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CHAPTER 1

THE GASEOUS STATE

Experiment 1–1

Place some ammonium chloride, litmus papers and asbestos wool in a long test-tube as shown in Fig 1. Gently warm the whole tube and heat the ammonium chloride more strongly. Note and explain the behaviour of the litmus papers.

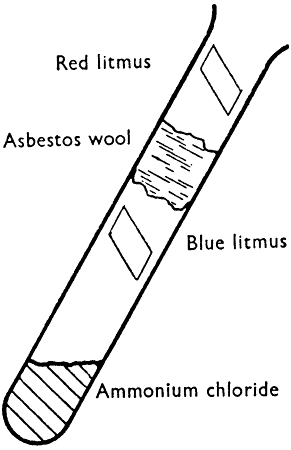

Fig. 1

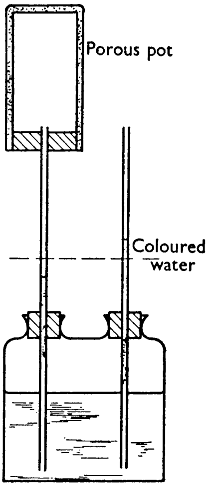

Fig. 2

Experiment 1–2

Set up the apparatus shown in Fig. 2. Displace the air from a large beaker with coal-gas or hydrogen, covering the mouth of the beaker with a card. Invert the beaker, remove the card and quickly place the beaker over the porous pot attached to the Woulfe's bottle. Note and interpret the behaviour of the coloured liquid in the tubes. Remove the beaker and again note what happens to the liquid. Repeat the experiment, using carbon dioxide in the beaker instead of hydrogen.

Experiment 1–3

Fill a gas jar with nitrogen peroxide or sulphur dioxide and invert it over a jar of air. After a few seconds, test for the presence of the heavier gas in the lower jar. Repeat the experiment, but place the jar of air above the jar containing the heavy gas. Test for the presence of the latter in the upper jar after (*a*) a few seconds, (*b*) a few minutes.

Experiment 1–4

Seal a little bromine in a thin glass bulb. Place it in a glass bottle fitted with a rubber stopper carrying a tap and a vaselined brass rod with which the bulb can be broken. Compare the rates of diffusion of the vapour through the bottle when (*a*) it is full of air, (*b*) the air has been pumped out.

Experiment 1–5. *Molecular motion in mercury vapour*

Prepare a Pyrex or Monax glass tube about 20 cm. long and 1 cm. internal diameter, with one end closed and the other drawn to a thick-walled constriction to be sealed off later. Place about 5 ml. of mercury in the tube and cover this with about ½ cm. of crushed glass of about 1 mm. particle size (no glass dust should be included). Clamp the tube vertically and evacuate it by means of a good vacuum pump. Warm the tube with a Bunsen burner and boil the mercury *in vacuo* for a few minutes. Then seal off the tube at the constriction. Boil the mercury and note that the glass particles gather in a cloud well above the mercury surface, buoyed up by bombardment by the mercury atoms.

THE GASEOUS STATE AND THE GAS LAWS

The above experiments illustrate one of the most striking characteristics of gases, namely, their power of diffusion. The ability of gases to mix freely and rapidly with each other, and to pass readily through many solid substances, strongly suggests that view of their inner structure which is now called the

Kinetic-Molecular Theory. This section reviews the facts upon which the theory is based and recalls the historic experiments and reasoning of Boyle and his successors.

The gaseous state was first formally recognized early in the seventeenth century by van Helmont, who introduced the name 'gas'. The Hon. Robert Boyle made the first quantitative studies of the behaviour of gases (1661). Having observed the distension of a lamb's bladder when placed under the receiver of an air-pump, he measured the changes in volume of a sample of air confined in a closed limb of a U-tube when mercury was poured into the other limb. When the volume of the enclosed air had been reduced to half its value at atmospheric pressure, he 'observed, not without delight and satisfaction', that its pressure was then 2 atm. The results of his measurements are summarized in Boyle's law: 'The volume of a certain mass of gas at a constant temperature is inversely proportional to its pressure.'

The effect of heat on the volume of a given mass of gas was observed by Priestley, Cavendish and Charles, and, about 15 years later (1802), by Dalton and Gay Lussac. Priestley concluded from 'a very coarse experiment' that 'fixed and common air expand alike with the same degree of heat'. Gay Lussac published the relation, known alternatively as 'Charles's law' or 'Gay Lussac's law', 'The volume of a certain mass of gas at constant pressure increases linearly with the temperature, and the increase of a given volume per degree rise in temperature is the same for all gases'. The discovery embodied in the latter part of the statement, i.e. that all gases have the same coefficient of expansion, has been of far-reaching consequence, as shown in the next paragraph.

