

## chapter ten

### Gases

IN this chapter we shall be concerned with the relationship between the temperature, pressure and volume of a gas. Unlike the case of a solid or liquid this can be expressed in very simple laws, called the Gas Laws, and reduced to a simple equation, called the Equation of State. We shall also deal in this chapter with the specific heat capacities of gases.

#### THE GAS LAWS AND THE EQUATION OF STATE

##### Pressure and Volume: Boyle's Law

In 1660 Robert Boyle—whose epitaph reads 'Father of Chemistry, and Nephew of the Earl of Cork'—published the results of his experiments on the natural spring of air. In the vigorous language of the seventeenth century, he meant what we now tamely call the relationship between the pressure of air and its volume. Similar results were published in 1676 by Mariotte, who had not heard of Boyle's work. Boyle trapped air in the closed limb of a U-tube, with mercury (Fig. 10.1 (a)). He first adjusted the amount of mercury until its level was the same in each limb, so that the trapped air was at atmospheric pressure. He next

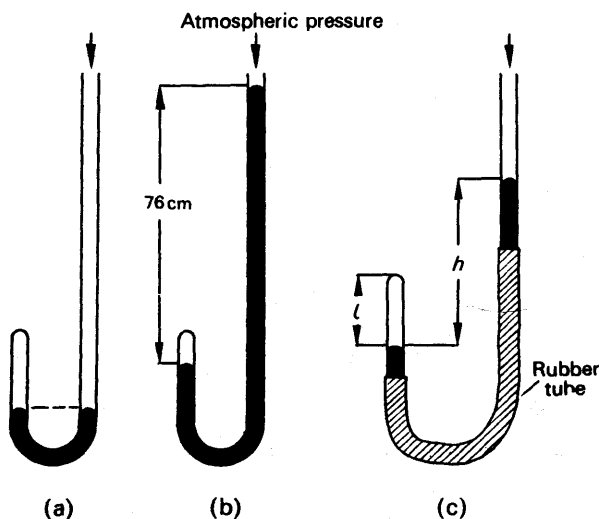


FIG. 10.1. Boyle's law apparatus.

poured in more mercury, until he had halved the volume of the trapped air (Fig. 10.1 (b)). Then 'not without delight and satisfaction' he found that the mercury in the open limb stood 740 mm above the mercury in the closed limb. Since he knew that the height of the barometer was about 740 mm of mercury, he realized that to halve the volume of his air he had had to double the pressure on it.

We can repeat Boyle's experiment with the apparatus shown in Fig. 10.1 (c); its form makes the pouring of mercury unnecessary. We set the open limb of the tube at various heights above and below the closed limb and measure the difference in level,  $h$ , of the mercury. When the mercury in the open limb is below that in the closed, we reckon  $h$  as negative. At each value of  $h$  we measure the corresponding length  $l$  of the air column in the closed limb. To find the pressure of the air we add the difference in level  $h$  to the height of the barometer,  $H$ ; their sum gives the pressure  $p$  of the air in the closed limb:

$$p = g\rho(H+h)$$

where  $g$  is the acceleration of gravity and  $\rho$  is the density of mercury.

If  $S$  is the area of cross-section of the closed limb, the volume of the trapped air is

$$V = lS.$$

To interpret our measurements we may either plot  $H+h$ , which is a measure of  $p$  against  $1/l$  or tabulate the product  $(H+h)l$ . We find that the plot is a straight line, and therefore

$$(H+h) \propto \frac{1}{l} \quad \dots \quad (1)$$

Alternatively, we find

$$(H+h)l = \text{constant}, \quad \dots \quad (2)$$

which means the same as (1).

Since,  $g$ ,  $\rho$ , and  $S$  are constants, the relationships (1) and (2) give

$$p \propto \frac{1}{V}$$

or

$$pV = \text{constant}.$$

A little later in this chapter we shall see that the pressure of a gas depends on its temperature as well as its volume. To express the results of the above experiments, therefore, we say that *the pressure of a given mass of gas, at constant temperature, is inversely proportional to its volume. This is Boyle's Law.*

### Mixture of Gases: Dalton's Law

Fig. 10.2 shows an apparatus with which we can study the pressure of a mixture of gases. A is a bulb, of volume  $V_1$ , containing air at atmospheric pressure,  $p_1$ . C is another bulb, of volume  $V_2$ , containing

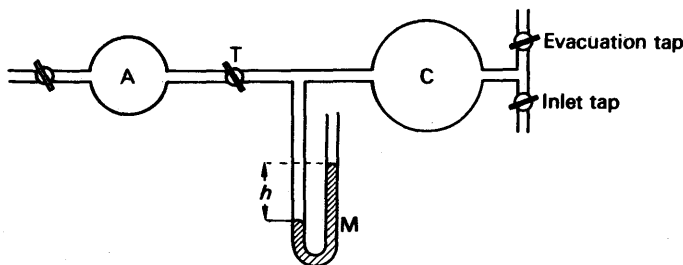


FIG. 10.2. Apparatus for demonstrating Dalton's law of partial pressures.

carbon dioxide at a pressure  $p_2$ . The pressure  $p_2$  is measured on the manometer M; in millimetres of mercury it is

$$p_2 = h + H,$$

where  $H$  is the height of the barometer. (In the same units, the air pressure,  $p_1 = H$ .)

When the bulbs are connected by opening the tap T, the gases mix, and reach the same pressure,  $p$ ; this pressure is given by the new height of the manometer. Its value is found to be given by

$$p = p_1 \frac{V_1}{V_1 + V_2} + p_2 \frac{V_2}{V_1 + V_2}.$$

Now the quantity  $p_1 V_1 / (V_1 + V_2)$  is the pressure which the air originally in A would have, if it expanded to occupy A and C; for, if we denote this pressure by  $p'$ , then  $p'(V_1 + V_2) = p_1 V_1$ . Similarly  $p_2 V_2 / (V_1 + V_2)$  is the pressure which the carbon dioxide originally in C would have, if it expanded to occupy A and C. Thus the total pressure of the mixture is the sum of the pressures which the individual gases exert, when they have expanded to fill the vessel containing the mixture.

The pressure of an individual gas in a mixture is called its *partial pressure*: it is the pressure which would be observed if that gas alone occupied the volume of the mixture, and had the same temperature as the mixture. The experiment described shows that *the pressure of a mixture of gases is the sum of the partial pressures of its constituents*. This statement was first made by Dalton, in 1801, and is called *Dalton's Law of Partial Pressures*.

### Volume and Temperature: Charles's Law

Measurements of the change in volume of a gas with temperature, at constant pressure, were published by Charles in 1787 and by Gay-Lussac in 1802. Fig. 10.3 shows an apparatus which we may use for repeating their experiments. Air is trapped by mercury in the closed limb C of the tube AC; a scale engraved upon C enables us to measure the length of the air column,  $l$ . The tube is surrounded by a water-bath W, which we can heat by passing in steam. After making the temperature uniform by stirring, we level the mercury in the limbs A and C, by pouring mercury in at A, or running it off at B. The air

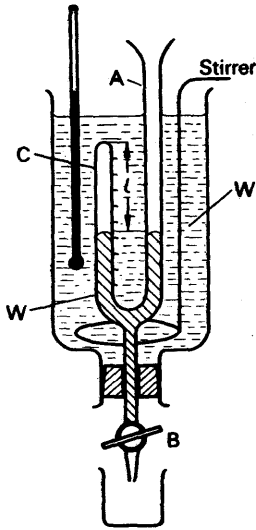


FIG. 10.3. Charles' law experiment.

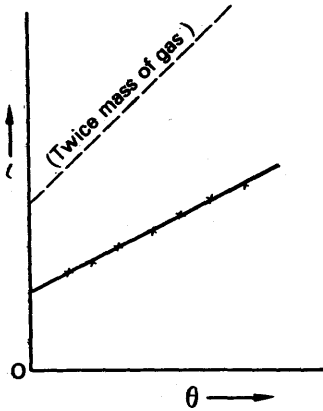


FIG. 10.4. Results of experiment.

in C is then always at atmospheric (constant) pressure. We measure the length  $l$  and plot it against the temperature,  $\theta$  (Fig. 10.4).

If  $S$  is the cross-section of the tube, the volume of the trapped air is

$$V = lS.$$

The cross-section  $S$ , and the distance between the divisions on which we read  $l$ , both increase with the temperature  $\theta$ . But their increases are very small compared with the expansion of the gas, and therefore we may say that the volume of the gas is proportional to the scale-reading of  $l$ . The graph then shows that the volume of the gas, at constant pressure, increases uniformly with its temperature. A similar result is obtained with twice the mass of gas, as indicated in Fig. 10.4.

