setter:

1. There should be 9 questions in the term-end examinations question paper.
2. The first unit will be compulsory and cover the entire syllabus. This question will have Five sub-parts, and the students will be required to answer any THREE parts of 5 marks each. This unit will have a total weightage of 15 marks.
3. Apart from unit 1 which is compulsory, the rest of the paper shall consist of 4 units as per the syllabus. Every unit shall have two questions covering the corresponding unit of the syllabus. However, the student shall be asked to attempt only one of the two questions in the unit. Individual questions may contain up to 5 sub-parts / sub-questions. Each Unit shall have a marks weightage of 15.
4. The questions are to be framed keeping in view the learning outcomes of the course/paper. The standard / level of the questions to be asked should be at the level of the prescribed textbook.
5. The requirement of (scientific) calculators / log-tables / data - tables may be specified if required.

Course Objectives:

1:	To impart knowledge about understanding and modeling atomic structure and chemical bonding.
2:	To impart knowledge about understanding and modeling Thermochemistry and Reaction Kinetics.
3:	To impart knowledge about understanding and modeling organic compound structure and reactions.
4:	To impart knowledge about understanding and modeling Stereochemistry.

Course Outcomes (CO):

CO1:	Ability to understand and model atomic structure and chemical bonding.
CO2:	Ability to understand and model Thermochemistry and Reaction Kinetics.
CO3:	Ability to understand and model organic compound structure and reactions.
CO4:	Ability to understand and model Stereochemistry.

Course Outcomes (CO to Programme Outcomes (PO) Mapping (scale 1: low, 2: Medium, 3: High

CO/PO	PO01	PO02	PO03	PO04	PO05	PO06	PO07	PO08	PO09	PO10	PO11	PO12
CO1	2	2	3	3	2	-	-	-	1	1	-	1
CO2	2	2	3	3	2	-	-	-	1	1	-	1
CO3	2	2	3	3	2	-	-	-	1	1	-	1
CO4	2	2	3	3	2	-	-	-	1	1	-	1

Unit I

Atomic Structure: Introduction to wave mechanics, the Schrödinger equation as applied to hydrogen atom, origin of quantum numbers, Long form of periodic table on the basis of Electronic configuration s, p, d, f block elements periodic trends, Ionization potential, atomic and ionic radii electron affinity & electro-negativity. Chemical Bonding: Ionic bond, energy changes, lattice energy Born Haber Cycle, Covalent bond-energy changes, Potential energy curve for H2 molecule, characteristics of covalent compound, co-ordinate bond-Werner's Theory, effective atomic numbers, A hybridization and resonance, Valence Shell Electron Repulsion theory (VSEPR), Discussion of structures of H2O, NH3, BrF3, SiF4, Molecular orbital theory, Linear combination of atomic orbitals (LCAO) method. Structure of simple homo nuclear diatomic molecule like H2, N2, O2, F2.

[12Hrs]

Unit II

Thermochemistry: Hess's Law, heat of reaction, effect of temperature on heat of reaction at constant pressure (Kirchhoff's Equation) heat to dilution, heat of hydration, heat of neutralization and heat of combustion, Flame temperature. Reaction Kinetics: Significance of rate law and rate equations, order and molecularity, Determinations of order of simple reactions-experimental method, Equilibrium constant and reaction rates -Lindermann, collision and activated complex theories, complex reactions of 1st order characteristics of consecutive, reversible and parallel reactions-Steady state and non-steady state approach.

[10 Hrs]

Unit III

Basic concepts of Organics: Inductive, electromeric, mesomeric and hyperconjugative effects. Stability of reaction intermediates. Electrophiles and nucleophiles, concepts of acids and bases. Arrhenius, Lowry-Bronsted and Lewis theory of acids and bases (HSAB), Carbon acids (active methylene groups), super acids. Bonds weaker than covalent bond: Hydrogen bonding - nature, types stability and effects. IUPAC Nomenclature.[8Hrs]

Unit IV

Stereochemistry: Classification of stereoisomers, diastereomers, Separation of enantiomers. Absolute configuration (R and S), Projection formulae. Stereochemistry of compounds containing two asymmetric C-atoms. Elements of symmetry - center, plane and axis of symmetry, Conformations: Conformations around a C-C bond in acyclic and cyclic compounds.