THE ABSOLUTE SCALE OF TEMPERATURE

When graphs showing the effect of temperature change on the volume of a given mass of any gas are extrapolated, they all cut the temperature axis at the same point, namely, at about −273° C., no matter what the nature of the gas. If this temperature is taken as the zero of a new scale of temperatures, it is clear that the volume of a given mass of gas will be directly proportional to its temperature measured on this new scale.

The zero on the Centigrade scale was an arbitrarily chosen temperature, namely, the melting-point of ice, but this new zero emerges from an experimental study of the behaviour of gases as something fundamental and inherent in the nature of matter. It is called the 'Absolute Zero', and the new scale is called the 'Absolute Scale' of temperature. One degree absolute is the same difference of temperature as one degree Centigrade. The laws of Boyle and Gay Lussac may now be combined in the form $pv = kT$, where k is a constant and T is the temperature on the absolute scale.

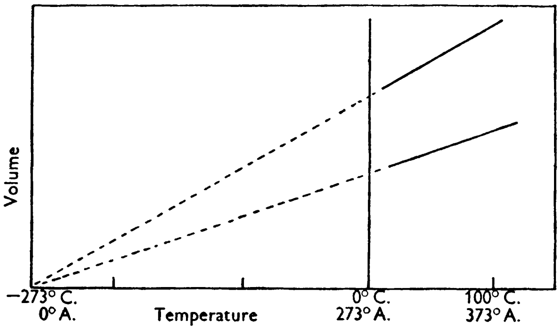

Fig. 3

THE KINETIC THEORY OF GASES

Sir Isaac Newton (1680) believed in an atomic theory of matter (see Chapter 4) and held that the atoms in the gaseous state were widely spaced from each other. He attributed the pressure exerted by a gas to the mutual repulsion of its constituent particles. On reducing the space containing the gas, the particles were forced nearer together, the force of repulsion increased and an increase in pressure was thereby produced. The kinetic-molecular theory of gases, which was developed largely from the ideas of Bernoulli (1738), pictures a gas as consisting of widely separated particles of small volume compared with the space occupied by the gas. The particles, to which the term 'molecules' was applied, are in a state of continuous and rapid random motion. The pressure exerted by the gas on the walls of the containing vessel is due to the bombardment of the walls of the vessel by the molecules. Reduction of the volume (at constant temperature) causes an increase in the frequency of bombardment and hence an increase in pressure. If the gas is heated, the heat energy is converted into kinetic energy of the molecules and, if the volume is constant, the pressure consequently rises.

In its simple form, the theory assumes that the molecules are spheres, that they exert no forces on each other, and that their collisions with each other and with the walls of the containing vessel are perfectly elastic. On these assumptions an expression for the pressure exerted by a gas can be derived as follows.

Consider n particles, each of mass m, contained in a cube of side, length l. Since the particles are in random motion, there is a normal probability distribution of velocities among them (see p. 8). Consider a particle moving with a velocity c in some arbitrary direction. Its velocity can be resolved into three components u_x, u_y and u_z, normal to the faces of the cube. Then

$$u_x^2+u_y^2+u_z^2=c^2.$$

Each time this particle collides with a wall of the cube normal to the x-axis, its momentum changes from mu_x to $-mu_x$, i.e. there is a change in momentum of $2mu_x$. Before colliding with the same wall again, it must travel a distance of $2l$; therefore it will undergo $u_x/2l$ collisions in unit time. Its rate of change of momentum at the wall is thus $\dfrac{2mu_xu_x}{2l}$.

If c^2 represents a mean value for all the particles, the force exerted by n molecules on one wall is $\dfrac{nmu_x^2}{l}$. The pressure exerted on the wall of the cube is therefore $\dfrac{nmu_x^2}{l^3}$. Since there is no drift of the gas in any particular direction, $u_x=u_y=u_z$, and therefore $u_x^2=\frac{1}{3}c^2$. If v is the volume of the cube (l^3), the pressure p is given by

$$p=\frac{nm}{v}\tfrac{1}{3}c^2.$$

The total mass of gas, M, is mn, hence

$$p=\frac{1}{3}\frac{M}{v}c^2.$$

The density of the gas, ρ, is equal to M/v, so an alternative expression for the pressure is

$$p=\tfrac{1}{3}\rho c^2.$$

It should be noted that this expression results from the application of the principles of mechanics to the hypotheses of the kinetic-molecular theory. It is therefore very interesting to observe how the relationships between the volume, pressure, and temperature of a given mass of gas observed by Boyle and Charles are consistent with the above equation:

Boyle's law. At constant temperature, the mean kinetic energy of the molecules is constant, i.e. for a given mass, M, of gas, $\frac{1}{2}Mc^2$ is constant. Therefore pv is constant.