### Expansivity of Gas (Volume Coefficient)

We express the rate at which the volume of a gas increases with temperature by defining a quantity called its *expansivity at constant pressure*,  $\alpha_p$ , or *volume coefficient*:

$$\alpha_p = \frac{\text{volume at } \theta^\circ\text{C} - \text{volume at } 0^\circ\text{C}}{\text{volume at } 0^\circ\text{C}} \times \frac{1}{\theta}$$

Thus, if  $V$  is the volume at  $\theta^\circ\text{C}$ , and  $V_0$  the volume at  $0^\circ\text{C}$ , then

$$\alpha_p = \frac{V - V_0}{V_0 \theta},$$

whence

$$V - V_0 = V_0 \alpha_p \theta,$$

or

$$V = V_0(1 + \alpha_p \theta).$$

The expansivity  $\alpha_p$  has the dimensions

$$\frac{[\text{volume}]}{[\text{volume}] \times [\text{temperature}]} = \frac{1}{[\text{temperature}]}$$

Its value is about  $\frac{1}{273}$  when the temperature is measured in  $^{\circ}\text{C}$ , and we therefore say that

$$\alpha_p = \frac{1}{273} \text{ per deg C, or } \frac{1}{273} \text{ K}^{-1}.$$

Charles, and Gay-Lussac, found that  $\alpha_p$  had the same value,  $\frac{1}{273}$ , for all gases. This observation is now called Charles's or Gay-Lussac's Law: *The volume of a given mass of any gas, at constant pressure, increases by  $\frac{1}{273}$  of its value at  $0^{\circ}\text{C}$ , for every degree Centigrade rise in temperature.*

### Absolute Temperature

Charles's Law shows that, if we plot the volume  $V$  of a given mass of any gas at constant pressure against its temperature  $\theta$ , we shall get a straight line graph A as shown in Fig. 10.5. If we produce this line back-

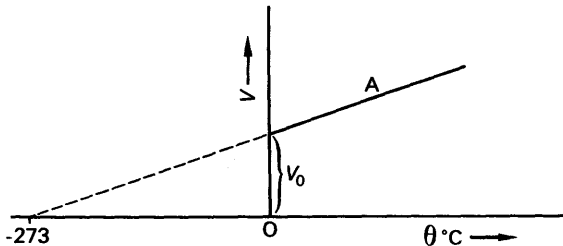


FIG. 10.5. Absolute zero.

wards, it will meet the temperature axis at  $-273^{\circ}\text{C}$ . This temperature is called the *absolute zero*. If a gas is cooled, it liquefies before it reaches  $-273^{\circ}\text{C}$ , and Charles's Law no longer holds; but that fact does not affect the form of the relationship between the volume and temperature at higher temperatures. We may express this relationship by writing

$$V \propto (273 + \theta).$$

The quantity  $(273 + \theta)$  is called the *absolute temperature* of the gas, and is denoted by  $T$ . The idea of absolute temperature was developed by Lord Kelvin, and absolute temperatures are hence expressed in degrees Kelvin:

$$TK = (273 + \theta)^{\circ}\text{C}.$$

From Charles's Law, we see that the volume of a given mass of gas at constant pressure is proportional to its absolute temperature, since

$$V \propto (273 + \theta) \propto T.$$

Thus if a given mass of gas has a volume  $V_1$  at  $\theta_1^{\circ}\text{C}$ , and is heated at constant pressure to  $\theta_2^{\circ}\text{C}$ , its new volume is given by

$$\frac{V_1}{V_2} = \frac{273 + \theta_1}{273 + \theta_2} = \frac{T_1}{T_2}.$$

### Pressure and Temperature

The effect of temperature on the pressure of a gas, at constant volume, was investigated by Amontons in 1702. His work was forgotten, however, and was re-discovered only after the work of Gay-Lussac and Charles on the effect of temperature on volume.

An apparatus for measuring the pressure of a constant volume of gas at various known temperatures is shown in Fig. 10.6 (a). The bulb B

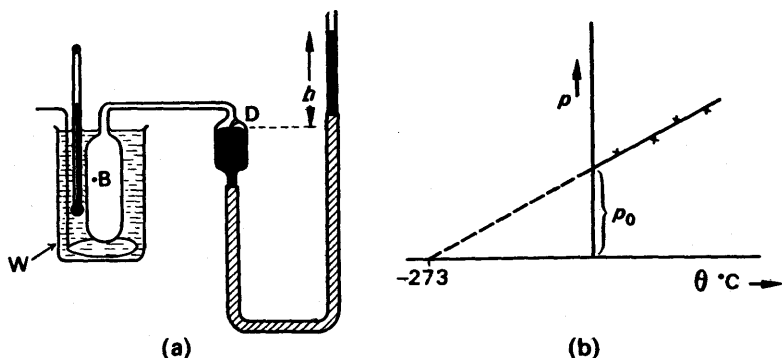


FIG. 10.6. Pressure and temperature.

contains air, which can be brought to any temperature  $\theta$  by heating the water in the surrounding bath W. When the temperature is steady, the mercury in the closed limb of the tube is brought to a fixed level D, so that the volume of the air is fixed. The difference in level,  $h$ , of the mercury in the open and closed limbs is then added to the height of the barometer,  $H$ , to give the pressure  $p$  of the gas in cm of mercury. If  $p$ ,  $(h + H)$ , is plotted against the temperature, the plot is a straight line (Fig. 10.6 (b)).

The coefficient of pressure increase at constant volume,  $\alpha_v$ , known as the *pressure coefficient*, is given by

$$\alpha_v = \frac{p - p_0}{p_0 \theta},$$

where  $p_0$  is the pressure at  $0^\circ\text{C}$ . The coefficient  $\alpha_v$ , which expresses the change of pressure with temperature, at constant volume, has practically the same value for all gases:  $\frac{1}{273} \text{K}^{-1}$ . It is thus numerically equal to the expansivity,  $\alpha_p$ . We may therefore say that, at constant volume, the pressure of a given mass of gas is proportional to its absolute temperature  $T$ , since

$$p \propto (273 + \theta).$$

$$\therefore \frac{p_1}{p_2} = \frac{273 + \theta_1}{273 + \theta_2} = \frac{T_1}{T_2}.$$

### Equality of Pressure and Volume Coefficients

If a gas obeys Boyle's Law, its coefficient of pressure change at constant volume,  $\alpha_v$ , and of volume change at constant pressure,  $\alpha_p$ ,

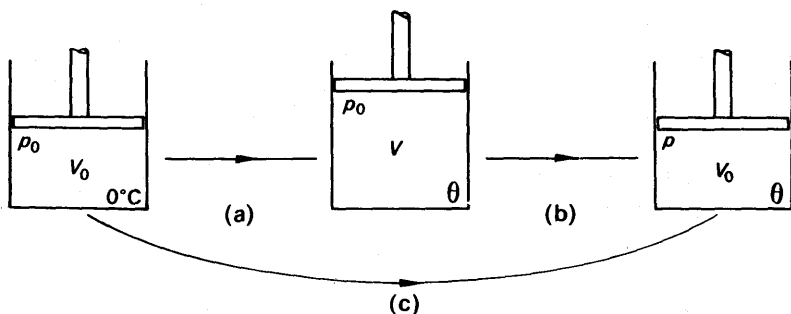


FIG. 10.7. Showing that  $\alpha_v = \alpha_p$ .

must be equal. For let us suppose that a given mass of gas is warmed at constant pressure,  $p_0$ , from  $0^\circ\text{C}$  to  $\theta^\circ\text{C}$  (Fig. 10.7 (a)). Its volume expands from  $V_0$  to  $V$ , where

$$V = V_0(1 + \alpha_p \theta).$$

Now let us suppose that it is compressed, at constant temperature, until its volume returns to  $V_0$  (Fig. 10.7 (b)). Then its pressure rises to  $p$ , where

$$\begin{aligned} pV_0 &= p_0V \\ &= p_0V_0(1 + \alpha_p \theta) \end{aligned}$$

or

$$p = p_0(1 + \alpha_p \theta) \quad (3)$$

The condition of the gas is now the same as if it had been warmed at constant volume from  $0^\circ\text{C}$  to  $\theta^\circ\text{C}$  (Fig. 10.7 (c)). Therefore

$$p = p_0(1 + \alpha_v \theta);$$

and, by equation (3), it follows that

$$\alpha_v = \alpha_p.$$

We shall see later that gases do not obey Boyle's law exactly, although at moderate pressures they do so very nearly. The difference between  $\alpha_p$  and  $\alpha_v$  provides a sensitive test for departures from Boyle's Law.

### The Equation of State

Fig. 10.8 illustrates the argument by which we may find the general relationship between pressure, volume and temperature of a given mass of gas. This relationship is called the *equation of state*.

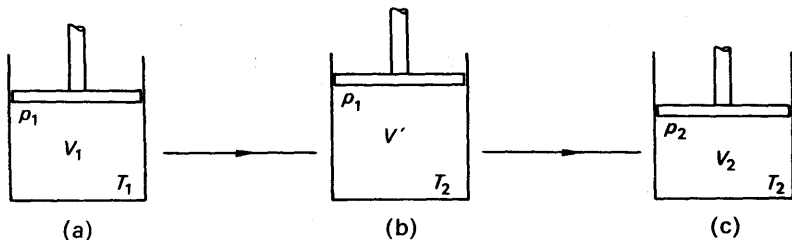


FIG. 10.8. Changing temperature and pressure of a gas.