[10Hrs]

Textbooks / References:

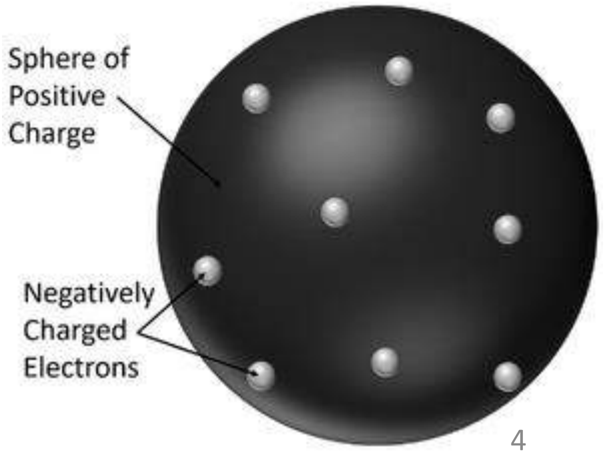
1. Engineering Chemistry (16th Edition) Jain, Jain, Dhanpat Rai Publishing Company, 2013.
2. Textbook of Engineering Chemistry by Jaya Shree Anireddy, Wiley, 2017
3. Engineering Chemistry by E.R. Nagarajan and S. Ramalingam, Wiley, 2017.

Atom:

- John Dalton said matter to be composed of indivisible particles called atoms.
- According to modern research, atoms are the smallest indivisible particles which cannot be further subdivided into smaller particles.
- However, it has been broken into smaller fragments like electrons, protons and neutrons. And in present "Quarks" represent the smallest known subatomic particles.
- Dalton was not able to explain the formation of chemical bond.
- Then, various model were discussed

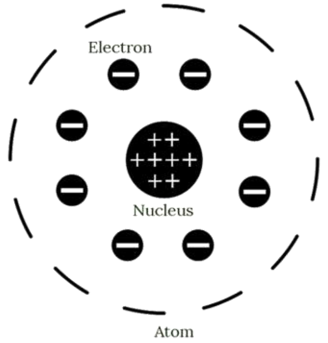
Thomson Atomic Model or Plum Pudding Model:

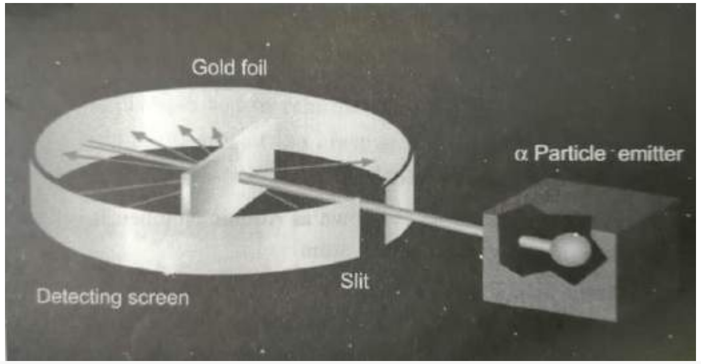
- In 1906, Thomson proposed atom is composed of the negative charge which is surrounded by a cloud of the positive charge so as to balance the negative charges.
- It appear as if the negatively charge of plums are surrounded by the positively charged pudding.
- Drawback: did not have any experimental evidence in its support.

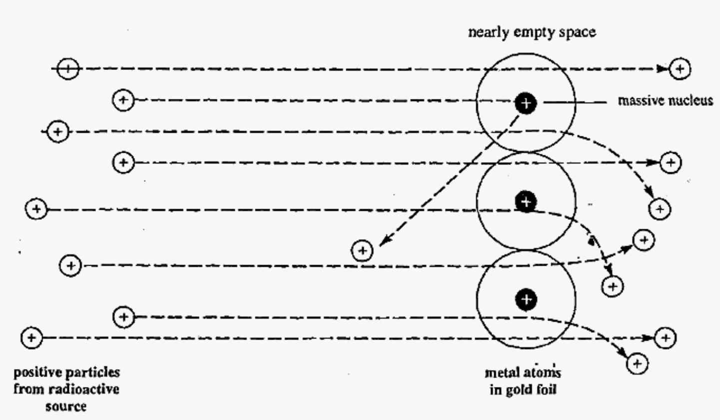


Rutherford Atomic Model:

