How this Book helps in CSIR NET/ICMR/other exams preparation?

Atomic Structure and Chemical Bonding

CHAPTER
1

LEARNING OBJECTIVES **EXAM INDEX** ⌛⌛⌛

- Atom, sub-atomic particles and their organisation.
- Various models of atom, salient features and drawbacks.
- Chemical bonds, their formation and types.
- Comparison between all types of interactions in terms of their strength.
- Distance dependence on the magnitude of interaction/bond.

1.1. INTRODUCTION

Biomolecules are characterised by their biological origin and may appear to be more complex than basic chemical entities often seen in chemistry textbooks, yet their fundamental constituents are atoms and their chemical properties are governed by the same rules of chemistry.

In order to understand the stability of biomolecules, their interactions and the mechanism of biochemical reactions, it is essential to revisit the atomic structure and basic atomic/molecular interactions that are essential for the existence of every chemical entity in this universe. In this chapter, we will also focus on biological relevance of atomic structure and their interactions.

The word atom has originated from the Greek word '**a-tomio**' which means uncutable or non-divisible. The details of the atom could be elucidated only after the discovery of sub-atomic particles such as electron (JJ Thomson), proton (Goldstein) and neutrons (Chadwick). Since early 1800, the atomic structure has been extensively revised and elaborated by several classical experiments. Chronologically, initial model was **plum pudding model** given by JJ Thomson, followed by **Rutherford's atomic model,** which was later refined by Neil's Bohr. The most recent model of atom is based on quantum mechanics and called as **quantum mechanical model.** Let us now understand the key ideas proposed in these model and refine our understanding about the structure of atom.

Interesting Fact

The "God particle" is the nickname of a subatomic particle called the Higgs boson. In layman's terms, different subatomic particles are responsible for giving matter different properties. One of the most mysterious and important properties is mass. Some particles, like protons and neutrons, have mass. Others, like photons, do not. The Higgs boson or "God particle," is believed to be the particle which gives mass to matter. The "God particle" nickname grew out of the long, drawn-out struggles of physicists to find this elusive piece of the cosmic puzzle. What follows is a very brief and simplified explanation of how the Higgs boson fits into modern physics, and how science is attempting to study it.

1.1.1. Plum Pudding Model

J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius ~ 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. This may be understood similar to plums as electrons present in positively charged pudding or seeds as electrons present in

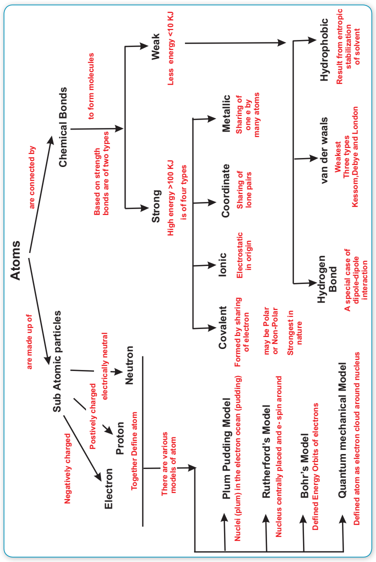
EXAM INDEX

This books has been custom written for assisting students in their preparation for competitive exams. Starting of each chapter is gives a detailed view of each chapter and it weightage in exams. We have also provided an exam weightage icon on the scale of 5 which helps readers to know the impact and importance of particular topic based on previous trends.

INTERESTING FACT

Another opening shot in the chapter is the column called interesting fact, which include some of the unique facts that will excite the students giving them some unique information on the topic.

CONCEPT MAP



CONCEPT MAP

Most Importantly, Last part of each chapter is provided with a small concept map of everything that could summaries the chapter. This would provide a bird's eye view of chapter and help students to revise faster.

The seminal work of Heisenberg and Schrödinger with ways of describing the quantized energy levels of atoms explained a much better model of atom. Heisenberg used matrices and Schrödinger developed a wave equation. It was solutions of Schrödinger's equation that provided pictures of electrons' probability densities around the nucleus of an atom.

Relative organization of atom and chorological development is shown below in the Fig. 1.3

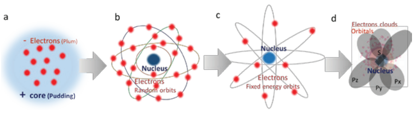


Fig 1.3. Chronological advent in the structure of atom **a.** plum pudding model of JJ Thomson – No defined position of electrons and protons, **b.** Rutherford's atomic Model – centrally located nucleus, spinning electrons but not defined orbits **c.** Neil Bohr's atomics structure – defined orbits and energy levels. **d.** Quantum mechanical model – position of electrons/probability is calculated from Schrodinger equation, and electron density varies at different places surrounding nucleus.

▶ **Online Support**

Video Lecture Available: You tube channel: video 1.1: Atomic structure

In extension to the quantum mechanical model, there are certain rules that govern the filling and positioning of electron into an atoms as described below.

SELF-TEST

Q: The order. of radius of the nucleus of an atom is **[CEEB, JNU Biotech entrance 2011]**

a. 10^{-10} m **b.** 10^{-12} m **c.** 10^{-15} m **d.** 10^{-17} m

[**HINT:** c is correct answer]

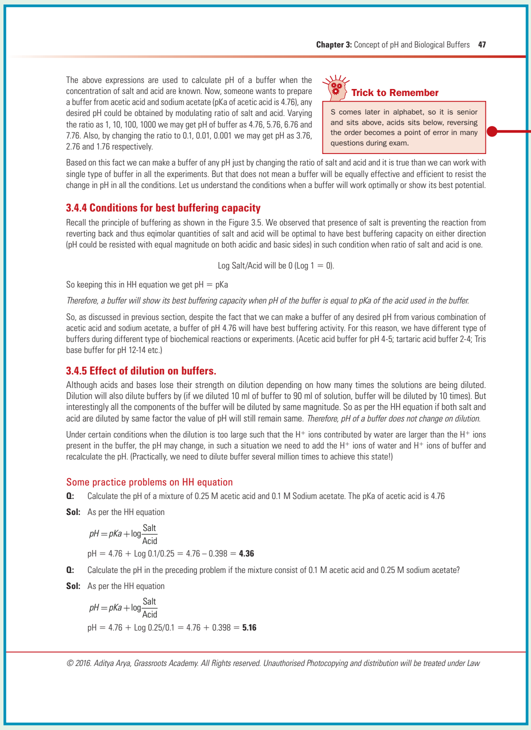
Quantum Numbers

These are used to get complete information about electron, i.e., location, energy, spin, etc. These quantum numbers also help to designate the electron present in an orbital.