At (a) we have the gas occupying a volume  $V_1$  at a pressure  $p_1$ , and an absolute temperature  $T_1$ . We wish to calculate its volume  $V_2$  at an absolute temperature  $T_2$  and pressure  $p_2$ , as at (c). We proceed via (b), raising the temperature of  $T_2$  while keeping the pressure constant at  $p_1$ . If  $V'$  is the volume of the gas at (b), then, by Charles's law:

$$\frac{V'}{V_1} = \frac{T_2}{T_1} \quad \dots \quad (4)$$

We proceed now to (c), by increasing the pressure to  $p_2$ , while keeping the temperature constant at  $T_2$ . By Boyle's law,

$$\frac{V_2}{V'} = \frac{p_1}{p_2} \quad \dots \quad (5)$$

Eliminating  $V'$  between equations (4) and (5), we find

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \cdot \frac{p_1}{p_2}$$

or

$$\frac{p_2 V_2}{T_2} = \frac{p_1 V_1}{T_1}$$

In general therefore,

$$\frac{pV}{T} = R \quad \dots \quad (6)$$

where  $R$  is a constant. This equation is often given in the form

$$pV = RT \quad \dots \quad (7)$$

Equation (7) is the *equation of state* for a perfect gas. The value of the constant  $R$  depends on the nature of the gas—air, hydrogen, etc.—and on the mass of the gas concerned. If we consider *unit mass* of a gas, we can denote its volume by  $V$  and write

$$pV = RT \quad \dots \quad (8)$$

$R$  is called the gas-constant for unit mass of the gas. If  $\rho$  is the density of the gas, at absolute temperature  $T$  and pressure  $p$ , then

$$\rho = \frac{1}{V},$$

and equation (8) becomes  $\frac{p}{\rho} = RT \quad \dots \quad (9)$

The volume  $V$  of an arbitrary mass  $M$  of the gas, at absolute temperature  $T$  and pressure  $p$ , is

$$V = MV;$$

therefore, by (8)  $pV = MRT;$   $\dots \quad (10)$

and, by (7),  $R = MR.$



### Magnitude of the Gas Constant

To calculate the constant  $R$  for a gas, we need to know the density of the gas at a given temperature and pressure. Very often, in dealing with gases, we specify the pressure not in newton per metre<sup>2</sup> ( $\text{N m}^{-2}$ ) but simply in millimetres of mercury. 1 mm mercury pressure is called 1 *torr*. We do so because we are concerned only with relative values. A pressure of 760 mm of mercury, which is about the average pressure of the atmosphere, is sometimes called 'standard' or 'normal' pressure. A temperature of 0°C, or 273 K, is likewise called standard or normal temperature. The conditions 273 K and 760 mm pressure are together called standard temperature and pressure (s.t.p.). A pressure of 760 mm mercury is given, in newton per metre<sup>2</sup>, by

$$p = g\rho H$$

$$= 9.8 \times 13600 \times 0.76 = 1.013 \times 10^5 \text{ N m}^{-2},$$

since  $\rho$  = mercury density = 13600 kg m<sup>-3</sup>;  $g$  = 9.8 m s<sup>-2</sup>;  $H$  = 0.76 m.

At s.t.p. the density of hydrogen is about 0.09 g/litre, or 0.09 kg m<sup>-3</sup>. The gas-constant for unit mass of hydrogen, from (9), is therefore

$$R = \frac{p}{\rho T} = \frac{1.013 \times 10^5}{0.09 \times 273}$$

$$= 4.16 \times 10^3, \text{ in the appropriate units.}$$

We will now discuss the units in which  $R$  is expressed.

### The Gas-constant Units: Work done in Expansion

The gas-constant  $R$  for an *arbitrary mass* of gas is defined by the equation

$$pV = RT$$

or

$$R = \frac{pV}{T}.$$

Its unit is therefore that of

$$\frac{\text{pressure} \times \text{volume}}{\text{temperature}}$$

In SI units, the pressure is in  $\text{N m}^{-2}$ , the volume in  $\text{m}^3$  and the temperature in K. If we are given values of  $p$ ,  $V$  and  $T$  and work out the value of  $R$ , we express it in the corresponding units. The constant per unit mass,  $R$ , for 1 kg has the unit of

$$\frac{\text{pressure} \times \text{volume}}{\text{temperature} \times \text{mass}} = \frac{\text{N m}^{-2} \times \text{m}^3}{\text{K} \times \text{kg}} = \text{N m kg}^{-1} \text{K}^{-1}$$

$$= \text{J kg}^{-1} \text{K}^{-1}.$$

since 1 newton  $\times$  1 metre = 1 joule. The gas constant may thus be expressed in the same units as specific heat capacity (p. 199).

The gas constant depends on the mass of gas. For 1 kg, the unit is

$\text{J kg}^{-1} \text{K}^{-1}$ . For 1 mole, the unit is  $\text{J mol}^{-1} \text{K}^{-1}$ ; for 1 kmol, the unit is  $\text{J kmol}^{-1} \text{K}^{-1}$ .

**Work Done.** The product of pressure and volume has the dimensions of *work*. To see this, let us imagine some gas, at a pressure  $p$ , in a cylinder fitted with a piston (Fig. 10.9).

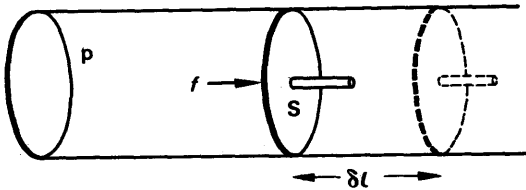


FIG. 10.9. Work done in expansion.

If the piston has an area  $S$ , the force on it is

$$f = pS.$$

If we allow the piston to move outwards a distance  $\delta l$ , the gas will expand, and its pressure will fall. But by making the distance very short, we can make the fall in pressure so small that we may consider the pressure constant. The force  $f$  is then constant, and the work done is

$$\delta W = f \cdot \delta l = pS \cdot \delta l.$$

The product  $S \cdot \delta l$  is the increase in volume,  $\delta V$ , of the gas, so that

$$\delta W = p \cdot \delta V \quad \dots \quad (11)$$

*The product of pressure and volume, in general, therefore represents work.* If the pressure  $p$  is in newton  $\text{m}^{-2}$ , and the area  $S$  is in  $\text{m}^2$ , the force  $f$  is in newtons. And if the movement  $\delta l$  is in  $\text{m}$ , the work  $f \cdot \delta l$  is in newton  $\times$  metre or *joule* (J). The increase of volume,  $\delta V$ , is in  $\text{m}^3$ . Thus the product of pressure in  $\text{N m}^{-2}$ , and volume in  $\text{m}^3$ , represents work in joules.

Consequently, if we express the pressure of a gas in newton  $\text{m}^{-2}$  and its volume in  $\text{m}^3$ , the gas-constant  $R$ ,  $= pV/T$ , is in joule (J) per degree. The constant for 1 kg,  $R$ , is in joule per kg per degree. The value of  $R$  for hydrogen, which we calculated on p. 228, is

$$R = 4.16 \times 10^3 \text{ J kg}^{-1} \text{K}^{-1} = 4.16 \text{ kJ kg}^{-1} \text{K}^{-1}.$$

**Avogadro's Hypothesis: Molecular Weight**

Amedeo Avogadro, with one simple-looking idea, illuminated chemistry as Newton illuminated mechanics. In 1811 he suggested that chemically active gases, such as oxygen, existed not as single atoms, but as pairs: he proposed to distinguish between an atom, O, and a molecule,  $\text{O}_2$ . Ampere proposed the same distinction, independently, in 1814. Avogadro also put forward another idea, now called *Avogadro's hypothesis*: that equal volumes of all gases, at the same temperature and pressure, contained equal numbers of molecules. The number of molecules in  $1 \text{ cm}^3$  of gas at s.t.p. is called Loschmidt's number; it is  $2.69 \times 10^{19}$ .

Avogadro's hypothesis became accepted in the middle of the nineteenth century. Because molecules could not be observed, their masses could not be measured directly; but they could be compared, by chemical methods. The molecular mass of a substance,  $\mu$ , was at first defined as the ratio of the mass of its molecule,  $m$ , to the mass of a hydrogen atom. Later, for the convenience of chemists, it was defined as the ratio of the molecular mass to the mass of an imaginary atom, this atom having  $\frac{1}{12}$ th the mass of a carbon atom  $^{12}\text{C}$ :

$$\mu = \frac{\text{mass of molecule}}{\frac{1}{12} \text{ mass of C-atom}} = \frac{m}{\frac{1}{12}m_{\text{C}}} = \frac{12m}{m_{\text{C}}}$$

On this scale, the mass of a hydrogen atom is 1.008 times the mass of the imaginary atom. And since the hydrogen molecule contains two atoms, its molar mass is

$$\mu_{\text{H}_2} = 2.016.$$

The unit of molecular mass,  $m_{\text{C}}/12$ , is also the unit of atomic mass; its value is  $1.66 \times 10^{-24}$  g.

### The Mole: Molar Gas-constant

The amount of a substance which contains as many elementary units as there are atoms in 0.012 kg (12 g) of carbon-12 is called a *mole*, symbol 'mol'. The number of molecules in a mole,  $N_{\text{A}}$ , is given, if  $m$  is the mass of a molecule in grammes, by

$$\mu = N_{\text{A}}m,$$

whence

$$\begin{aligned} N_{\text{A}} &= \frac{\mu}{m} = \frac{12m/m_{\text{C}}}{m} \\ &= \frac{12}{m_{\text{C}}}. \end{aligned}$$

The number of molecules per mole is thus the same for all substances. It is called Avogadro's constant, and is equal to  $6.02 \times 10^{23} \text{ mol}^{-1}$ .

