1. Details of Module and its structure

Module Detail		
Subject Name	Chemistry	
Course Name	Chemistry 01 (Class XI, Semester - 1)	
Module Name/Title	States of Matter: Part 1	
Module Id	kech_10501	
Pre-requisites	Classification of states of matter (Solid, Liquid and Gas)	
Objectives	 After going through this module, the learner will be able to: Explain the existence of different states of matter, Understand the intermolecular forces and thermal energy of particles of different states of matter. Understand the general properties of Gaseous state. 	
Keywords	Intermolecular forces, Van der Waals forces, Dispersion forces, Dipole-dipole interactions, Induced dipole interaction, Hydrogen bond, Thermal energy, Gaseous state	

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1. **General Introduction:** In previous units we have learnt about the properties related to single particle of matter, such as atomic size, ionization enthalpy, electronic charge density, molecular shape and polarity, etc. Most of the observable characteristics of chemical systems with which we are familiar represent bulk properties of matter, i.e., the properties associated with a collection of a large number of atoms, ions or molecules. For example, an individual molecule of a liquid does not boil but the bulk boils. A Collection of water molecules has wetting properties; individual molecules do not wet. Water can exist as ice, which is a solid; it can exist as liquid; or it can exist in the gaseous state as water vapour or steam (Fig.1).



Fig. 1. Different states of water (H₂O).

(Source:http://www.balticnet-plasmatec.org/wpcontent/uploads/2014/05/what is plama.jpg)

Physical properties of ice, water and steam are very different. In all the three states of water chemical composition of water remains the same i.e., H₂O. Characteristics of the three states

of water depend on the energies of molecules and on the manner in which water molecules aggregate.

The snowflake falls, yet lays not long Its feath'ry grasp on Mother Earth Ere Sun returns it to the vapors Whence it came, Or to waters tumbling down the rocky slope

The above pleasing lines were delivered by an american radio and television announcer, *Rod O'Connor* which delightfully explain the phenomenon of inter-conversion of different

states of water using natural process. Same is true for other substances also.

Chemical properties of a substance do not change with the change of its physical state; but rate of chemical reactions do depend upon the physical state. Many times in calculations while dealing with data of experiments we require knowledge of the state of matter. Therefore, it becomes necessary for a chemist to know the physical laws which govern the behaviour of matter in different states. In this unit, we will learn more about these three different physical states of matter more particularly liquid and gaseous states. To begin with, it is necessary to understand the nature of intermolecular forces, molecular interactions and effect of thermal energy on the motion of particles because a balance between these determines the state of a substance.

1. **Intermolecular Forces:** Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds.

Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837 - 1923) (Fig. 2), who explained the deviation of real gases from the ideal behaviour through these forces. We will learn about this later in this unit. van der Waals forces vary considerably in magnitude and include dispersion forces or London forces, dipole-dipole forces, and dipole-induced dipole forces. A particularly strong type of dipole-dipole interaction is hydrogen bonding. Only a few elements can participate in hydrogen bond formation, therefore it is treated as a separate category.



Fig. 2. Dutch scientist Johannes van der Waals (1837 - 1923).

(Source: https://upload.wikimedia.org/wikipedia/commons/3/32/Van_der_Waals.jpg)

At this point, it is important to note that attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces. We will now learn about different types of van der Waals forces. The foreword of different intermolecular forces of attraction is shown in a tabular form (Table 1).

Intermolecular	formed between the	Examples:
forces	atoms/molecules or ions	
Ion - Dipole	An ion and a polar molecule	Na^{+} (aqueous): Na^{+} and H_2O
Hydrogen Bond	Molecules which have H	H_2O and H_2O , H_2O and alcohol
	directly bonded to N, O or F	(ethyl alcohol C_2H_5OH), NH_3 and
	atoms	H ₂ O
Dipole - Dipole	Two polar molecules	CH ₃ Br and ICl, CH ₃ Br and H ₂ O
Ion – induced dipole	An ion and a non polar	Fe^{2+} and O_2
	molecule	
Dipole – induced	A polar molecules and a non	HCl and Cl ₂
dipole	polar molecule	
London forces or	Two non polar molecules	CH_4 and CH_4 , F_2 and F_2 , CH_4 and
Dispersion forces		F ₂

Table 1. Summary of the inter-molecular forces of attraction.

2. **Dispersion Forces or London Forces:** Atoms and non polar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other (Fig. 3 a). It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical i.e., the charge cloud is more on one side than the other (Fig. 3 (b) and (c)). This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient

dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'.



Fig. 3. Dispersion forces or London forces between atoms.