- *Principal quantum number.* It specifies the location and energy of an electron. It is measure of the effective volume of the electron cloud. It is denoted by *n*'. Its possible values are 1, 2, 3, 4.
- *Angular momentum quantum number.* It is also called azimuthal quantum number. It determines the shape of the orbital. It is denoted by *l*'. The permitted values of *l* are 0, 1, 2, etc., up to $n - 1$. For a given value of n, $l = 0$ to $n - 1$. e.g., if value of *n* is 4, *l* can have values 0, 1, 2, 3. It determines angular momentum.
- *Magnetic quantum number.* It is denoted by *m*' and its value depends on value of *l*' since magnetism is due to angular momentum. It determines the magnetic orientation of an orbital, i.e., the direction of orbital relative to magnetic field in which it is placed. Its permitted values are $-l$ to $+l$ including zero, e.g., when $l = 1$, then $m = -1, 0, +1$. It has total number of values equal to $2l + 1$.
- *Spin quantum number.* It indicates, the direction in which electron revolves. Spin is magnetic property and is also quantized. It has two permitted values + ½ or –½. The spin angular momentum of an electron is constant and cannot be changed.

ONLINE SUPPORT

All videos referring to online support are freely available at You tube channel https://www.youtube.com/channel/UCamj_DLY1sy7OvGwo8WkdXw which can be searched on google/you tube with key words " Aditya Arya Biochemistry"



Chapter 3: Concept of pH and Biological Buffers **47**

The above expressions are used to calculate pH of a buffer when the concentration of salt and acid are known. Now, someone wants to prepare a buffer from acetic acid and sodium acetate (pKa of acetic acid is 4.76), any desired pH could be obtained by modulating ratio of salt and acid. Varying the ratio as 1, 10, 100, 1000 we may get pH of buffer as 4.76, 5.76, 6.76 and 7.76. Also, by changing the ratio to 0.1, 0.01, 0.001 we may get pH as 3.76, 2.76 and 1.76 respectively.

Trick to Remember

S comes later in alphabet, so it is senior and sits above, acids sits below, reversing the order becomes a point of error in many questions during exam.

Based on this fact we can make a buffer of any pH just by changing the ratio of salt and acid and it is true than we can work with single type of buffer in all the experiments. But that does not mean a buffer will be equally effective and efficient to resist the change in pH in all the conditions. Let us understand the conditions when a buffer will work optimally or show its best potential.

3.4.4 Conditions for best buffering capacity

Recall the principle of buffering as shown in the Figure 3.5. We observed that presence of salt is preventing the reaction from reverting back and thus eqimolar quantities of salt and acid will be optimal to have best buffering capacity on either direction (pH could be resisted with equal magnitude on both acidic and basic sides) in such condition when ratio of salt and acid is one.

Log Salt/Acid will be 0 (Log 1 = 0).

So keeping this in HH equation we get pH = pKa

Therefore, a buffer will show its best buffering capacity when pH of the buffer is equal to pKa of the acid used in the buffer.

So, as discussed in previous section, despite the fact that we can make a buffer of any desired pH from various combination of acetic acid and sodium acetate, a buffer of pH 4.76 will have best buffering activity. For this reason, we have different type of buffers during different type of biochemical reactions or experiments. (Acetic acid buffer for pH 4-5; tartaric acid buffer 2-4; Tris base buffer for pH 12-14 etc.)

3.4.5 Effect of dilution on buffers.

Although acids and bases lose their strength on dilution depending on how many times the solutions are being diluted. Dilution will also dilute buffers by (if we diluted 10 ml of buffer to 90 ml of solution, buffer will be diluted by 10 times). But interestingly all the components of the buffer will be diluted by same magnitude. So as per the HH equation if both salt and acid are diluted by same factor the value of pH will still remain same. *Therefore, pH of a buffer does not change on dilution.*

Under certain conditions when the dilution is too large such that the H^+ ions contributed by water are larger than the H^+ ions present in the buffer, the pH may change, in such a situation we need to add the H^+ ions of water and H^+ ions of buffer and recalculate the pH. (Practically, we need to dilute buffer several million times to achieve this state!)

Some practice problems on HH equation

Q: Calculate the pH of a mixture of 0.25 M acetic acid and 0.1 M Sodium acetate. The pKa of acetic acid is 4.76

Sol: As per the HH equation

$$pH = pKa + \log\frac{\text{Salt}}{\text{Acid}}$$

pH = 4.76 + Log 0.1/0.25 = 4.76 – 0.398 = **4.36**

Q: Calculate the pH in the preceding problem if the mixture consist of 0.1 M acetic acid and 0.25 M sodium acetate?

Sol: As per the HH equation

$$pH = pKa + \log\frac{\text{Salt}}{\text{Acid}}$$

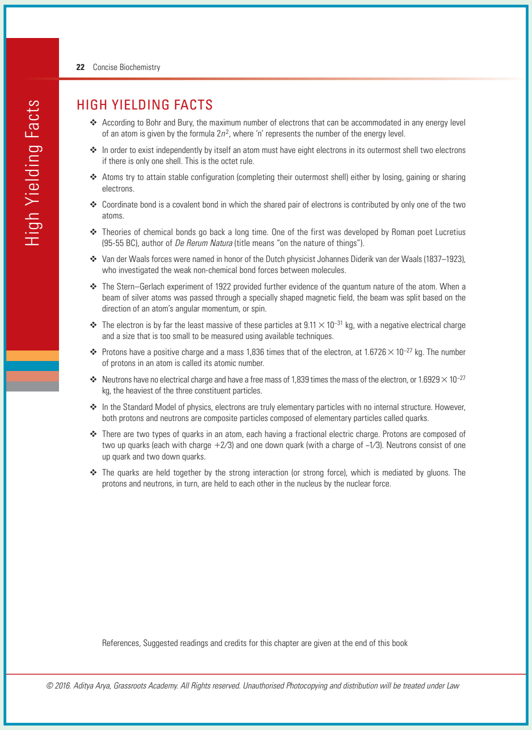
pH = 4.76 + Log 0.25/0.1 = 4.76 + 0.398 = **5.16**

TRICK TO REMEMBER

Further during the entire text some tricks to remember the difficult topics have also been added, which is unique feature of this book usually not found in standard texts.

HIGH YIELDING FACTS

The chapter ends with a section called high yielding facts, this includes some of the unique small points about the topic that may be remembered by the students especially for memory based questions asked in many competitive examinations.