From Avogadro's hypothesis, it follows that the mole of all gases, at the same temperature and pressure, occupy equal volumes. Experiment confirms this; at s.t.p. 1 mole of any gas occupies 22.4 litres. Consequently, if we denote by  $V$  the volume of 1 mole, then the ratio  $\frac{pV}{T}$  is the same for all gases. We call it the *molar gas constant*,  $R$ , and

$$R = \frac{pV}{T}.$$

$$\text{At s.t.p. } V = 22.4 \text{ litres} = 22.4 \times 10^{-3} \text{ m}^3$$

$$p = 760 \text{ mm mercury} = 1.013 \times 10^5 \text{ N m}^{-2} \text{ (p. 228)}$$

$$T = 273 \text{ K.}$$

$$\therefore R = \frac{1.013 \times 10^5 \times 22.4 \times 10^{-3}}{273}$$

$$= 8.31 \text{ J mol}^{-1} \text{ K}^{-1}.$$

The value of  $R$  is the same for the moles of all substances. If  $\mu$  g is the molar mass of a gas, the constant for 1 g is thus

$$R = \frac{R}{\mu} \quad (12)$$

### KINETIC THEORY

The kinetic theory of matter, which regards all bodies as assemblies of particles in motion—either vibrating or flying about—is an old one. Lucretius described it in the first century A.D. and Gassendi and Hooke revived it in the seventeenth century. In 1738 D. Bernoulli applied it in detail to a gas, and from it deduced Boyle's law, which was already known from experiment. Another century passed, however, before the kinetic view of a gas was fully developed—mainly by Clausius (1822–88), Boltzmann (1844–1906), and Maxwell (1831–79).

In the kinetic theory of gases, we seek to explain the behaviour of gases by considering the motion of their molecules. In particular, we suppose that the pressure of a gas is due to the molecules bombarding the walls of its container. Whenever a molecule bounces off a wall, its momentum at right-angles to the wall is reversed; the force which it exerts on the wall is equal to the rate of change of its momentum. The average force exerted by the gas on the whole of its container is the average rate at which the momentum of its molecules is changed by collision with the walls.

To find the pressure of the gas we must find this force, and then divide it by the area of the walls. The following assumptions are made to simplify the calculation:

- (a) The attraction between the molecules is negligible.
- (b) The volume of the molecules is negligible compared with the volume occupied by the gas.
- (c) The molecules are like perfectly elastic spheres.
- (d) The duration of a collision is negligible compared with the time between collisions.

#### Calculation of Pressure

Consider for convenience a cube of side  $l$  containing  $N$  molecules of gas each of mass  $m$ . Fig. 10.10. A typical molecule will have a velocity  $c$  at any instant and this will have components of  $u$ ,  $v$ ,  $w$  respectively in the direction of the three perpendicular axes  $Ox$ ,  $Oy$ ,  $Oz$  as shown. Thus  $c^2 = u^2 + v^2 + w^2$ .

Consider the force exerted on the face X of the cube due to the component  $u$ . Just before impact, the momentum of the molecule due to  $u$  is  $mu$ . After impact, the momentum is  $-mu$ , since the momentum reverses. Thus

$$\text{momentum change on impact} = mu - (-mu) = 2mu.$$

The time taken for the molecule to move across the cube to the opposite face and back to X is  $2l/u$ . Hence

$$\text{momentum change per second} = \frac{\text{momentum change}}{\text{time}}$$

$$= \frac{2mu}{2l/u} = \frac{mu^2}{l}$$

$$\therefore \text{force on X} = \frac{mu^2}{l}$$

$$\therefore \text{pressure on X} = \frac{\text{force}}{\text{area}} = \frac{mu^2}{l \times l^2} = \frac{mu^2}{l^3} \quad (\text{i})$$

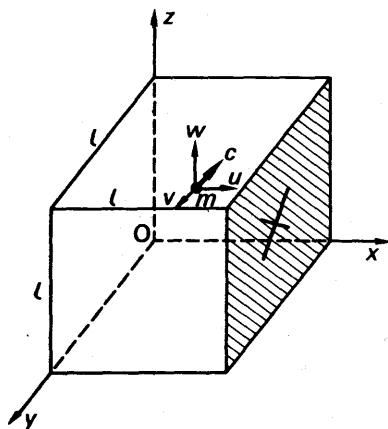


FIG. 10.10. Calculation of gas pressure.

We now take account of the  $N$  molecules in the cube. Each has a different velocity and hence a component of different magnitude in the direction  $Ox$ . If these are represented by  $u_1, u_2, u_3, \dots, u_N$ , it follows from (i) that the total pressure on X,  $p$ , is given by

$$p = \frac{mu_1^2}{l^3} + \frac{mu_2^2}{l^3} + \frac{mu_3^2}{l^3} + \dots + \frac{mu_N^2}{l^3}$$

$$= \frac{m}{l^3}(u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2) \quad (\text{ii})$$

Let the symbol  $\bar{u}^2$  represent the average or mean value of all the squares of the components in the  $Ox$  direction, that is,

$$\bar{u}^2 = \frac{u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2}{N}$$

Then 
$$N\bar{u}^2 = u_1^2 + u_2^2 + u_3^2 + \dots + u_N^2.$$

Hence, from (ii),

$$p = \frac{Nmu^2}{l^3} \dots \dots \dots \quad (iii)$$

Now with a large number of molecules of varying speed in random motion, the mean square of the component speed in any one of the three axes is the *same*.

$$\therefore \bar{u}^2 = \bar{v}^2 = \bar{w}^2.$$

But, for each molecule,  $c^2 = u^2 + v^2 + w^2$ , so that the mean square  $\bar{c}^2$  is given by  $\bar{c}^2 = \bar{u}^2 + \bar{v}^2 + \bar{w}^2$ .

$$\therefore \bar{u}^2 = \frac{1}{3}\bar{c}^2.$$

Hence, from (iii),

$$p = \frac{1}{3} \frac{Nmc^2}{l^3}.$$

The *number of molecules per unit volume*,  $n$ , =  $N/l^3$ . Thus we may write

$$p = \frac{1}{3} nmc^2 \dots \dots \dots \quad (13)$$

If  $n$  is in molecules per metre<sup>3</sup>,  $m$  is in kilogramme and  $c$  in metre per second, then the pressure  $p$  is in *newton per metre*<sup>2</sup> ( $N\ m^{-2}$ ).

It should be carefully noted that the pressure  $p$  of the gas depends on the 'mean square' of the speed. This is because (a) the momentum change at a wall is proportional to  $u$ , as previously explained, and (b) the time interval before this change is repeated is *inversely*-proportional to  $u$ . Thus the rate of change of momentum is proportional to  $u \div 1/u$  or to  $u^2$ . Further, the mean-square speed is *not* equal to the square of the average speed. As an example, let us suppose that the speeds of six molecules are, 1, 2, 3, 4, 5, 6 units. Their mean speed is

$$\bar{c} = \frac{1+2+3+4+5+6}{6} = \frac{21}{6} = 3.5,$$

and its square is 
$$(\bar{c})^2 = 3.5^2 = 12.25.$$

Their mean square speed, however is

$$\bar{c}^2 = \frac{1^2+2^2+3^2+4^2+5^2+6^2}{6} = \frac{91}{6} = 15.2.$$

This differs by about 25 per cent from the square of the mean speed.

In our calculation, we assumed that molecules of a gas do not collide with other molecules as they move to-and-fro across the cube. If,

however, we assume that their collisions are perfectly elastic, both the kinetic energy and the momentum are conserved in them. The average momentum with which all the molecules strike the walls is then not changed by their collisions with one another; what one loses, another gains. The important effect of collisions between molecules is to distribute their individual speeds; on the average, the fast ones lose speed to the slow. We suppose, then, that different molecules have different speeds, and that the speeds of individual molecules vary with time, as they make collisions with one another; but we also suppose that the average speed of all the molecules is constant. These assumptions are justified by the fact that the kinetic theory leads to conclusions which agree with experiment.

### Root-mean-square (R.M.S.) Speed

In equation (13) the factor  $nm$  is the product of the molecules per unit volume and the mass of one molecule. It is therefore the total mass of the gas per unit volume: its density  $\rho$ . Thus the equation gives

$$p = \frac{1}{3}\rho\bar{c}^2 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

or

$$\frac{p}{\rho} = \frac{1}{3}\bar{c}^2 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

If we substitute known values of  $p$  and  $\rho$  in equation (15), we can find  $\bar{c}^2$ . For hydrogen at s.t.p.,

$$\rho = 0.09 \text{ kg m}^{-3}.$$

The pressure in newton per  $\text{m}^2$ , is  $p = g\rho H$ , where  $g$  = acceleration of gravity =  $9.81 \text{ m s}^{-2}$ ,  $\rho$  = density of mercury =  $13600 \text{ kg m}^{-3}$ ,  $H$  = barometer height =  $760 \text{ mm} = 0.76 \text{ m}$ .

$$\begin{aligned} \therefore \bar{c}^2 &= \frac{3p}{\rho} = \frac{3 \times 9.81 \times 13600 \times 0.76}{9 \times 10^{-2}} \\ &= 3.37 \times 10^6 \text{ m}^2 \text{ s}^{-2}. \end{aligned}$$

The square root of  $\bar{c}^2$  is called the *root-mean-square speed*; it is of the same magnitude as the average speed, but not quite equal to it. Its value is

$$\begin{aligned} \sqrt{\bar{c}^2} &= \sqrt{3.37 \times 10^6} = 1840 \text{ m s}^{-1} \text{ (approx.)} \\ &= 1.84 \text{ km s}^{-1} \end{aligned}$$

Molecular speeds were first calculated in this way by Joule in 1848; they turn out to have a magnitude which is high, but reasonable. The value is reasonable because it has the same order of magnitude as the speed of sound ( $1.30 \text{ km s}^{-1}$  in hydrogen at  $0^\circ\text{C}$ ); the speed of sound is the speed with which the molecules of a gas pass on a disturbance from one to another, and this we may expect to be of the same magnitude as the speeds of their natural motion.