- In 1909, Rutherford gave the first successful model of the arrangement of electrons, protons and neutrons based on alpha-ray scattering experiment.
- The model described the atom as a tiny, dense, positively charged core called a *nucleus*, in which nearly all the mass is concentrated around which light, negatively charged constituents, called *electrons*, circulate at some distance.







Rutherford Experiment:

- a thin gold foil was placed in the path of the beam.
- Expectation as per Thomson model was that alpha particles would go undeflected.
- But found that
  - some particles are deflected by small angles,
  - some deflected at fairly large angles,
  - few particles are rebounded back along their path at 180^{o}.

Conclusion of Rutherford experiment:

- The α -particle which is deflected largely is meeting a center of very high mass within the atom.
- The center of high mass is also positively charged, is very small, and extremely dense region which is called atomic nucleus.
- Most of the α-radiations pass through the metal foil unreflected in straight lines. This shows that there is a lot of empty space around the nucleus.
- This is extra nuclear part, where electrons revolve in high speed in fixed part called orbit.

From Rutherford's experiment it becomes clear

- ✓ that the entire mass of an atom is concentrated in a small region. Hence all the protons and neutrons which account for the mass of an atom, must be present in this region.
- ✓ Consequently this region is positively charged. This portion of the atom is known as the nucleus.
- ✓ The number of protons in the nucleus tells the number of positive charges on the nucleus. This number is called Atomic number of the element.
- ✓ the total number of protons (P) and neutrons (N) present in the nucleus is called the mass number of the element. The mass number thus, can be calculated as = N + P.
- ✓ atom as a whole is electrically neutral, so obviously, it is necessary that the number of electrons present in an atom must be equal to the number of protons present in its nucleus.

Drawbacks of the Rutherford model: as electron is revolving around the nucleus with a high speed, therefore must loses energy and it speed is decreased and electron should fall into the nucleus, thus making atom unstable. But this is not the case, and Rutherford model *could not explain the stability of an atom.*

Bohr Model of an Atom

- To overcome the drawbacks of the Rutherford's model and production of spectrum of H and hydrogen like species (eg. He^+, Li^{2+}) in 1913 utilized the concept of quantization and proposed a new model of an atom.
- Postulates of the model are
  - An electron revolves around the nucleus in a certain fixed energy level, it does not radiate any energy.
  - An electron does not emit energy continuously but it does so only when it jumps from a higher energy level to a lower energy level. This energy loss is in terms of discrete units of energy called quantum. So these energy levels were also named as the **principal quantum numbers** later on.
  - The electron can only move in those circular orbits where the angular momentum (*mvr*) is a whole number multiple of h/2π or it is quantized. This is called the *Principle of Quantization of Angular Momentum*.

$$mvr = \frac{nh}{2\pi}$$

Where, m ismass of electron; v is velocity of electron; r is radius of the orbit in which electron is moving; n is principle quantum number and h is Planck's constant.

- Based on these principles, *explained the emission spectrum of hydrogen* (Lyman series, Balmer series, Paschen series, Brackett series and Pfund series).

Limitations of Bohr's Postulates

- Explain the spectra of species having only one electron
- No explanation for Zeeman and Stark effect : effect of electric and magnetic fields on the spectral atoms.

  (When a magnetic field is applied on an atom, its usually observed spectral lines split. This effect is known as Zeeman's effect)

  (Spectral lines also get split in the presence of electric field. This effect is known as Stark effect.)
- Bohr's theory predicts the origin of only one spectral line from an electron between any two given energy states. But under spectroscope of strong resolution, a single line was found to split in a number of very close related lines. Therefore, Bohr could not explain this multiple or fine structure of spectral lines. These multiple lines indicated the energy level of similar energy for each Principal quantum number, n. **Due to this concept of quantum numbers came into existence.**

Dual Nature of Electron-Particles and Wave

To overcome the inadequacies of Bohr's model, the modern structure of atom was developed in the light of observation by de-Broglie and Heisenberg Uncertainty Principle.