Charles's law. At constant pressure, v is proportional to $\frac{1}{2}Mc^2$, so the latter is directly proportional to the absolute temperature.

Graham's Law of Diffusion also follows, for if two gases are at the same temperature and pressure, the rates of free diffusion, assumed to be proportional to the mean velocity of the molecules, will be inversely proportional to the square roots of the densities of the gases.

The kinetic-molecular theory also embraces the important hypothesis of Avogadro, namely, that equal volumes of all gases at the same temperature and pressure contain the same number of molecules. (The truth of Avogadro's hypothesis had been so well established by chemists that Clausius, in 1857, used it as the basis of his proof that temperature is measured by kinetic energy.) For equal volumes of two gases at the same pressure, $n_1m_1c_1^2=n_2m_2c_2^2$. It was shown by Clerk Maxwell that, at a given temperature, the mean kinetic energy per molecule in a gas is constant, even if the masses of the molecules differ. Hence, $\frac{1}{2}m_1c_1^2=\frac{1}{2}m_2c_2^2$, and therefore $n_1=n_2$. Comparison of the densities of gases is thus a comparison of the weights of their molecules.

It is worth emphasizing that the pressure of a certain volume of gas at constant temperature is directly proportional to the number of molecules and is independent of their nature. For a quantity of gas containing n molecules, the gas laws may be written

$$p=\frac{nkT}{v},$$

where k is a constant. For that special quantity of gas called a 'gram-molecule' (i.e. the molecular weight expressed in grams) the constant R is used, and the equation becomes $p=\frac{RT}{v}$. For any other mass of gas, say x gram-molecules, the pressure will be given by $p=x\frac{RT}{v}$. For w grams of gas of molecular weight M, $p=\frac{w}{M}\frac{RT}{v}$.

An approximate value of R can be obtained from the measurement of the density of a permanent gas and a knowledge of its molecular weight. For example, the density of hydrogen at S.T.P. (273° A. and 76 cm. of mercury) is 0·090 g. per litre. Hence 1 gram-molecule (2 g.) will occupy 2/0·090 litres, and therefore $R=\frac{76\times 13{\cdot}6\times 981\times 2000}{273\times 0{\cdot}09\times 4{\cdot}2\times 10^7}$, which comes to about 2 calories per °C.

THERMAL DISSOCIATION

It is found that when certain gases (e.g. dinitrogen tetroxide) are heated at constant volume the increase in pressure is greater than would be expected if the gas laws were followed. It is clear from the expression for the pressure derived above that one possible explanation is that the number of particles present is increasing. The molecules of dinitrogen tetroxide (N_2O_4) tend to dissociate on heating into molecules of nitrogen dioxide (NO_2), so that the hot gas consists of a mixture of double and single molecules in equilibrium, the extent of the dissociation becoming greater as the temperature is raised. The degree of dissociation at any particular temperature may be found as follows.

Suppose that a fraction α of the total number of molecules present, n, has split into two parts. There will then be a total of $n(1-\alpha)+2\alpha n=(1+\alpha)n$ particles. The measured pressure, p_0, will be $(1+\alpha)$ times as great as the pressure, p_t, to be expected from the gas laws, i.e., $p_0=(1+\alpha)p_t$.

It will be noticed that the calculation of p_t requires a knowledge of the molecular weight, M, of the undissociated substance, $p_t=w/M.RT/v$.

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In practice, α is usually obtained from the density of the gas, ρ_0, and the density, ρ_t, it would have at the same temperature and pressure if no dissociation had occurred.

$$\rho_t=(1+\alpha)\rho_0 \quad \text{and thus} \quad \alpha=\frac{\rho_t-\rho_0}{\rho_0}.$$

Real Gases

The gas laws will only be expected to hold for a gas of which the assumptions of the kinetic theory are true. Such a gas is called an 'ideal gas'. The behaviour of real gases deviates from the gas laws, the deviations being due mainly to the fact that real molecules exert attractive forces on each other, and also that the volume of the molecules of a real gas is finite. As would be expected, the deviations become larger at higher pressures and lower temperatures, when the molecules are closer together. The behaviour of real gases has been expressed by various equations, of which the best known is that of Van der Waals:

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT.$$

The constant b makes allowance for the volume of the molecules. The existence of attractive forces between the molecules renders the pressure exerted by a real gas less than that for an ideal gas under the same conditions, so a term, a/v^2, is added to the measured pressure and represents this 'internal pressure'.