**Introduction of the Temperature**

Let us consider a volume  $V$  of gas, containing  $N$  molecules. The number of molecules per unit volume is

$$n = \frac{N}{V},$$

and therefore the pressure of the gas, by equation (13) is

$$p = \frac{1}{3}nmc^2 = \frac{1}{3}\frac{N}{V}mc^2$$

$$\therefore pV = \frac{1}{3}Nmc^2. \quad (16)$$

Equation (16) reminds us of the equation combining Boyle's and Charles's laws:

$$pV = RT.$$

We can therefore make the kinetic theory consistent with the observed behaviour of a gas, if we write

$$\frac{1}{3}Nmc^2 = RT \quad (17)$$

Essentially, we are here assuming that the mean square speed of the molecules,  $c^2$ , is proportional to the absolute temperature of the gas. This is a reasonable assumption, because we have learnt that heat is a form of energy; and the kinetic energy of a molecule, due to its random motion within its container, is proportional to the square of its speed. When we heat a gas, we expect to speed-up its molecules. See p. 237.

The kinetic energy of a molecule moving with a speed  $c$  is  $\frac{1}{2}mc^2$ ; the average kinetic energy of translation of the random motion of the molecule of a gas is therefore  $\frac{1}{2}mc^2$ . To relate this to the temperature, we put equation (17) into the form

$$RT = \frac{1}{3}Nmc^2 = \frac{2}{3}N(\frac{1}{2}mc^2),$$

whence

$$\frac{1}{2}mc^2 = \frac{3}{2}\frac{R}{N}T \quad (18)$$

Thus, *the average kinetic energy of translation of a molecule is proportional to the absolute temperature of the gas.*

The ratio  $R/N$  in equation (18) is a universal constant. To see that it is, we have only to consider a mole. We have already seen that, for a mole, the gas constant  $R$ , and number of molecules  $N$ , are universal constants. If our arbitrary mass of gas is  $x$  moles, then  $R = xR$ , and  $N = xN$ ; therefore

$$\frac{R}{N} = \frac{R}{N} = k.$$

The constant  $k$ , the gas constant per molecule, is also a universal constant; it is often called *Boltzmann's constant*. In terms of  $k$  equation (18) becomes

$$\frac{1}{2}mc^2 = \frac{3}{2}kT \quad (19)$$



Boltzmann's constant is usually given in joules per degree, since it relates energy to temperature:

$$k = \frac{\frac{1}{2}mc^2}{\frac{3}{2}T}.$$

Its value is  $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ .

### Diffusion: Graham's Law

When a gas passes through a porous plug, a cotton-wool wad, for example, it is said to 'diffuse'. Diffusion differs from the flow of a gas through a wide tube, in that it is not a motion of the gas in bulk, but is a result of the motion of its individual molecules.

Fig. 10.11 shows an apparatus devised by Graham (1805–69) to compare the rates of diffusion of different gases. D is a glass tube, closed with a plug P of plaster of Paris. It is first filled with mercury, and inverted over mercury in a bowl. Hydrogen is then passed into it until the mercury levels are the same on each side; the hydrogen is then at atmospheric pressure. The volume of hydrogen,  $V_H$ , is proportional to the length of the tube above the mercury. The apparatus is now left; hydrogen diffuses out through P, and air diffuses in. Ultimately no hydrogen remains in the tube D. The tube is then adjusted until the level of mercury is again the same on each side, so that the air within it is at atmospheric pressure. The volume of air,  $V_A$ , is proportional to the new length of the tube above the mercury.

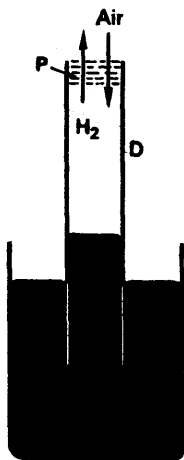


FIG. 10.11. Graham's apparatus for diffusion.

The volumes  $V_A$  and  $V_H$  are, respectively, the volumes of air and hydrogen which diffused through the plug in the same time. Therefore the rates of diffusion of the gases air and hydrogen are proportional to the volumes  $V_A$  and  $V_H$ :

$$\frac{\text{rate of diffusion of air}}{\text{rate of diffusion of hydrogen}} = \frac{V_A}{V_H}.$$

Graham found in his experiments that the volumes were inversely proportional to the square roots of the densities of the gases,  $\rho$ :

$$\frac{V_A}{V_H} = \sqrt{\frac{\rho_H}{\rho_A}}$$

thus

$$\frac{\text{rate of diffusion of air}}{\text{rate of diffusion of hydrogen}} = \sqrt{\frac{\rho_H}{\rho_A}}$$

In general:

$$\text{rate of diffusion} \propto \frac{1}{\sqrt{\rho}};$$

and in words: *the rate of diffusion of a gas is inversely proportional to the square root of its density. This is Graham's Law.*

Graham's law of diffusion is readily explained by the kinetic theory. At the same Kelvin temperature  $T$ , the mean kinetic energies of the molecules of different gases are equal, since

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}kT$$

and  $k$  is a universal constant. Therefore, if the subscripts A and H denote air and hydrogen respectively,

$$\frac{1}{2}m_A\overline{c_A^2} = \frac{1}{2}m_H\overline{c_H^2},$$

whence

$$\frac{\overline{c_A^2}}{\overline{c_H^2}} = \frac{m_H}{m_A}.$$

At a given temperature and pressure, the density of a gas,  $\rho$ , is proportional to the mass of its molecule,  $m$ , since equal volumes contain equal numbers of molecules:

Therefore

$$\frac{m_H}{m_A} = \frac{\rho_H}{\rho_A},$$

whence

$$\frac{\overline{c_A^2}}{\overline{c_H^2}} = \frac{\rho_H}{\rho_A}.$$

$$\therefore \frac{\sqrt{\overline{c_A^2}}}{\sqrt{\overline{c_H^2}}} = \frac{\sqrt{\rho_H}}{\sqrt{\rho_A}} \quad \dots \quad (20)$$

The average speed of the molecules of a gas is roughly equal to—and strictly proportional to—the square root of its mean square speed. Equation (20) therefore shows that the average molecular speeds are inversely proportional to the square roots of the densities of the gases. And so it explains why the rates of diffusion—which depend on the molecular speeds—are also inversely proportional to the square roots of the densities.

### Thermal Agitations and Internal Energy

The random motion of the molecules of a gas, whose kinetic energy depends upon the temperature, is often called the *thermal agitation* of the molecules. And the kinetic energy of the thermal agitation is called the *internal energy* of the gas. We must appreciate that this energy is quite independent of any motion of the gas in bulk: when a cylinder of oxygen is being carried by an express train, its kinetic energy as a whole is greater than when it is standing on the platform; but the random motion of the molecules within the cylinder is unchanged—and so is the temperature of the gas. The same is true of a liquid; in a water-churning experiment to convert mechanical energy into heat, baffles must be used to prevent the water from acquiring any mass-motion—all the work done must be converted into random motion, if it is to appear as heat. Likewise, the internal energy of a solid is the kinetic energy of its atoms' vibrations about their mean positions: throwing a lump of metal through the air does not raise its temperature, but hitting it with a hammer does.

The internal energy of a gas depends on the number of atoms in its molecule. A gas whose molecules consist of single atoms is said to be monatomic: for example, chemically inert gases and metallic vapours, Hg, Na, He, Ne, A. A gas

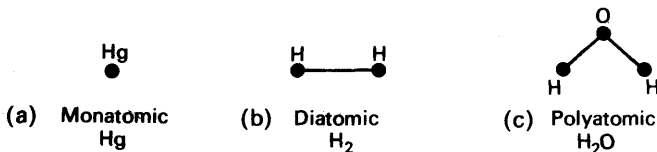


FIG. 10.12. Types of gas molecule.

with two atoms to the molecule is said to be diatomic: O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub>, CO. And a gas with more than two atoms to the molecule is said to be polyatomic: H<sub>2</sub>O, O<sub>3</sub>, H<sub>2</sub>S, CO<sub>2</sub>, CH<sub>4</sub>. The molecules of a monatomic gas we may regard as points, but those of a diatomic gas we must regard as 'dumb-bells', and those of a polyatomic gas as more complicated structures (Fig. 10.12). A molecule which extends appreciably in space—a diatomic or polyatomic molecule—has an appreciable moment of inertia. It may therefore have kinetic energy of rotation, as well as of translation. A monatomic molecule, however, must have a much smaller moment of inertia than a diatomic or polyatomic; its kinetic energy of rotation can therefore be neglected.

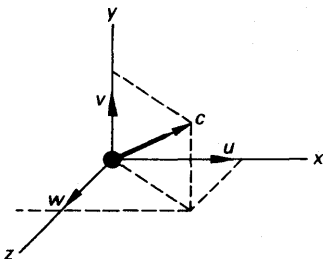


FIG. 10.12A. Components of velocity.

The  $x$ ,  $y$ ,  $z$  axes are called the molecules' degrees of freedom: they are three directions such that the motion of the molecule along any one is independent of its motion along the others.