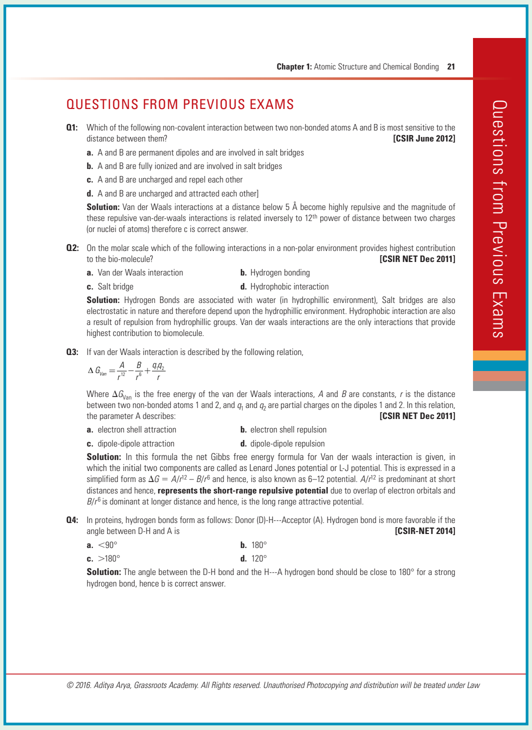
High Yielding Facts

22 Concise Biochemistry

HIGH YIELDING FACTS

- According to Bohr and Bury, the maximum number of electrons that can be accommodated in any energy level of an atom is given by the formula $2n^2$, where 'n' represents the number of the energy level.
- In order to exist independently by itself an atom must have eight electrons in its outermost shell two electrons if there is only one shell. This is the octet rule.
- Atoms try to attain stable configuration (completing their outermost shell) either by losing, gaining or sharing electrons.
- Coordinate bond is a covalent bond in which the shared pair of electrons is contributed by only one of the two atoms.
- Theories of chemical bonds go back a long time. One of the first was developed by Roman poet Lucretius (95-55 BC), author of *De Rerum Natura* (title means "on the nature of things").
- Van der Waals forces were named in honor of the Dutch physicist Johannes Diderik van der Waals (1837–1923), who investigated the weak non-chemical bond forces between molecules.
- The Stern–Gerlach experiment of 1922 provided further evidence of the quantum nature of the atom. When a beam of silver atoms was passed through a specially shaped magnetic field, the beam was split based on the direction of an atom's angular momentum, or spin.
- The electron is by far the least massive of these particles at 9.11×10^{-31} kg, with a negative electrical charge and a size that is too small to be measured using available techniques.
- Protons have a positive charge and a mass 1,836 times that of the electron, at 1.6726×10^{-27} kg. The number of protons in an atom is called its atomic number.
- Neutrons have no electrical charge and have a free mass of 1,839 times the mass of the electron, or 1.6929×10^{-27} kg, the heaviest of the three constituent particles.
- In the Standard Model of physics, electrons are truly elementary particles with no internal structure. However, both protons and neutrons are composite particles composed of elementary particles called quarks.
- There are two types of quarks in an atom, each having a fractional electric charge. Protons are composed of two up quarks (each with charge +2/3) and one down quark (with a charge of –1/3). Neutrons consist of one up quark and two down quarks.
- The quarks are held together by the strong interaction (or strong force), which is mediated by gluons. The protons and neutrons, in turn, are held to each other in the nucleus by the nuclear force.

References, Suggested readings and credits for this chapter are given at the end of this book



Chapter 1: Atomic Structure and Chemical Bonding **21**

Questions from Previous Exams

QUESTIONS FROM PREVIOUS EXAMS

Q1: Which of the following non-covalent interaction between two non-bonded atoms A and B is most sensitive to the distance between them? **[CSIR June 2012]**

a. A and B are permanent dipoles and are involved in salt bridges
b. A and B are fully ionized and are involved in salt bridges
c. A and B are uncharged and repel each other
d. A and B are uncharged and attracted each other]

Solution: Van der Waals interactions at a distance below 5 Å become highly repulsive and the magnitude of these repulsive van-der-waals interactions is related inversely to 12th power of distance between two charges (or nuclei of atoms) therefore c is correct answer.

Q2: On the molar scale which of the following interactions in a non-polar environment provides highest contribution to the bio-molecule? **[CSIR NET Dec 2011]**

a. Van der Waals interaction **b.** Hydrogen bonding
c. Salt bridge **d.** Hydrophobic interaction

Solution: Hydrogen Bonds are associated with water (in hydrophillic environment), Salt bridges are also electrostatic in nature and therefore depend upon the hydrophillic environment. Hydrophobic interaction are also a result of repulsion from hydrophillic groups. Van der waals interactions are the only interactions that provide highest contribution to biomolecule.

Q3: If van der Waals interaction is described by the following relation,

$$\Delta G_{Van} = \frac{A}{r^{12}} - \frac{B}{r^6} + \frac{q_1 q_2}{r}$$

Where ΔG_{Van} is the free energy of the van der Waals interactions, A and B are constants, r is the distance between two non-bonded atoms 1 and 2, and q_1 and q_2 are partial charges on the dipoles 1 and 2. In this relation, the parameter A describes: **[CSIR NET Dec 2011]**

a. electron shell attraction **b.** electron shell repulsion
c. dipole-dipole attraction **d.** dipole-dipole repulsion

Solution: In this formula the net Gibbs free energy formula for Van der waals interaction is given, in which the initial two components are called as Lenard Jones potential or L-J potential. This is expressed in a simplified form as $\Delta G = A/r^{12} - B/r^6$ and hence, is also known as 6–12 potential. A/r^{12} is predominant at short distances and hence, **represents the short-range repulsive potential** due to overlap of electron orbitals and B/r^6 is dominant at longer distance and hence, is the long range attractive potential.

Q4: In proteins, hydrogen bonds form as follows: Donor (D)-H---Acceptor (A). Hydrogen bond is more favorable if the angle between D-H and A is **[CSIR-NET 2014]**