DISTRIBUTION OF VELOCITIES AMONG THE MOLECULES

The velocity of an individual molecule is constantly changing owing to collisions; it may momentarily be zero, low, medium or high. The distribution of velocities among the molecules was calculated by Clerk Maxwell from probability laws. The result is shown in Fig. 4 for two temperatures. It is clear that at any instant, most molecules, of course, have a velocity not far removed from the most probable velocity, a few are moving very slowly and a few very fast. The kinetic-energy distribution follows the velocity distribution, as the particles are all of the same mass.

If the temperature is raised, the number of molecules of higher kinetic energy is increased, the number having the most

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probable velocity decreases. Maxwell's distribution law may be simplified to the approximate form $n/n_0 = e^{-E/RT}$, where n_0 is the total number of molecules, and n is the total number having an energy greater than any particular value E at the temperature $T°$ abs.

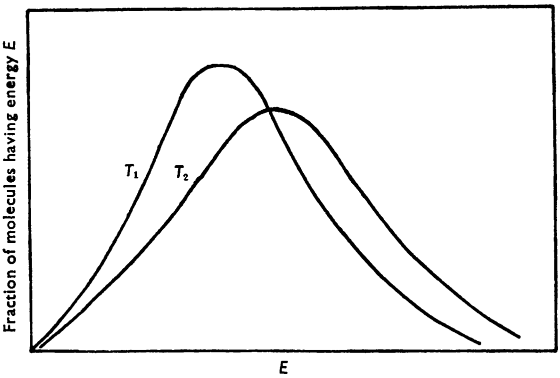

Fig. 4

Experiment 1–6. *Change of volume with pressure*

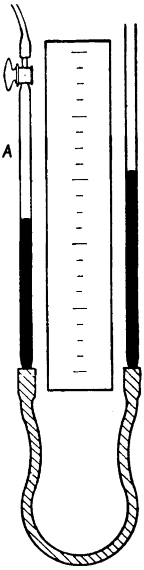

Fig. 5

The apparatus can be assembled either from nitrometer tubes, a gas burette with a stopcock, or from a burette. In the latter case, the volume of the space between the tap and the '50' mark must first be measured. Admit 50 ml. of dry air at atmospheric pressure and read the mercury levels accurately. Increase the pressure of the air in A by raising the open tube, and again read off the mercury levels. Obtain several sets of readings ranging from the lowest to the highest pressures obtainable with the apparatus. Measure the barometric pressure and calculate the pressures of the gas in A corresponding to the various measured volumes. Calculate the product pv in each case.

Now repeat the measurements on 50 ml. (at atmospheric pressure) of another gas; dry hydrogen, carbon dioxide or sulphur dioxide are suitable. The temperature should be the same for all the experiments. Are the values of pv constant for one gas? Is the value of the constant the same for the other gases?

Experiment 1–7. *Change of volume with temperature*

Draw out one end of a piece of glass tubing about 9 in. long and not more than 2 mm. internal diameter, and pass a stream of dry carbon dioxide through it for about 2 min. Seal off the end. Rapidly immerse the other end in a little pure sulphuric acid and warm the tube to expel about 20 bubbles of gas. On cooling, a pellet of acid will be drawn in. Arrange to have a pellet about $\frac{1}{2}$ in. long about half-way down the tube when it is at room temperature.

Prepare similar tubes containing air and another containing hydrogen. Fix the tubes to a centimetre scale together with a thermometer by means of rubber bands and immerse in a tall 1 litre beaker of water. Warm slowly with a small flame, keeping the water stirred. The volume of the gas is proportional to the length of tube occupied, so read the position of the bottom of the pellet on the scale and the corresponding temperature every 2 or 3 min. Plot a graph of volume against temperature, and extrapolate the straight line obtained to cut the temperature axis. It should be found that the graphs obtained are straight lines, and, for each of the gases used, cut the temperature axis at about the same point, which should be within 3 degrees of −273° C., the absolute zero.

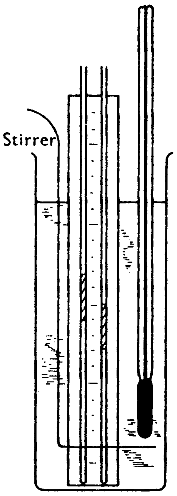

Fig. 6

Experiment 1–8. *Gas thermometers*

By means of a short length of pressure tubing A attach the bulb, which should have a volume of at least 200 ml., to a