

CHAPTER THIRTEEN

KINETIC THEORY

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13.1 INTRODUCTION

Boyle discovered the law named after him in 1661. Boyle, Newton and several others tried to explain the behaviour of gases by considering that gases are made up of tiny atomic particles. The actual atomic theory got established more than 150 years later. Kinetic theory explains the behaviour of gases based on the idea that the gas consists of rapidly moving atoms or molecules. This is possible as the inter-atomic forces, which are short range forces that are important for solids and liquids, can be neglected for gases. The kinetic theory was developed in the nineteenth century by Maxwell, Boltzmann and others. It has been remarkably successful. It gives a molecular interpretation of pressure and temperature of a gas, and is consistent with gas laws and Avogadro's hypothesis. It correctly explains specific heat capacities of many gases. It also relates measurable properties of gases such as viscosity, conduction and diffusion with molecular parameters, yielding estimates of molecular sizes and masses. This chapter gives an introduction to kinetic theory.

13.2 MOLECULAR NATURE OF MATTER

Richard Feynman, one of the great physicists of 20th century considers the discovery that "Matter is made up of atoms" to be a very significant one. Humanity may suffer annihilation (due to nuclear catastrophe) or extinction (due to environmental disasters) if we do not act wisely. If that happens, and all of scientific knowledge were to be destroyed then Feynman would like the 'Atomic Hypothesis' to be communicated to the next generation of creatures in the universe. Atomic Hypothesis: All things are made of atoms - little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.

Speculation that matter may not be continuous, existed in many places and cultures. Kanada in India and Democritus

Atomic Hypothesis in Ancient India and Greece

Though John Dalton is credited with the introduction of atomic viewpoint in modern science, scholars in ancient India and Greece conjectured long before the existence of atoms and molecules. In the Vaisheshika school of thought in India founded by Kanada (Sixth century B.C.) the atomic picture was developed in considerable detail. Atoms were thought to be eternal, indivisible, infinitesimal and ultimate parts of matter. It was argued that if matter could be subdivided without an end, there would be no difference between a mustard seed and the Meru mountain. The four kinds of atoms (**Paramanu** — Sanskrit word for the smallest particle) postulated were Bhoomi (Earth), Ap (water), Tejas (fire) and Vayu (air) that have characteristic mass and other attributes, were propounded. Akasa (space) was thought to have no atomic structure and was continuous and inert. Atoms combine to form different molecules (e.g. two atoms combine to form a diatomic molecule *dyavanuka*, three atoms form a *tryanuka* or a triatomic molecule), their properties depending upon the nature and ratio of the constituent atoms. The size of the atoms was also estimated, by conjecture or by methods that are not known to us. The estimates vary. In *Lalitavistara*, a famous biography of the Buddha written mainly in the second century B.C., the estimate is close to the modern estimate of atomic size, of the order of 10^{-10} m.

In ancient Greece, Democritus (Fourth century B.C.) is best known for his atomic hypothesis. The word 'atom' means 'indivisible' in Greek. According to him, atoms differ from each other physically, in shape, size and other properties and this resulted in the different properties of the substances formed by their combination. The atoms of water were smooth and round and unable to 'hook' on to each other, which is why liquid /water flows easily. The atoms of earth were rough and jagged, so they held together to form hard substances. The atoms of fire were thorny which is why it caused painful burns. These fascinating ideas, despite their ingenuity, could not evolve much further, perhaps because they were intuitive conjectures and speculations not tested and modified by quantitative experiments - the hallmark of modern science.

in Greece had suggested that matter may consist of indivisible constituents. The scientific 'Atomic Theory' is usually credited to John Dalton. He proposed the atomic theory to explain the laws of definite and multiple proportions obeyed by elements when they combine into compounds. The first law says that any given compound has, a fixed proportion by mass of its constituents. The second law says that when two elements form more than one compound, for a fixed mass of one element, the masses of the other elements are in ratio of small integers.

To explain the laws Dalton suggested, about 200 years ago, that the smallest constituents of an element are atoms. Atoms of one element are identical but differ from those of other elements. A small number of atoms of each element combine to form a molecule of the compound. Gay Lussac's law, also given in early 19th century, states: When gases combine chemically to yield another gas, their volumes are in the ratios of small integers. Avogadro's law (or hypothesis) says: Equal volumes of all gases at equal temperature and pressure have the same number of molecules. Avogadro's law, when combined with Dalton's theory explains Gay Lussac's law. Since the elements are often in the form of molecules, Dalton's atomic theory can also be referred to as the molecular theory

of matter. The theory is now well accepted by scientists. However even at the end of the nineteenth century there were famous scientists who did not believe in atomic theory !