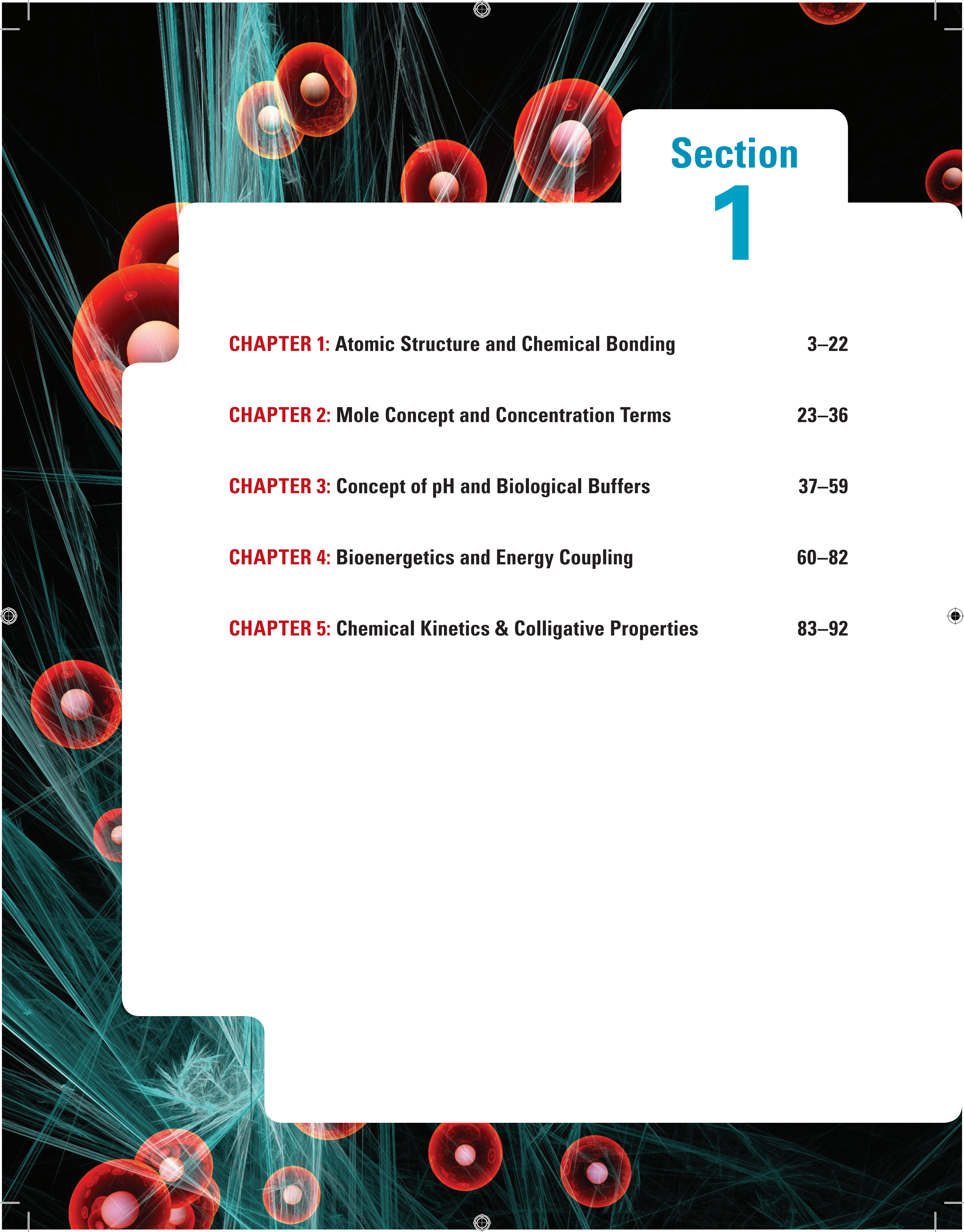
a. <90° **b.** 180°
c. >180° **d.** 120°

Solution: The angle between the D-H bond and the H---A hydrogen bond should be close to 180° for a strong hydrogen bond, hence b is correct answer.

QUESTION FROM PREVIOUS EXAM

This is followed by another important segment containing previous year questions from CSIR-NET from that particular chapter, providing students a recap of what need to be focused in the chapter and detailed solution of each previous year question.

Additionally, as an innovative approach, some of the difficult topics are aided with online support. Readers may visit you tube channel of author or the publisher to watch curtailed classroom videos for clarity.



Section
1

CHAPTER

1

Atomic Structure and Chemical Bonding

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1.1. INTRODUCTION

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The word atom has originated from the Greek word '**a-tomio**' which means uncutable or non-divisible. The details of the atom could be elucidated only after the discovery of sub-atomic particles such as electron (JJ Thomson), proton (Goldstein) and neutrons (Chadwick). Since early 1800, the atomic structure has been extensively revised and elaborated by several classical experiments. Chronologically, initial model was **plum pudding model** given by JJ Thomson, followed by **Rutherford's atomic model,** which was later refined by Neil's Bohr. The most recent model of atom is based on quantum mechanics and called as **quantum mechanical model.** Let us now understand the key ideas proposed in these model and refine our understanding about the structure of atom.

Interesting Fact

The "God particle" is the nickname of a subatomic particle called the Higgs boson. In layman's terms, different subatomic particles are responsible for giving matter different properties. One of the most mysterious and important properties is mass. Some particles, like protons and neutrons, have mass. Others, like photons, do not. The Higgs boson or "God particle," is believed to be the particle which gives mass to matter. The "God particle" nickname grew out of the long, drawn-out struggles of physicists to find this elusive piece of the cosmic puzzle. What follows is a very brief and simplified explanation of how the Higgs boson fits into modern physics, and how science is attempting to study it.

1.1.1. Plum Pudding Model

JJ Thomson, in 1898, proposed that an atom possesses a spherical shape (radius ~ 10^{-10} m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement. This may be understood similar to plums as electrons present in positively charged pudding or seeds as electrons present in when electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.

- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by (v – frequency; h – planks constant)

$$v = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Here E_2 is the energy of orbit from where electron returns and E_1 is the energy of the orbit to which electron returns. The difference between these energies is ΔE and therefore the frequency can be calculated using planks equation ($E = h\upsilon$) or $E = hc/\lambda$.

Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+, Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the following equation:

$$E_n = -2.18 \times 10^{-13} \frac{Z^2}{N^2} \quad \text{[here } Z \text{ is the no. of protons and } N \text{ is no. of electrons]}$$

As described above, the atomic structure of hydrogen atom was determined with the help of absorption spectra analysis. An **absorption spectrum** is like the photographic negative / invert of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths.

Line Spectrum of Hydrogen: When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced, emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. These series were the basis of determination of atomic structure as proposed by Bohr. Various spectral series and their corresponding energies are depicted in Fig. 1.1.

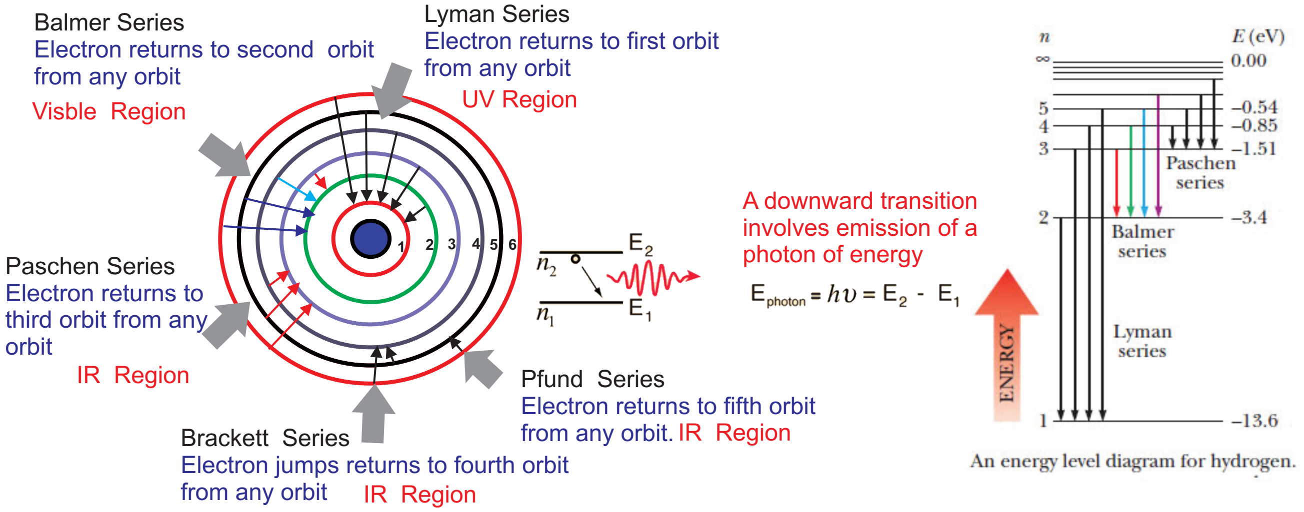

Fig. 1.1. Spectral lines and series obtained in hydrogen spectra with corresponding energies represented as region of electromagnetic spectrum.