In 1924, the French physicist, Louis de Broglie suggested that if light has electron, behaves both as a material particle and as a wave.

This presented a new wave mechanical theory of matter. According to this theory, small particles like electrons when in motion possess wave properties.

According to de-Broglie, the wavelength associated with a particle of mass m, moving with velocity v is given by the relation

$$\lambda = \frac{h}{mv}$$

where h = Planck's constant.

Derivation of de-Broglie's equation

Energy of photon $E = hv = \frac{hc}{\lambda}$ (Planck's equation)

According to Einstein equation , $E = mc^2$

So, from both equations, $\frac{hc}{\lambda} = mc^2$ so, $\frac{h}{\lambda} = mc$ Therefore, $\lambda = \frac{h}{mc}$

According to wave mechanical model of the atom, an electron behaves as a standing wave which goes around the nucleus in a circular orbit. The only condition need to be followed is that the length of the orbit should be a whole number multiple of the wavelength of electron

If r is the radius of the orbit,

$$2\pi r = n\lambda$$

Now,

$$\lambda = h/mv$$

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

$$mvr = nh//2\,\pi$$

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

Since, ‘mvr’ is the angular momentum of electron. (This seen in Bohr’s postulate)

Wave nature of electron experimentally verified by Davisson and Germer

Davisson and Germer designed and built a vacuum apparatus for the purpose of measuring the energy of electrons scattered from a metal surface. Electrons from a heated filament were accelerated by a voltage, and allowed to strike the surface of nickel metal.

The electrons were scattered and were obtained on the photographic plate on which electron produced the diffraction rings suggesting that electrons have the wave character.

Significance of the de-Broglie equation:

Significance of the de-Broglie equation

- The wave character is only significant in case of small particles like atoms, electrons, protons etc., having small mases. The wave nature is of no significance in case of large microscopic objects.

$$\lambda \propto 1/m$$

Heisenberg Uncertainty Principle

- In 1926, Wernel Heisenberg, suggested that *simultaneous measurement of the position and momentum of sub-atomic particle like electron with complete accuracy is not possible.*
- Inother words, the product of uncertainty in momentum (Δp) and that in position (Δx) almost remains constant.

Mathematically, principle can be expressed as

$$\Delta x.\Delta p \geq h/4\pi$$

Also, can be written as $\Delta x.m\Delta v \geq h/4\pi$

This limitation is not due to lacking in experimental techniques but due to nature of sub-atomic particle itself.

- On the bases of this principle, Bohr's model of atoms no longer stand. The best way is to predict the probability of finding an electron with probable velocity with definite energy in a given region of space in given time. Thus, the uncertainty principle which gave the wave nature of the electron only provides probability of finding an electron in a given space .Thus, atomic model has been replace by probability approach.

Postulates of the wave mechanical model

- Electron wave is compared to a stationary or standing wave.
- Energy values of an electron are quantized.
- The wave length of electron is associated with a wave given by de-Broglie relation.
- The term probability distribution or mathematical wave function is used to describe the motion of an electron.

<u>Quantum Numbers</u>

- In general "address of the electron is given by the quantum number"
- **The set of four integers required to define the state of electron in an atom are called quantum numbers**. OR "*A group of numerical values which provide solutions that are acceptable by the Schrodinger wave equation for hydrogen atoms*."
- The set of quantum numbers are:

1. <u>Principal Quantum number (**n**):</u> proposed by *Bohr*, determines the main energy level, the averge distance of electron from the nucleus, the magnitude of energy of the electron, and describes the size of orbital. n = 1,2,3…….

   The maximum number of electrons in any principal shell is given by $2n^2$.

2. <u>Azimuthal Quantum number (***l***):</u> proposed by Sommerfeld, also known as orbital or angular momentum number. It describes the shape of the orbital.

   Orbital have shapes that are best described as **spherical** (l=0), **dumb-bell** (l=1), or double dumb-bell (l=2). More complex shapes at higher angular momentum quantum number.