If we average the speed  $c$ , and the components  $u$ ,  $v$ ,  $w$ , over all the molecules in a gas, we have

$$\overline{c^2} = \overline{u^2} + \overline{v^2} + \overline{w^2}.$$

And since the molecules do not pile up in any corner of the vessel containing the gas, their average velocities in all directions must be the same. We may therefore write

$$\overline{u^2} = \overline{v^2} = \overline{w^2},$$

$$\overline{c^2} = 3\overline{u^2} = 3\overline{v^2} = 3\overline{w^2},$$

$$\text{whence} \quad \overline{u^2} = \overline{v^2} = \overline{w^2} = \frac{1}{3}\overline{c^2}.$$

The average kinetic energy of a molecule of the gas is given by equation (19):

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}kT.$$

Therefore the average kinetic energy of a monatomic molecule, in each degree of freedom, is

$$\frac{1}{2}m\overline{u^2} = \frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{w^2} = \frac{1}{2}kT.$$

Thus the molecule has kinetic energy  $\frac{1}{2}kT$  per degree of freedom.

### Rotational Energy

Let us now consider a diatomic or polyatomic gas. When two of its molecules collide, they will, in general, tend to rotate, as well as to deflect each other. In some collisions, energy will be transferred from the translations of the molecules

to their rotations; in others, from the rotations to the translations. We may assume, then, that the internal energy of the gas is shared between the rotations and translations of its molecules.

To discuss the kinetic energy of rotation, we must first extend the idea of degrees of freedom to it. A diatomic molecule can have kinetic energy of rotation about any axis at right-angles to its own. Its motion about any such axis can be resolved into motions about two such axes at right-angles to each other (Fig. 10.13 (a)). Motions about these axes are independent of each other, and a diatomic

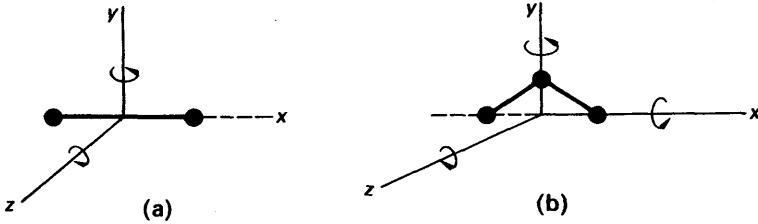


FIG. 10.13. Rotation of molecules.

molecule therefore has two degrees of rotational freedom. A polyatomic molecule, unless it happens to consist of molecules all in a straight line, has no axis about which its moment of inertia is negligible. It can therefore have kinetic energy of rotation about three mutually perpendicular axes (Fig. 10.13 (b)). It has three degrees of rotational freedom.

We have seen that the internal energy of a gas is shared between the translations and rotations of its molecules. Maxwell assumed that the average kinetic energy of a molecule, in each degree of freedom, *rotational as well as translational*, was  $\frac{1}{2}kT$ . This assumption is called the *principle of equipartition of energy*; experiment shows, as we shall find, that it is true at room temperature and above. At very low temperatures, when the gas is near liquefaction, it fails. At ordinary temperatures, then, we have:

$$\text{average K.E. of monatomic molecule} = \frac{3}{2}kT (\text{trans.});$$

$$\text{average K.E. of diatomic molecule} = \frac{3}{2}kT (\text{trans.}) + \frac{2}{2}kT (\text{rot.}) = \frac{5}{2}kT;$$

$$\text{average K.E. of polyatomic molecule} = \frac{3}{2}kT (\text{trans.}) + \frac{3}{2}kT (\text{rot.}) = \frac{6}{2}kT.$$

### Internal Energy of any Gas

From the average kinetic energy of its molecules, we can find the internal energy of a mass  $M$  of a gas. The number of molecules in this mass is, if  $m$  is the mass of one molecule.

$$N = \frac{M}{m}.$$

Its internal energy,  $U$ , is the total kinetic energy of its molecules' random motions; thus

$$U = N \times \text{average K.E. of molecule.}$$

For a monatomic gas, therefore,

$$U = \frac{3}{2}NkT (\text{monatomic}).$$

The constant  $k$  is the gas-constant per molecule; the product  $Nk$  is therefore the gas-constant  $R$  for the mass  $M$  of the gas. Thus

$$U = \frac{3}{2}RT \text{ (monatomic).}$$

In particular, if  $R$  is the gas-constant per kg, the internal energy per kg is

$$U = \frac{3}{2}RT \text{ (monatomic)} \quad . \quad . \quad . \quad (21)$$

Similarly, for a diatomic gas,

$$U = \frac{5}{2}NkT = \frac{5}{2}RT \quad . \quad . \quad . \quad (22)$$

$$U = \frac{5}{2}RT$$

And for a polyatomic gas,

$$U = \frac{6}{2}NkT = \frac{6}{2}RT \quad . \quad . \quad . \quad (23)$$

$$U = \frac{6}{2}RT$$

### Internal Energy and Volume

In our simple account of the kinetic theory of gases, we have implicitly assumed that the molecules of a gas do not attract one another. If they did, any molecule approaching the boundary of the gas would be pulled towards the body of it, as is a molecule of water approaching the surface (see Chapter 6, *Surface Tension*, p. 128). The attractions of the molecules would thus reduce the pressure of the gas.

Since the molecules of a substance are presumably the same whether it is liquid or gas, the molecules of a gas must attract one another somewhat. But except for brief instants when they collide, the molecules of a gas are much further apart than those of a liquid. In 1 cubic centimetre of gas at s.t.p. there are  $2.69 \times 10^{19}$  molecules, and in 1 cubic centimetre of water there are  $3.33 \times 10^{22}$ ; there are a thousand times as many molecules in the liquid, and so the molecules in the gas are ten times further apart. We may therefore expect that the mutual attraction of the molecules of a gas, for most purposes, can be neglected, as experiment, in fact, shows.

The experiment consists in allowing a gas to expand without doing external work; that is, to expand into a vacuum. Then, if the molecules attract one another, work is done against their attractions, as they move further apart. But if the molecular attractions are negligible, the work done is also negligible. If any work is done against the molecular attractions, it will be done at the expense of the molecular kinetic energies; as the molecules move apart, they will exert retarding forces on one another. Thus the internal energy of the gas, and therefore its temperature, will fall.

The expansion of a gas into a vacuum is called a 'free expansion'. If a gas does not cool when it makes a free expansion, then the mutual attractions of its molecules are negligible.

### Joule's Experiments

Experiments on the free expansion of a gas were made in 1807 by Gay-Lussac; they showed no fall in temperature. Joule repeated these experiments with a better vacuum in 1845; he got the same negative result, and the greater accuracy of his experiments made them more trustworthy. Joule used two forms of apparatus, as shown in Fig. 10.14 (a) and (b). Each consisted of a cylinder of air, R, at 22 atmospheres, connected by a stop-cock S to an evacuated cylinder E. In the apparatus (a) both cylinders stood in the same tin can C, which contained  $16\frac{1}{2}$  lb water. In (b) the cylinders stood in different cans, and the stop-cock in a third, also containing water. When the stop-cock was opened, gas expanded from R to E. With the apparatus (a) Joule found, after stirring the water, that its temperature was unchanged. The expanding gas had therefore neither liberated heat nor absorbed it. With the apparatus (b) Joule found that heat was absorbed from the water round R, and given to the water round S and E; the heat given out was equal to the heat

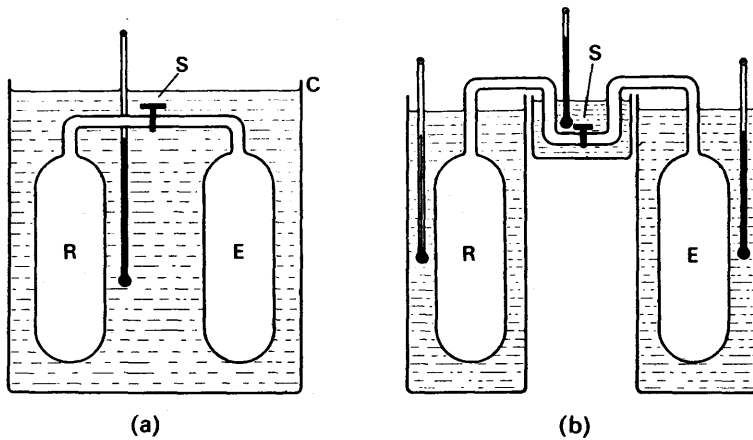


FIG. 10.14. Joule's experiment on internal energy.

taken in. The heat taken in represented the work done by the gas from R, expanding against the rising pressure of the gas in E and in the pipe beyond S. The heat given out represented the work done on the gas in E and S by the gas flowing in, against the rising pressure. The equality of the two showed that the total mass of gas neither gained nor lost energy in making its free expansion. Joule's experiments, therefore, showed that *the internal energy of a gas is independent of its volume*.

From Joule's results we may argue back to show that the mutual attractions of the molecules of the gas are negligible; in practice, however, it is the property of the bulk gas which is important—the fact that its internal energy does not depend on its volume.

Joule's experiments, though more reliable than Gay-Lussac's, were crude; with so much water, a small amount of heat would not produce a measurable temperature rise. Between 1852 and 1862, Joule worked with William Thomson, later Lord Kelvin, on more delicate experi-

ments. They found that most gases, in expanding from high pressure to low, do lose a little of their internal energy. The loss represents work done against the molecular attractions, which are therefore not quite negligible.

If the internal energy of a gas is independent of its volume, it is determined only by the temperature of the gas. The simple expression for the pressure,  $p = \frac{1}{3}\rho c^2$ , then holds; and the gas obeys Boyle's and Charles's laws. Its pressure coefficient,  $\alpha_p$ , is equal to its volume coefficient,  $\alpha_v$ . Such a gas is called an ideal, or perfect, gas. All gases, when far from liquefaction, behave for most practical purposes as though they were ideal.