The Swedish spectroscopist, **Johannes Rydberg,** noted that all series of lines in the hydrogen spectrum could be described by the following expression

$$\bar{\upsilon} = 109.6777\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ cm}^{-1}$$

Here $\bar{\upsilon}$ is the wave number (wave number is inverse of wave length), n_1 is the orbit in which electron returns back and n_2 is the orbit from which electron returns back.

SELF-TEST

Q: The Ground state energy of hydrogen atom is –13.6 eV. Assume *hc* = 1240 eV.nm. The maximum wavelength in Balmer series (in nm) is approximately. **[IIT-JAM 2010]**

a. 103 **b.** 122 **c.** 244 **d.** 653

[**HINT:** Balmer Series always produces the photos in visible range and here d is correct option]

Q: The radius of the first 'Bohr's stationary orbit' for the hydrogen atom is 0.53 A, The radius of the second orbit is **[IIT-JAM 2013]**

a. 1.06 A° **b.** 1.59 A° **c.** 2.12 A° **d.** 4.24 A°

[**HINT:** use the formula for calculation of atomic radii.]

Shortcomings of Bohrs Model of atom

The first drawback of Bohr's model was that it could not describe the structure of multi-electron systems, i.e. atom containing more than one electrons.

The second question was raised by the uncertainty principle given by Heisenberg, which states that "It is not possible to determine the position and velocity simultaneously for a sub-atomic particle like electron at any given instant to an arbitrary degree of precision. Consequently, it is not possible to talk of path of the electron in which it moves, which was in contradiction to Bohr's atomic orbits.

Furthermore, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or an electric field (**Stark effect).** Another limitation was the dual nature of matter (i.e. matter has both particle and wavelike properties) which could not explain the exact positioning of electron around an atom (as electrons now have not only particle but wave nature also). The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties. $\lambda = h/mv = h/p$, Where p is the momentum of particle = mass (m) × velocity (v).

To answer these drawbacks the latest model of atom called quantum mechanical model was proposed, which is discussed below.

1.1.4. Quantum mechanical model of atom

Quantum mechanical model of atom is the latest and most accepted model of an atom. As discussed earlier that the Bohr's model of atom could not explain the structure of multi-electron systems, as this creates a complex interfering environment. These shortcomings were answered by complex theories of physics collectively called quantum mechanics. In this model, the electrons were considered as wave and therefore electron is present in the form of a cloud around nucleus. Just like two or more waves can interfere with each other and show increase or decrease in amplitude. The multiple electrons of an atom can also interact and interfere with each other, hence the probability of finding an electron varies around the nuclii. These situation were mathematically studied by famous scientist Erwin Schrodinger who, based on the mathematical equations proposed how the electron clouds will be organized around nuclei. The probability graphs of finding electrons around nuclei are known as electron orbitals. This model is illustrated in the Fig. 1.2.

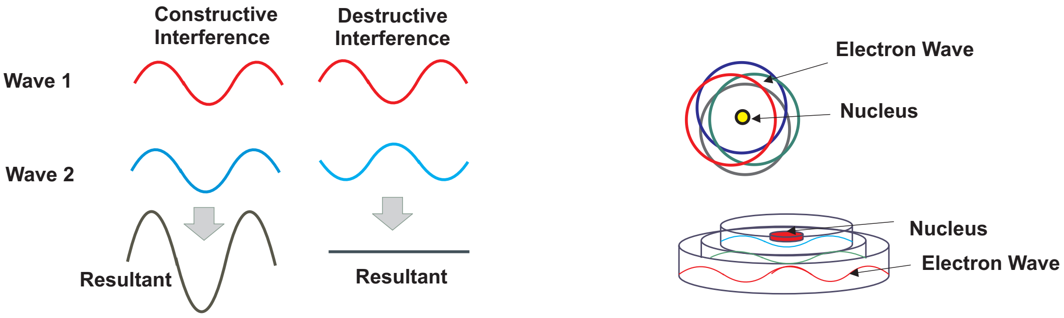

Fig. 1.2. Two or more waves may interact to show constructive and destructive interference, similarly electron waves in an atom interact and show interference which results in high and low probability regions for finding an electron in an atom.

The seminal work of Heisenberg and Schrödinger with ways of describing the quantized energy levels of atoms explained a much better model of atom. Heisenberg used matrices and Schrödinger developed a wave equation. It was solutions of Schrödinger's equation that provided pictures of electrons' probability densities around the nucleus of an atom.

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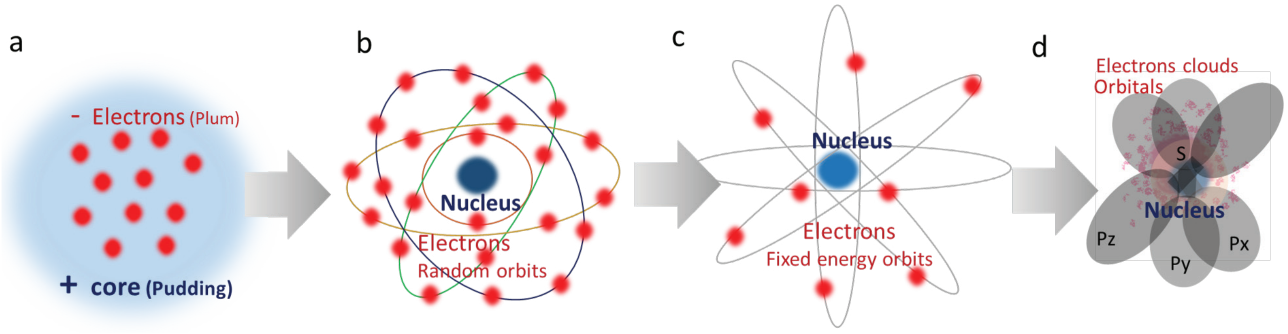