(Source: Fig 5.1, Chapter 5: States of matter, page no.133, Class XI Textbook, NCERT) The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as London force. Another name for this force is dispersion force. These forces are always attractive and interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., $1/r^6$ where r is the distance between two particles). These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle. For larger molecules, due to more dispersed electron clouds between atoms, polarizability is large and resulting London or dispersion forces become more prominent. For example, in a halogen family the size of the molecule increases from fluorine (F_2) to iodine (I_2) and hence resultant london or dispersion forces family. Due increases down the to this reason. Fluorine and chlorine are found to be gases at room temperature, bromine is a liquid,

and iodine is a solid. The London or Dispersion forces are also directly proportional to the area of the surface in contact. Greater surface area means closer interaction between different molecules.

3. Dipole - Dipole Forces: Dipole-dipole forces act between the molecules possessing permanent dipole. Partial charges are always less than the unit electronic charge (1.610⁻¹⁹ C). The polar molecules interact with neighbouring molecules (Fig. 4).





(Source: http://www.buzzle.com/images/diagrams/dipole-dipole-interactions.jpg)

Fig 5 (a) shows electron cloud distribution in the dipole of hydrogen chloride and Fig. 5 (b) shows dipole-dipole interaction between two HCl molecules. This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved. The attractive force decreases with the increase of distance between the dipoles. As in the above case here also, the interaction energy is inversely proportional to distance between polar molecules. Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to $1/r^3$ and that between rotating polar molecules is proportional to $1/r^6$, where r is the distance between polar molecules. Besides dipole - dipole interaction, polar molecules can interact by London forces also. Thus cumulative effect is that the total of intermolecular forces in polar molecules increases.



Fig. 5. (a) Distribution of electron cloud in HCl – a polar molecule, (b) Dipole – dipole interaction between two HCl molecules.

(Source: Fig 5.2, Chapter 5: States of matter, page no.134, Class XI textbook NCERT)

4. Dipole – Induced Dipole Forces: This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud (Fig. 6). Thus an induced dipole is developed in the other molecule. In this case also interaction energy is proportional to 1/r⁶ where r is the distance between two molecules. Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule. We have already learnt in Unit 4 that molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.



Fig. 6. Dipole – induced dipole interaction between permanent dipole – induced dipole. (Source: Fig 5.3, Chapter 5: States of matter, page no.134, Class XI textbook, NCERT) The example for dipole – induced dipole interaction is interaction between xenon and water molecule (Fig. 7). Another example of such interaction between permanent dipole and induced dipole is the interaction between HCl and Ar.



Fig. 7. An example of Dipole – induced dipole interaction. (Source: http://cdn1.askiitians.com/Images/2014917-162813349-3592-Untitled.png)

The dipole – induced dipole interactions are weaker than the interaction between permanent dipoles. In this case also cumulative effect of dispersion forces and dipole-induced dipole interactions exists.

5. **Hydrogen bond:** As already mentioned in earlier section; this is special case of dipoledipole interaction. We have already learnt about this in Unit 4. This is found in the molecules in which highly polar N–H, O–H or H–F bonds are present. Although hydrogen bonding is regarded as being limited to N, O and F; but species such as Cl may also participate in hydrogen bonding. Energy of hydrogen bond varies between 10 to 100 kJ. mol⁻¹. This is quite a significant amount of energy; therefore, hydrogen bonds are powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids. Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of other molecule. Following diagram shows the formation of hydrogen bond.

$$\begin{split} \delta^+ & \delta^- & \delta^+ & \delta^- \\ H - F & \cdots & H - F \end{split}$$

The pictorial representation of water molecules showing hydrogen bonding is shown in Fig. 8. The dashed lines between hydrogen of one water molecule and oxygen of the another molecule illustrate the hydrogen bonding.



Fig. 8. Water molecules: an example of hydrogen bonding.

(Source: <u>https://upload.wikimedia.org/wikipedia/commons/0/0b/Miri9.jpg</u>) As we studied in previous unit, the hydrogen bonding is of two types:

- (1) Inter-molecular hydrogen bonding
- (2) Intra-molecular hydrogen bonding

Intermolecular hydrogen bonding is the interaction between two different molecules (as shown in Fig. 8). The examples for intermolecular hydrogen bonding are HF molecules, alcohol and water molecules. On the other hand, intramolecular hydrogen bonding is formed when hydrogen atom is in between the two highly electronegative (F, O, N) atoms present

within the same molecule. For example, o-nitro phenol exhibits both inter- as well as intramolecular hydrogen bonding (Fig. 9).