### Van der Waals' Equation

In deriving the ideal gas equation  $pV = RT$  from the kinetic theory of gases, a number of assumptions were made. These are listed on p. 231. Van der Waals modified the ideal gas equation to take account that two of these assumptions may not be valid. Thus, as explained on p. 127, to which the student should refer:

- (1) *The volume of the molecules may not be negligible in relation to the volume  $V$  occupied by the gas.*
- (2) *The attractive forces between the molecules may not be negligible.*

Molecules have a particular diameter or volume because repulsive forces occur when they approach very closely and hence they can not be compressed indefinitely. The volume of the space inside a container occupied by the molecules is thus not  $V$  but  $(V - b)$ , where  $b$  is a factor depending on the actual volume of the molecules.

If the attractive forces between molecules are not negligible, the molecules approaching the container walls are attracted by the molecules behind them. This reduces the momentum of the approaching molecules and hence the pressure. The observed pressure  $p$  is thus less than the ideal gas pressure, where there are no molecular forces, by a pressure  $p'$ . Hence we write  $(p + p')$  in place of  $p$  in the ideal gas equation. As explained on p. 127, the 'pressure defect'  $p' \propto \rho^2$ , where  $\rho$  is the density of the gas, or  $p = a/V^2$ , where  $a$  is a constant. Thus *van der Waals' equation* for real gases is:

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

At high pressures, when the molecules are relatively numerous and close together, the volume factor  $b$  and pressure 'defect'  $a/V^2$  both become important. Conversely, at low pressures, where the molecules are relatively few and far apart on the average, a gas behaves like an ideal gas and obeys the equation  $pV = RT$ .

### Critical Phenomena

A graph of pressure  $p$  v. volume  $V$  at constant temperature is called an *isotherm*. Fig. 10.15 (i) shows a number of isotherms for an ideal gas, which obeys the perfect gas law  $pV = RT$ . Fig. 10.15 (ii) shows a

number of isotherms for a gas which obeys van der Waals' equation,  $(p + a/V^2)(V - b) = RT$ .

At high temperatures the isotherms are similar. As the temperature is lowered, however, the isotherms in Fig. 10.15 (ii) change in shape. One curve has a point of inflexion at C, which corresponds to the *critical point* of a real gas. The isotherms thus approximate to those obtained by Andrews in his experiments on actual gases such as carbon dioxide, described on p. 314.

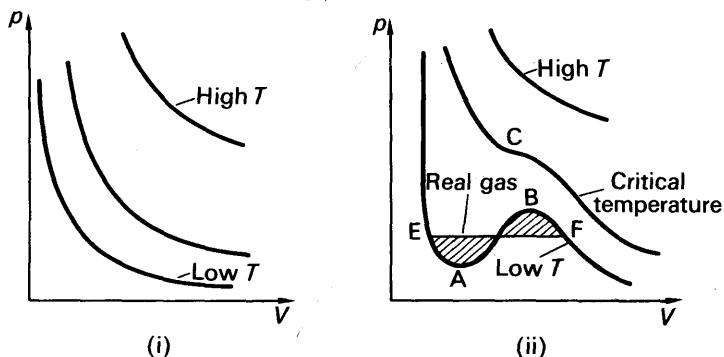


FIG. 10.15. Isotherms for ideal and van der Waals gases.

Below this temperature, however, isotherms such as EABF are obtained by using van der Waals' equation. These are unlike the isotherms obtained with real gases, because in the region AB the pressure increases with the volume, which is impossible. However, an actual isotherm in this region corresponds to a straight line EF, as shown. Here the liquid and vapour are in equilibrium (see p. 317) and the line EF is drawn to make the shaded areas above and below it equal. Thus van der Waals' equation roughly fits the isotherms of actual gases above the critical temperature but below the critical temperature it must be modified considerably. Many other gas equations have been suggested for real gases but quantitative agreement is generally poor.

## SPECIFIC HEAT CAPACITIES

### Specific Heat Capacities at Constant Volume and Constant Pressure

When we warm a gas, we may let it expand or not, as we please. If we do not let it expand—if we warm it in a closed vessel—then it does no external work, and all the heat we give it goes to increase its internal energy. *The heat required to warm unit mass of a gas through one degree, when its volume is kept constant, is called the specific heat capacity of the gas at constant volume.* It is denoted by  $c_v$ , and is generally expressed in  $\text{J kg}^{-1} \text{K}^{-1}$ .

If we allow a gas to expand as we warm it, then it does external work. The heat we give the gas appears partly as an increase to its internal energy—and hence its temperature—and partly as the heat equivalent of the work done. The work done depends on the increase in volume of the gas, which in turn depends on the way in which we allow the



gas to expand. We can get an important theoretical result by supposing that the pressure is constant, and defining the corresponding specific heat capacity. *The specific heat capacity of a gas at constant pressure is the heat required to warm unit mass of it by one degree, when its pressure is kept constant.* It is denoted by  $c_p$ , and is expressed in the same units as  $c_v$ .

**Specific Heat Capacities: their Difference**

Any number of heat capacities can be defined for a gas, according to the mass and the conditions imposed upon its pressure and volume. For unit mass, 1 kg or 1 g, of a gas, the heat capacities at constant pressure  $c_p$ , and at constant volume  $c_v$ , are the *specific heat capacities*.

Fig. 10.16 shows how we can find a relationship between the specific heat capacities of a gas. We first consider 1 kg of the gas warmed through

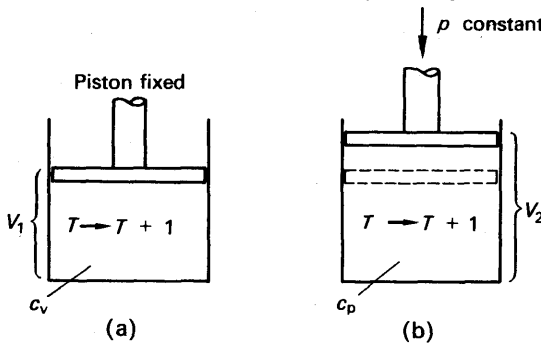


FIG. 10.16. Specific heat capacity at constant volume and pressure.

1°C at constant volume, (a). The heat required is  $c_v$  joules, and goes wholly to increase the internal energy.

We next consider 1 kg warmed through 1°C at constant pressure, (b). It expands from  $V_1$  to  $V_2$ , and does an amount of external work given by

$$W = p(V_2 - V_1) \quad (\text{equation (11), p. 229}).$$

The work  $W$  is in joules if  $p$  is in newton  $m^{-2}$ , and the volumes in  $m^3$ . Thus the amount of heat in joules required for this work is

$$W = p(V_2 - V_1).$$

Further, since the temperature rise of the gas is 1°C, and the internal energy of the gas is independent of volume, the rise in internal energy is  $c_v$ , the specific heat at constant volume. Hence, from  $\delta Q = \delta U + p \cdot \delta V$ , the total amount of heat required to warm the gas at constant pressure is therefore

$$c_p = c_v + p(V_2 - V_1) \quad \dots \dots \dots (24)$$

We can simplify the last term of this expression by using the equation of state for unit mass:

$$pV = RT,$$

where  $T$  is the absolute temperature of the gas, and  $R$  is the gas-

constant for unit mass of it in  $\text{J K}^{-1}$ . If  $T_1$  is the absolute temperature before warming, then

$$pV_1 = RT_1 \quad \dots \quad (25)$$

The absolute temperature after warming is  $T_1 + 1$ ; therefore

$$pV_2 = R(T_1 + 1), \quad \dots \quad (26)$$

and on subtracting (25) from (26) we find

$$p(V_2 - V_1) = R$$

Equation (24) now gives  $c_p = c_v + R$

or  $c_p - c_v = R \quad \dots \quad (27)$

Equation (27) was first derived by Robert Mayer in 1842. He used it, before Joule had done his water-churning experiments, to derive a relation between heat and mechanical energy.

**Ratio of Specific Heat Capacities**

We have seen that the internal energy of a gas, at a given temperature, depends on the number of atoms in its molecule. For a monatomic gas its value in joules per kg is

$$U = \frac{3}{2}RT \quad \dots \quad (i)$$

where  $U$  is the internal energy of the gas,  $R$  is the gas constant in  $\text{J kg}^{-1} \text{K}^{-1}$  and  $T$  is the absolute temperature of the gas.

The heat required to increase the internal energy of 1 kg of a monatomic gas, when it is warmed through 1 degree, is therefore  $\frac{3}{2}R$  joule. But this is the specific heat capacity at constant volume, and so

$$c_v = \frac{3}{2}R$$

The specific heat capacity of a monatomic gas at constant pressure is therefore

$$\begin{aligned} c_p &= c_v + R = \frac{3}{2}R + R \\ &= \frac{5}{2}R \end{aligned}$$

Let us now divide  $c_p$  by  $c_v$ ; their quotient is called the ratio of the specific heat capacities, and is denoted by  $\gamma$ .

For a monatomic gas, its value is

$$\begin{aligned} \gamma &= \frac{c_p}{c_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} \\ &= \frac{5}{3} = 1.667. \end{aligned}$$

Similarly, for a diatomic molecule,

$$U = \frac{5}{2}RT \quad \dots \quad (ii)$$

This was shown on p. 240.