The ***l*** value depends upon value of **n**, the value of the azimuthal quantum number ranges between 0 and (n-1).

Eg. **n** = 3, so *l* can be either 0,1 or 2.

The maximum number of orbitals in a sub-shell is given by (2*l*+1) and the number or orbitals in n^{th} shell = n^2.

3. Magnetic Quantum number (**m**): proposed by Lande, describes the orientation of these orbitals.

   For a given value of *l*, there can be 2*l*+1 values for m. eg. For *l* = 0, m=0; *l*=1, m= +1,0,-1.

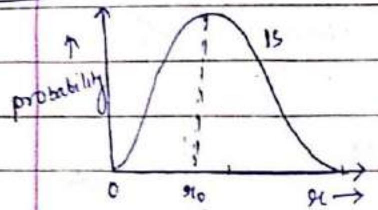
4. Spin Quantum number (**s**): proposed by Uhlenbeck and Goudsmith. This gives an idea about the electron spinning on its axis. Each spinning electron can have two values of spin quantum number i.e. +1/2 (clockwise spin) and -1/2 (anticlockwise spin).

→ Radial probability distribution → probable distance to find electron from nucleus.

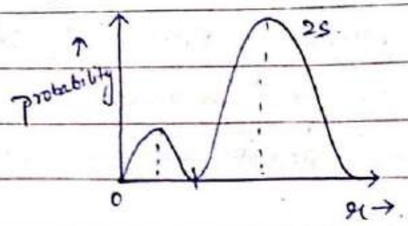
→ at nucleus, probability is zero.

→ larger value of principal quantum number, farther is electron.

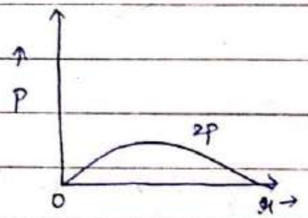
1s



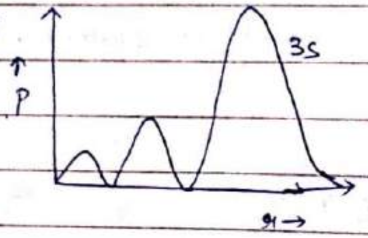
2s



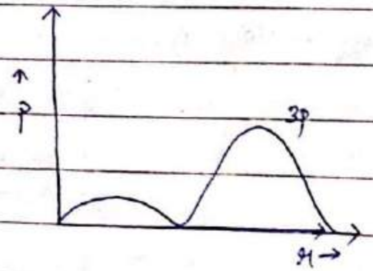
2p



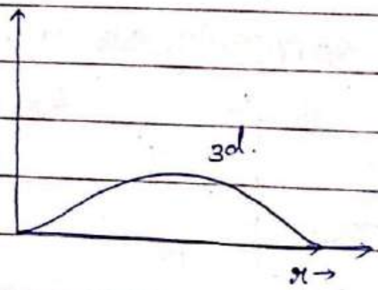
3s



3p



3d



1. Calculate and compare the energies of two radiations, having wavelength of 400Å and other with 800Å.

Ans→ $E = h\nu = \frac{hc}{\lambda}$

$$E_{400} = \frac{6.62 \times 10^{-34}\ Js \times 3 \times 10^{8}\ m/s}{400 \times 10^{-10}\ m} = 4.965 \times 10^{-18}\ J$$

$$E_{800} = \frac{6.62 \times 10^{-34}\ Js \times 3 \times 10^{8}\ m/s}{800 \times 10^{-10}\ m} = 2.482 \times 10^{-18}\ J$$

Hence, $\frac{E_{400}}{E_{800}} = \frac{4.965 \times 10^{-18}\ J}{2.482 \times 10^{-18}\ J} = 2$

Therefore, $E_{400} = 2E_{800}$.