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Online Support

You tube channel: video 1.1: Atomic structure

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- *Angular momentum quantum number.* It is also called azimuthal quantum number. It determines the shape of the orbital. It is denoted by *l*'. The permitted values of *l* are 0, 1, 2, etc., up to $n - 1$. For a given value of *n*, $l = 0$ to $n - 1$. e.g., if value of *n* is 4, *l* can have values 0, 1, 2, 3. It determines angular momentum.
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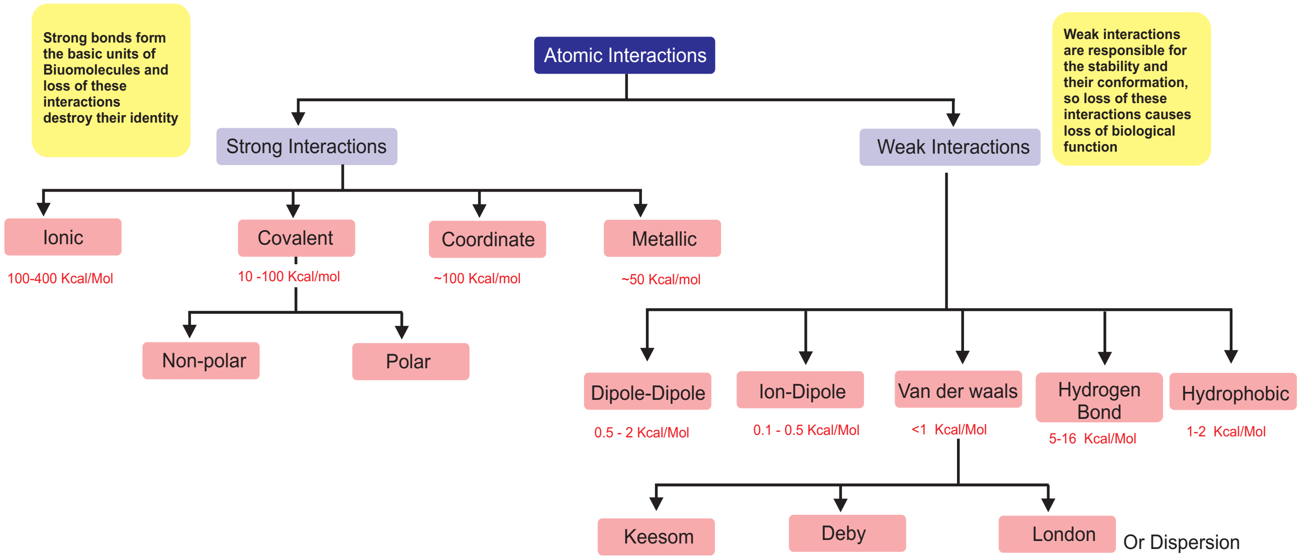
- *Spin quantum number.* It indicates, the direction in which electron revolves. Spin is magnetic property and is also quantized. It has two permitted values +½ or –½. The spin angular momentum of an electron is constant and cannot be changed.

1.2.1 Classification of Atomic Interactions

Online Support

You tube channel: video 1.2: Interactions in biomolecules



Atomic interactions (Chemical Bonds) may be classified into two broad categories based on the strength of the bonds; Strong and weak. Strong bonds may be more than 100 times stronger than weak bonds. For a chemist, the weak forces may be irrelevant for the stability or chemical reactivity of the molecules, but in biological systems, the weak interactions play a major role in their stability and therefore cannot be ignored. This is primarily due to a very large number of weak interactions existing within a single biomolecule. We will discuss here the detailed description of all major type of interactions. Further in Chapter 12 we will be evaluating the role of these interactions in special context of biomolecule stability.

Strong Bonds

Ionic Bond

Ionic bonding is a type of electrostatic interaction between atoms which have a large electronegativity difference. There is no precise value that distinguishes ionic from covalent bonding, but a difference of electronegativity of over 1.7 is likely to be ionic, and a difference of less than 1.7 is likely to be covalent. Ionic bonding leads to separate positive and negative ions. Ionic charges are commonly between –3e to +3e (e is the charge on one electron). Ionic bonding commonly occurs in metal salts such as sodium chloride (table salt). A typical feature of ionic compounds is that they are crystalline in which no ion is specifically paired with any single other ion in a specific directional bond, rather each species of ion is surrounded by many ions of the opposite charge forming an array of opposite charges forming a crystal lattice.

Origin of Ionic Interactions/Bonds: Ionic interactions are purely electrostatic in nature and therefore the force of interaction between two atoms may be calculated using a simple equation:

$$F = \frac{1}{4\pi\varepsilon} \times \frac{q_1 q_2}{r^2}$$

Here q_1 and q_2 are the charges on ions, r is the distance between them and ε is dielectric constant of the medium. Here q may remain constant for a charged molecule.

So we can say that force is **inversely proportional** to **dielectric constant** (ε), and therefore the interactions will be weaker in solvent with higher ε and vice versa. Also the solubility of an ionic compound is inversely proportional to the interactions, so in solvents of higher dielectric constant, ionic interactions will be weak and compound will be more soluble. This concept may be applicable in purification and separation of biomolecules in lab, as a biomolecule like DNA or protein will be quickly dissolved in formamide or water but will precipitate in solvents such as acetone, chloroform or hexane as force of ionic interaction will be stronger compelling the molecule to precipitate in solution. Dielectric constants of some of the common solvents are given below for quick reference.

Solvent	Dielectric constant (at 25°C)	Strength of ionic interactions	Solubility of biomolecules	Ability to precipitate biomolecules
Formamide	109	↓ Increases	Increases ↑	↓ Increases
Water	78.5			
Methyl Alcohol	32.6			
Ethyl Alcohol	24.3			
Acetone	20.7			
Acetic Acid	6.2			
Chloroform	5.0			
Hexane	1.9			

Examples of ionic interactions in biological systems

1. Several buffering systems (carbonate: bicarbonate buffer; Phosphate buffer)
2. Salt bridges in proteins (an interaction between amino side chains with carboxyl side chain)
3. Protein- DNA interactions (interaction of histone proteins (positive side chains) with phosphate)
4. Interaction of many divalent ions (such as Mg^{2+}, calcium etc with DNA and proteins)

It must be noted here that ionic bonds will be of poor strength in biological systems as water is prominent medium and it has high dielectric constant. However, in some biomolecules which maintain a local hydrophobic (water free) environment, ionic interactions may play an important role.