From many observations, in recent times we now know that molecules (made up of one or more atoms) constitute matter. Electron microscopes and scanning tunnelling microscopes enable us to even see them. The size of an atom is about an angstrom (10^{-10} m). In solids, which are tightly packed, atoms are spaced about a few angstroms (2 Å) apart. In liquids the separation between atoms is also about the same. In liquids the atoms are not as rigidly fixed as in solids, and can move around. This enables a liquid to flow. In gases the interatomic distances are in tens of angstroms. The average distance a molecule can travel without colliding is called the **mean free path**. The mean free path, in gases, is of the order of thousands of angstroms. The atoms are much freer in gases and can travel long distances without colliding. If they are not enclosed, gases disperse away. In solids and liquids the closeness makes the interatomic force important. The force has a long range attraction and a short range repulsion. The atoms attract when they are at a few angstroms but repel when they come closer. The static appearance of a gas

is misleading. The gas is full of activity and the equilibrium is a dynamic one. In dynamic equilibrium, molecules collide and change their speeds during the collision. Only the average properties are constant.

Atomic theory is not the end of our quest, but the beginning. We now know that atoms are not indivisible or elementary. They consist of a nucleus and electrons. The nucleus itself is made up of protons and neutrons. The protons and neutrons are again made up of quarks. Even quarks may not be the end of the story. There may be string like elementary entities. Nature always has surprises for us, but the search for truth is often enjoyable and the discoveries beautiful. In this chapter, we shall limit ourselves to understanding the behaviour of gases (and a little bit of solids), as a collection of moving molecules in incessant motion.

13.3 BEHAVIOUR OF GASES

Properties of gases are easier to understand than those of solids and liquids. This is mainly because in a gas, molecules are far from each other and their mutual interactions are negligible except when two molecules collide. Gases at low pressures and high temperatures much above that at which they liquefy (or solidify) approximately satisfy a simple relation between their pressure, temperature and volume given by (see Ch. 11)

$$PV = KT \quad (13.1)$$

for a given sample of the gas. Here T is the temperature in kelvin or (absolute) scale. K is a constant for the given sample but varies with the volume of the gas. If we now bring in the idea of atoms or molecules then K is proportional to the number of molecules, (say) N in the sample. We can write $K = Nk$. Observation tells us that this k is same for all gases. It is called Boltzmann constant and is denoted by k_B .

$$\text{As } \frac{P_1 V_1}{N_1 T_1} = \frac{P_2 V_2}{N_2 T_2} = \text{constant} = k_B \quad (13.2)$$

if P , V and T are same, then N is also same for all gases. This is Avogadro's hypothesis, that the number of molecules per unit volume is same for all gases at a fixed temperature and pressure. The number in 22.4 litres of any gas is 6.02×10^{23} . This is known as Avogadro number and is denoted by N_A . The mass of 22.4 litres of any gas is equal to its molecular weight in grams at S.T.P (standard temperature 273 K and pressure 1 atm). This amount of substance is called a mole (see Chapter 2 for a more precise definition). Avogadro had guessed the equality of numbers in equal volumes of gas at a fixed temperature and pressure from chemical reactions. Kinetic theory justifies this hypothesis.

The perfect gas equation can be written as

$$PV = \mu RT \quad (13.3)$$

where μ is the number of moles and $R = N_A k_B$ is a universal constant. The temperature T is absolute temperature. Choosing kelvin scale for



John Dalton (1766- 1844)

He was an English chemist. When different types of atoms combine, they obey certain simple laws. Dalton's atomic theory explains these laws in a simple way. He also gave a theory of colour blindness.

Amedeo Avogadro (1776 - 1856)

He made a brilliant guess that equal volumes of gases have equal number of molecules at the same temperature and pressure. This helped in understanding the combination of different gases in a very simple way. It is now called Avogadro's hypothesis (or law). He also suggested that the smallest constituent of gases like hydrogen, oxygen and nitrogen are not atoms but diatomic molecules.