Fig. 9. (a) inter-molecular hydrogen bonding and (b) intra-molecular hydrogen bonding in o-Nitro Phenol.

(Source: (a) <u>http://image.tutorvista.com/content/chemical-bonding/intermolecular-hydrogen-bond-illustration.gif</u> (b) <u>http://image.wistatutor.com/content/feed/tvcs/intramolecular-hydrogen-bond-o-nitrophenol-structure.gif</u>)

Intermolecular forces discussed so far are all attractive. Molecules also exert repulsive forces on one another. When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play. Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases. This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

6. **Thermal Energy:** Thermal energy is the energy of a body arising from motion of its atoms or molecules. Heat, temperature and thermal energy are inter-related but not the same thing. Thermal energy is directly proportional to the temperature of the substance. Also, it depends upon the matter we have. Temperature is the average kinetic energy of the particles while Thermal energy is the measure of the total kinetic energy of all the particles of the matter. For example, a glass of water can have the same temperature as a lake but the lake has much more thermal energy as lake contain more number of water molecules. Thermal energy is thus responsible for movement of particles and this movement of particles is called thermal motion. Thermal energy always moves from a hot place to a cold place. It is often measured in calories. One calorie (cal) is the amount of energy required to raise the temperature of 1 gram of substance by 1 degree Celsius (Fig. 10).



Fig. 10. Pictorial illustration for understanding the definition of Calorie (Source: <u>http://images.slideplayer.com/2/765846/slides/slide_30.jpg</u>)

Intermolecular Forces vs Thermal Interactions: We have already learnt that intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart. Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.

When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified. Predominance of thermal energy and the molecular interaction energy of a substance in three states is depicted as follows:



Predominance of thermal energy

Hence, a competition between the strength of intermolecular bonds and the thermal energy of the system depicts the difference between the different states of matter. For example, in case of water, as the temperature of the system increases, eventually the thermal energy of the water molecules becomes too large to allow these molecules to move out from the rigid structure of ice. At this point, the solid melts to form a liquid where intermolecular bonds are continuously broken and reformed as the molecules move through the liquid. With further increase in temperature, the thermal energy of the water molecules becomes so large that they move too rapidly to break intermolecular interactions and the liquid boils to form a gas where each of the particle moves more or less randomly through space (Fig. 11).



Fig. 11. Water molecules in three different states: Intermolecular forces vs Thermal energy. Source:

http://faculty.sdmiramar.edu/fgarces/zCourse/All Year/Ch100 OL/aMy FileLec/04OL Lec Notes Ch100/02 EnergyStateMatter/203 StMatter/203 pic/phasechangeexplained.gif) We have already learnt the cause for the existence of the three states of matter. Now we will learn more about gaseous and liquid states and the laws which govern the behaviour of matter in these states. We shall deal with the solid state in class XII.

7. **The Gaseous State:** This is the simplest state of matter. Throughout our life we remain immersed in the ocean of air which is a mixture of gases. We spend our life in the lowermost layer of the atmosphere called troposphere, which is held to the surface of the earth by gravitational force. The thin layer of atmosphere is vital to our life. It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc. Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure. A look at the periodic table shows that only eleven elements exist as gases under normal conditions (Fig 12).



Fig 12. Eleven elements that exists as gases

(Source: Fig 5.4, page 136, Chpater 5, Class XI textbook NCERT)

The gaseous state is characterized by the following physical properties.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible. Their behaviour is governed by same general laws, which were discovered as a result of their experimental studies. These laws are relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and mass are very important because relationships between these variables describe state of the gas. Interdependence of these variables leads to the formulation of gas laws which will be learnt in next module.

8. **Summary:** This module explained the importance of Chemistry and its domain in every sphere of life. Intermolecular forces operate between the particles of matter. These forces differ from pure electrostatic forces that exist between two oppositely charged ions. Also, these do not include forces that hold atoms of a covalent molecule together through covalent bond. Competition between thermal energy and intermolecular interactions determines the state of matter. "Bulk" properties of matter such as behaviour of gases, characteristics of solids and liquids and change of state depend upon energy of constituent particles and the type of interaction between them. At a given temperature, substances which contain strong intermolecular bonds are more likely to be solids and in other words, for a given intermolecular bond strength, the substance with higher temperature are more likely to be a gas. Chemical properties of a substance do not change with change of state, but the reactivity depends upon the physical state.

Forces of interaction between gas molecules are negligible and are almost independent of their chemical nature. Interdependence of some observable properties namely pressure, volume, temperature and mass leads to different gas laws obtained from experimental studies on gases.