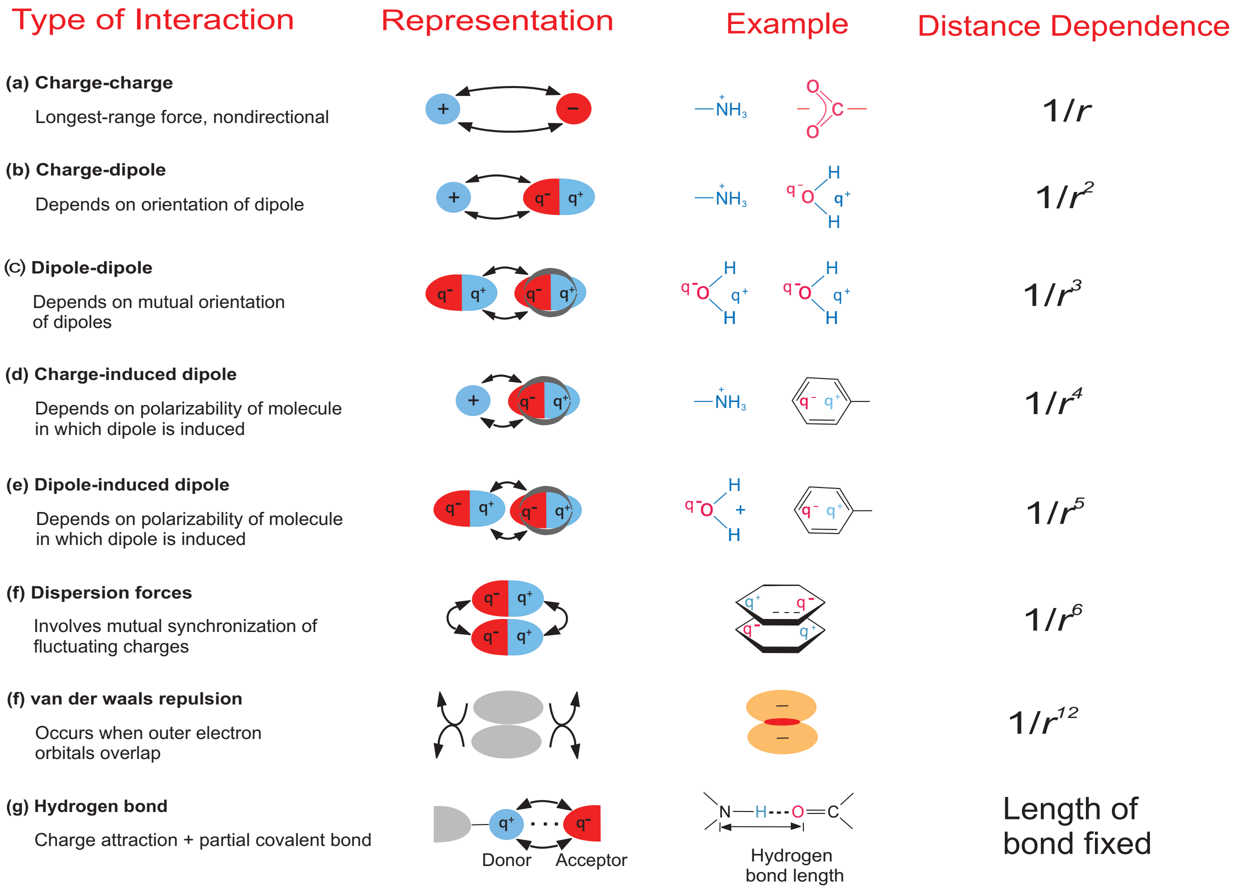
SELF-TEST

Q: Which kind of bond is the strongest: Ionic, or covalent.

Q: Which solvent will be most suitable for solubilising proteins/DNA or other biomolecules?
[**HINT:** Decide on the basis of dielectric constant of medium]

Covalent Bond

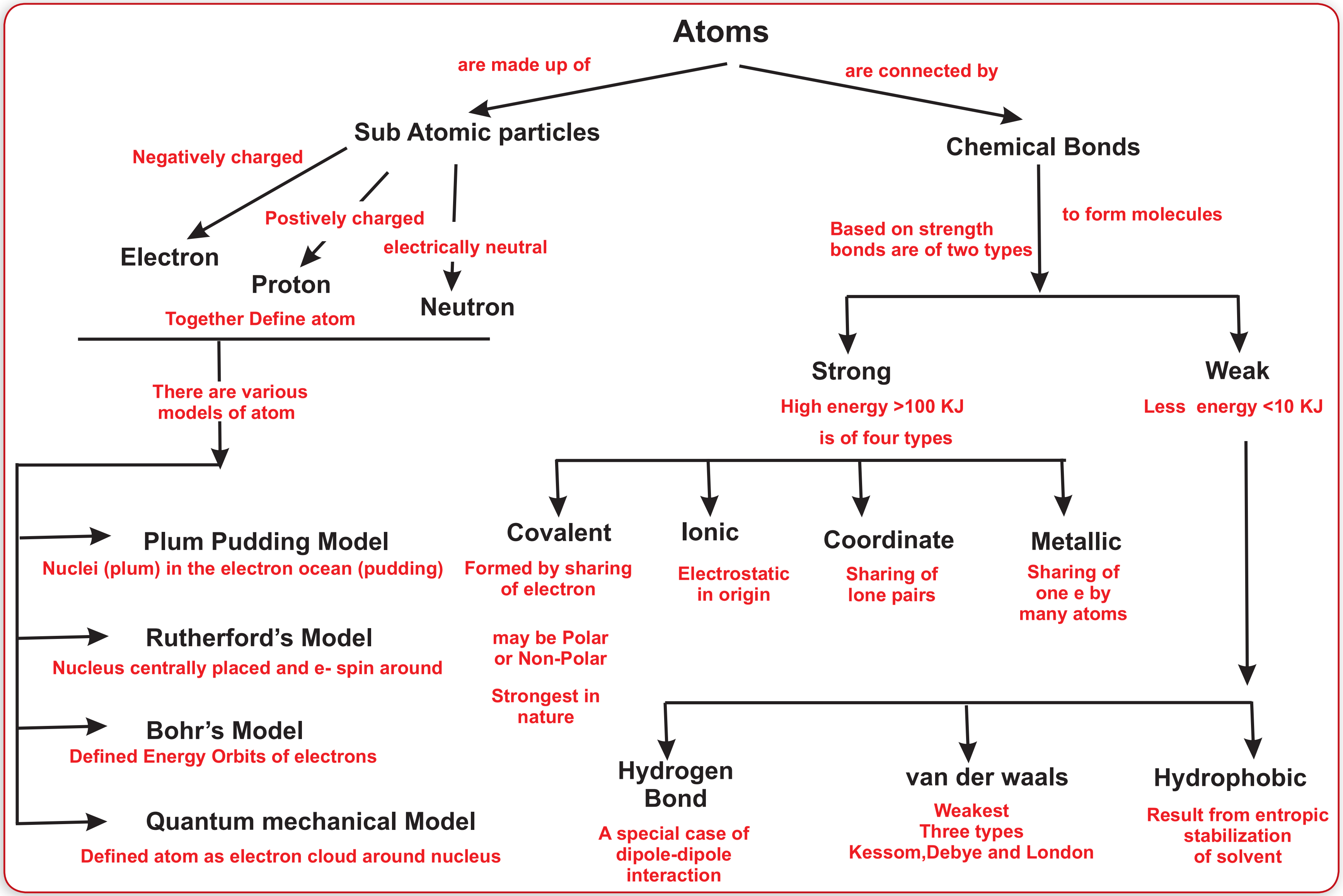
Covalent bonding is another strong bond between atoms which is not electrostatic in nature but arises due to mutual sharing of electrons between atoms. As we have learned above, the electrons have dual nature and behave as both particle and wave and therefore there are two views about the covalent bond formation. If we consider electron as particles, covalent bonds is defined as bond arising from sharing of electrons which means electron revolved around two atoms. While as per wave nature, covalent bond may be defined as the interaction of electronic waves or electron clouds. Therefore, the strength of a covalent bond depends upon the extent of overlap and the nature of overlap between the atomic orbitals. A head-on overlap of orbitals is most strong (called as **sigma bond),** while sideways overlap is relatively weaker (called **pi bond**).