2. Calculate the wavelength of 1000 Kg rocket moving with a velocity of 300 Km/h.

Ans → Mass of rocket = 1000 Kg

$$\text{Velocity} = 300\ \text{Km/h} = \frac{300 \times 1000}{60 \times 60} = 83.33\ \text{m/s}.$$

From, de-Broglie equation

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}\ \text{Js}}{1000\text{Kg} \times 83.33\ \text{m/s}} \qquad (\text{J} = \text{kg m}^2/\text{s}^2)$$

$$= 7.95 \times 10^{-39}\ \text{m}$$

3. A dustparticle having mass equal to 10^{-11} kg and velocity 10^{-4} cm sec^{-1}. The error in the measurement of velocity is 0.1 %. Calculate the uncertanity in its position.

Ans → Velocity, $v = 10^{-4}$ cm/sec

$$\Delta v = 0.1\% \times 10^{-4} = 1 \times 10^{-7}\ \text{cm/sec}$$

$$\Delta x \cdot m\Delta v = \frac{h}{4\pi}$$

$$\Delta v \cdot \Delta x = \frac{h}{4\pi m}$$

$$\Delta x = \frac{6.625 \times 10^{-34}}{4 \times 3.14 \times 10^{-11} \times 10^{-7}} = 0.527 \times 10^{9}\ \text{cm}.$$

4. Consider a ball of mass 1g moving with a speed 1 cm/s in one dimensional box of edge length equal to 10 cm.
(i) calculate its kinetic energy and number n corresponding to this kinetic energy.
(ii) if ball is prompted to next higher quantum level, then how much energy is required?

Ans- (i) K.E of ball $\Rightarrow E_n = \frac{1}{2}mv^2 = \frac{1}{2} \times (10^{-3} kg)(10^{-2} m/s)^2$

$$= 0.5 \times 10^{-7} J$$

Since, $E_n = \frac{n^2 h^2}{8ml^2}$,

$$\therefore n^2 = \frac{E_n \times 8ml^2}{h^2} = \frac{(0.5 \times 10^{-7} J)(8 \times 10^{-3} kg)(10^{-1} m)^2}{(6.626 \times 10^{-34} Js)^2}$$

$$= 9.11 \times 10^{54}$$

or $n \simeq 3.02 \times 10^{27}$

(ii) Now, $\Delta E = E_{n+1} - E_n = (2n+1)\left(\frac{h^2}{8ml^2}\right)$

$$= (2 \times 3.02 \times 10^{27} + 1)\left(\frac{(6.626 \times 10^{-34} Js)^2}{8 \times (10^{-3} kg)(10^{-1} m)^2}\right)$$

$$= 3.32 \times 10^{-35} J$$

5. An electron is confined to a molecule of length of 1 nm. (i) What is its minimum energy? (ii) What is the minimum excitation energy from this state.

Ans- (i) $$E_1 = \frac{h^2}{8ml^2} = \frac{(6.626 \times 10^{-34}\, Js)^2}{8 \times (10^{-9} m)^2 (9.109 \times 10^{-31} Kg)}$$

$$= 6.025 \times 10^{-20}\, J.$$

(ii) Now, $$E_2 = \frac{4h^2}{8ml^2} = 4(E_1) = 24.1 \times 10^{-20} J$$

$$\Delta E = E_2 - E_1 = 4E_1 - E_1 = 3E_1 = 18.075 \times 10^{-20} J.$$

6. What will happen if the walls of 1-D box are suddenly removed?

Ans If walls are removed, particles become free to move without any restriction on the value of potential energy (P.E.). Thus energy value are not quantised, and it will have continious energy spectrum.

7. What is the zero point energy of a particle in a one-dimensional box of infinite heigth? Is the occurance of zeropoint energy in accordance with the Heisenberg Uncertanity principle?

Ans → Since, $E = \frac{n^2 h^2}{8ml^2}$

$\therefore \boxed{E_1 = \frac{h^2}{8ml^2}} \Rightarrow$ zero point energy (Z.P.E)

Since, Z.P.E is finite (and not equal to zero) it means that the particle inside the box is not at rest even at 0K. This being so, the position of particle cannot be precisely known. Again, since only expectation value of $KE = \frac{1}{2}mv^2$ is known the linear momentum of particle is also not precisely known. Thus, occurance of Z.P.E implies uncertanity in the position, Δx and also uncertainty in x-component of linear momentum Δp_x.

This means, Z.P.E is keeping accordance with Heisenberg Uncertainity Principle.