Type of Interaction	Distance Dependence
(a) Charge-charge Longest-range force, nondirectional	$1/r$
(b) Charge-dipole Depends on orientation of dipole	$1/r^2$
(c) Dipole-dipole Depends on mutual orientation of dipoles	$1/r^3$
(d) Charge-induced dipole Depends on polarizability of molecule in which dipole is induced	$1/r^4$
(e) Dipole-induced dipole Depends on polarizability of molecule in which dipole is induced	$1/r^5$
(f) Dispersion forces Involves mutual synchronization of fluctuating charges	$1/r^6$
(f) van der waals repulsion Occurs when outer electron orbitals overlap	$1/r^{12}$
(g) Hydrogen bond Charge attraction + partial covalent bond	Length of bond fixed

Fig. 1.14. Summary of major chemical bonds/interactions and their relationship with distance.

CONCEPT MAP


Atoms
are made up of
are connected by
Sub Atomic particles
Chemical Bonds
Negatively charged
Postively charged
electrically neutral
Electron
Proton
Neutron
Together Define atom
There are various
models of atom
Plum Pudding Model
Nuclei (plum) in the electron ocean (pudding)
Rutherford's Model
Nucleus centrally placed and e- spin around
Bohr's Model
Defined Energy Orbits of electrons
Quantum mechanical Model
Defined atom as electron cloud around nucleus
to form molecules
Based on strength
bonds are of two types
Strong
High energy >100 KJ
is of four types
Weak
Less energy <10 KJ
Covalent
Formed by sharing
of electron
may be Polar
or Non-Polar
Strongest in
nature
Ionic
Electrostatic
in origin
Coordinate
Sharing of
lone pairs
Metallic
Sharing of
one e by
many atoms
Hydrogen
Bond
A special case of
dipole-dipole
interaction
van der waals
Weakest
Three types
Kessom,Debye and London
Hydrophobic
Result from entropic
stabilization
of solvent

QUESTIONS FROM PREVIOUS EXAMS

Q1: Which of the following non-covalent interaction between two non-bonded atoms A and B is most sensitive to the distance between them? **[CSIR June 2012]**

a. A and B are permanent dipoles and are involved in salt bridges

b. A and B are fully ionized and are involved in salt bridges

c. A and B are uncharged and repel each other

d. A and B are uncharged and attracted each other]

Solution: Van der Waals interactions at a distance below 5 Å become highly repulsive and the magnitude of these repulsive van-der-waals interactions is related inversely to 12th power of distance between two charges (or nuclei of atoms) therefore c is correct answer.

Q2: On the molar scale which of the following interactions in a non-polar environment provides highest contribution to the bio-molecule? **[CSIR NET Dec 2011]**

a. Van der Waals interaction **b.** Hydrogen bonding

c. Salt bridge **d.** Hydrophobic interaction

Solution: Hydrogen Bonds are associated with water (in hydrophillic environment), Salt bridges are also electrostatic in nature and therefore depend upon the hydrophillic environment. Hydrophobic interaction are also a result of repulsion from hydrophillic groups. Van der waals interactions are the only interactions that provide highest contribution to biomolecule.

Q3: If van der Waals interaction is described by the following relation,

$$\Delta G_{Van} = \frac{A}{r^{12}} - \frac{B}{r^{6}} + \frac{q_1 q_2}{r}$$

Where ΔG_{Van} is the free energy of the van der Waals interactions, A and B are constants, r is the distance between two non-bonded atoms 1 and 2, and q_1 and q_2 are partial charges on the dipoles 1 and 2. In this relation, the parameter A describes: **[CSIR NET Dec 2011]**

a. electron shell attraction **b.** electron shell repulsion

c. dipole-dipole attraction **d.** dipole-dipole repulsion

Solution: In this formula the net Gibbs free energy formula for Van der waals interaction is given, in which the initial two components are called as Lenard Jones potential or L-J potential. This is expressed in a simplified form as $\Delta G = A/r^{12} - B/r^{6}$ and hence, is also known as 6–12 potential. A/r^{12} is predominant at short distances and hence, **represents the short-range repulsive potential** due to overlap of electron orbitals and B/r^{6} is dominant at longer distance and hence, is the long range attractive potential.

Q4: In proteins, hydrogen bonds form as follows: Donor (D)-H---Acceptor (A). Hydrogen bond is more favorable if the angle between D-H and A is **[CSIR-NET 2014]**

a. $<90°$ **b.** 180°

c. $>180°$ **d.** 120°

Solution: The angle between the D-H bond and the H---A hydrogen bond should be close to 180° for a strong hydrogen bond, hence b is correct answer.

HIGH YIELDING FACTS

- According to Bohr and Bury, the maximum number of electrons that can be accommodated in any energy level of an atom is given by the formula $2n^2$, where 'n' represents the number of the energy level.
- In order to exist independently by itself an atom must have eight electrons in its outermost shell two electrons if there is only one shell. This is the octet rule.
- Atoms try to attain stable configuration (completing their outermost shell) either by losing, gaining or sharing electrons.
- Coordinate bond is a covalent bond in which the shared pair of electrons is contributed by only one of the two atoms.
- Theories of chemical bonds go back a long time. One of the first was developed by Roman poet Lucretius (95-55 BC), author of *De Rerum Natura* (title means "on the nature of things").
- Van der Waals forces were named in honor of the Dutch physicist Johannes Diderik van der Waals (1837–1923), who investigated the weak non-chemical bond forces between molecules.
- The Stern–Gerlach experiment of 1922 provided further evidence of the quantum nature of the atom. When a beam of silver atoms was passed through a specially shaped magnetic field, the beam was split based on the direction of an atom's angular momentum, or spin.
- The electron is by far the least massive of these particles at 9.11×10^{-31} kg, with a negative electrical charge and a size that is too small to be measured using available techniques.
- Protons have a positive charge and a mass 1,836 times that of the electron, at 1.6726×10^{-27} kg. The number of protons in an atom is called its atomic number.
- Neutrons have no electrical charge and have a free mass of 1,839 times the mass of the electron, or 1.6929×10^{-27} kg, the heaviest of the three constituent particles.
- In the Standard Model of physics, electrons are truly elementary particles with no internal structure. However, both protons and neutrons are composite particles composed of elementary particles called quarks.
- There are two types of quarks in an atom, each having a fractional electric charge. Protons are composed of two up quarks (each with charge $+2/3$) and one down quark (with a charge of $-1/3$). Neutrons consist of one up quark and two down quarks.
- The quarks are held together by the strong interaction (or strong force), which is mediated by gluons. The protons and neutrons, in turn, are held to each other in the nucleus by the nuclear force.

References, Suggested readings and credits for this chapter are given at the end of this book