Hence 
$$c_v = \frac{5}{2}R$$

and 
$$c_p = c_v + R = \frac{7}{2}R$$

Hence 
$$\gamma = \frac{c_p}{c_v} = \frac{7}{5} = 1.40.$$

And for a polyatomic molecule,

$$U = \frac{6}{2}RT, \quad \dots \dots \dots \quad \text{(iii)}$$

$$c_v = \frac{6}{2}R$$

and 
$$\gamma = \frac{c_p}{c_v} = \frac{8}{6} = 1.33.$$

In general, if the molecules of a gas have  $f$  degrees of freedom, the average kinetic energy of a molecule is  $f \times \frac{1}{2}kT$  (p. 238).

$$\therefore U = \frac{f}{2}RT,$$

$$c_v = \frac{f}{2}R,$$

$$c_p = c_v + R = \left(\frac{f}{2} + 1\right)R,$$

and 
$$\gamma = \frac{c_p}{c_v} = \frac{\frac{f}{2} + 1}{\frac{f}{2}} = 1 + \frac{2}{f} \quad \dots \dots \dots \quad \text{(iv)}$$

The ratio of the specific heat capacities of a gas thus gives us a measure of the number of atoms in its molecule, at least when that number is less than three. This ratio is fairly easy to measure, as we shall see later in this chapter. The poor agreement between the observed and theoretical values of  $\gamma$  for some of the polyatomic gases shows that, in its application to such gases, the theory is oversimple.

### Measurement of $c_v$ .

Fig. 10.17 shows an apparatus for measuring the specific heat capacity of a gas at constant volume, called a *differential steam calorimeter*. The calorimeter consists of two copper globes, A and B, as nearly identical as they can be made. They hang from the beam of a balance, and are surrounded by a chest C into which steam can be admitted at D. The sphere B is evacuated and A is filled with the gas whose specific heat is required. By filling A to a high pressure, the mass of gas can be made great enough to be accurately measurable on the balance. Let its value be  $M$ . Steam is now admitted to the chest, and condenses on both globes until they reach the temperature of the

steam. This will generally be about  $100^{\circ}\text{C}$ , but we shall denote it by  $\theta_1$ . The balance measures the excess steam condensed on A, over that condensed on B; let its mass be  $M_s$ . If the globes are identical, their heat capacities are equal, and the masses of steam required to warm the globes alone are equal. The excess steam condensed on A is then the mass required to warm the gas within it. Therefore if  $\theta_R$  is the room temperature, and  $l$  the specific latent heat of evaporation of water, the specific heat capacity  $c_v$  for the gas is given by

$$Mc_v(\theta_1 - \theta_R) = M_s l;$$

whence

$$c_v = \frac{M_s l}{M(\theta_1 - \theta_R)} \quad (28)$$

The calorimeter is called 'differential' for the reason that it measures the difference in mass of the steam on the two globes. This is an important feature of it, because the heat capacities of the globes may be much greater than that of the gas. If a single globe were used, two measurements would have to be made, one with and one without the

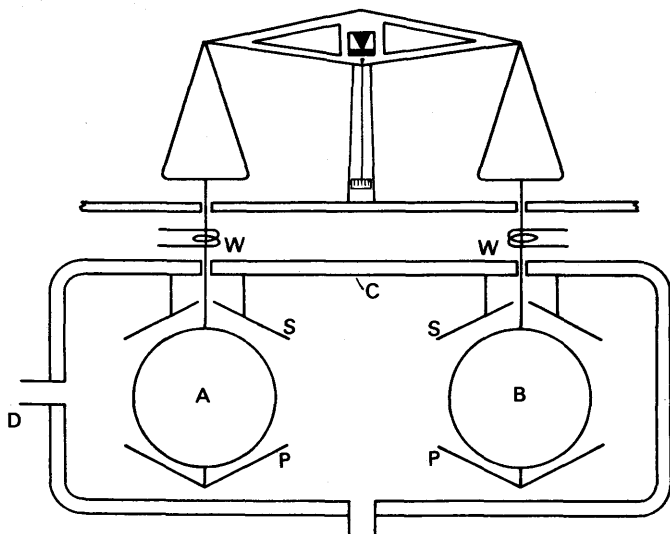


FIG. 10.17. Joly's differential steam calorimeter.

gas. The mass of steam condensed by the gas would then appear as the difference of two nearly equal masses, and could not be determined accurately. In practice the globes are not identical, and a control experiment with both evacuated is made to find the difference in mass of the steam condensed on them. This appears as a small correction to  $M_s$  in equation (28).

A small correction has also to be made to the result of the experiment, because the volume of the gas is not quite constant: the globe A expands when it is warmed.

The figure shows a few of the practical refinements of the apparatus. S, S are shields to prevent drops of moisture, condensed on the roof of

the chest, from falling on to the globes. P, P are pans to catch any drops which, having condensed on A or B, might fall off. W, W are platinum wires heated by an electric current, which prevent drops forming in the holes through which the suspension wires pass out of the chest.

### Measurement of $c_p$ .

The method of mixtures was used to determine the specific heat capacity of a gas at constant pressure by Regnault. Regnault was one of the greatest experimenters of the nineteenth century—the reader who sees pictures of his apparatus in other books should remember that he worked before Bunsen had invented his famous burner—but his method for  $c_p$  is now outmoded. We shall describe here only a continuous flow method, similar to Callendar and Barnes' for the specific heat capacity of water: It is due to Swann (1909).

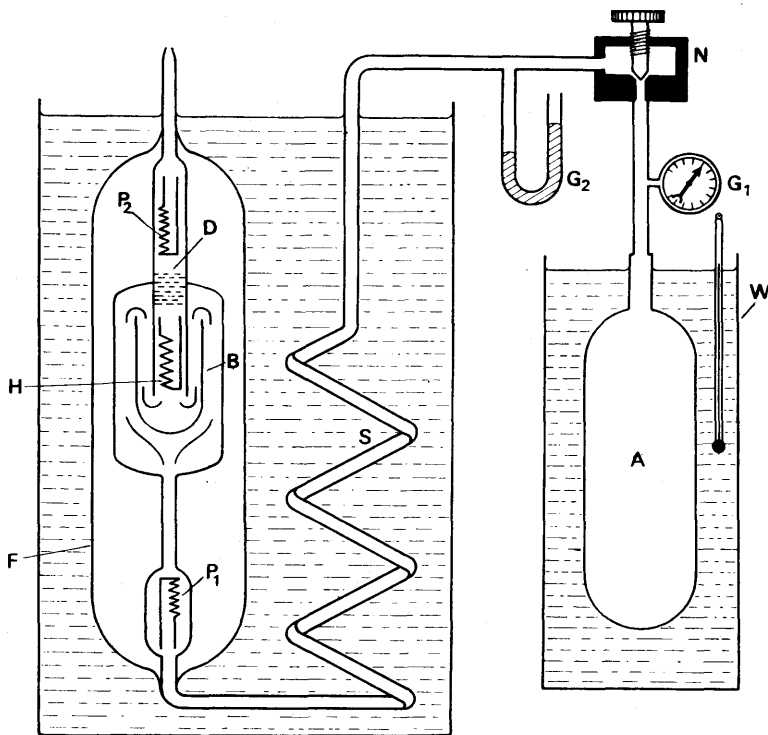


FIG. 10.18. Constant flow calorimeter for  $c_p$ .

Gas from a cylinder, A in Fig. 10.18, flows out through a needle valve N, which reduces its pressure to a little above atmospheric. If the pressure in the cylinder is high, it will fall slowly during an experiment, and the pressure of the emerging gas will be almost constant. Manometers  $G_1$ ,  $G_2$  indicate the pressure of the gas in the cylinder, and of the gas emerging. The gas passes through a coiled tube S, in a water bath,

which brings it to a uniform temperature. It then flows past a platinum resistance thermometer,  $P_1$ , which measures the temperature,  $\theta_1^\circ\text{C}$ . From there it goes to a heating coil  $H$ , past a baffle  $B$  which enables it to receive any heat that escapes from the neighbourhood of the coil. Beyond the coil it passes through copper gauze  $D$ , which mixes the stream of gas and so brings it to a uniform temperature. This temperature,  $\theta_2$ , is measured by the platinum resistance thermometer  $P_2$ . A vacuum jacket  $F$  makes the heat losses very small.

If  $M$  is the mass of gas flowing through the apparatus in  $t$  seconds, then the heat received by it is  $Mc_p(\theta_2 - \theta_1)$ . If the heat losses are negligible, the heat supplied by the coil in  $t$  seconds is  $IVt$  joule, where  $I$  is the current through it in ampere and  $V$  the potential difference across it in volt. Then

$$IVt = Mc_p(\theta_2 - \theta_1).$$

The mass of gas,  $M$ , is found from the fall of pressure in the cylinder. If  $v$  is the volume of the cylinder, and  $\rho_1$  the density of the gas at the initial pressure  $p_1$ , then the mass initially in the cylinder is

$$M_1 = \rho_1 v.$$

And if, after  $t$  seconds, the pressure has fallen to  $p_2$ , and the density to  $\rho_2$ , the mass remaining in the cylinder is

$$M_2 = \rho_2 v.$$

The mass of gas which has escaped is then

$$M = M_1 - M_2 = (\rho_1 - \rho_2)v.$$

The densities  $\rho_1$  and  $\rho_2$  can be readily calculated from the density  $\rho_0$  at s.t.p.: if  $\theta_3$  is the temperature of the cylinder, and the pressures are measured in mm mercury, then

$$\frac{p_1}{\rho_1(273 + \theta_3)} = \frac{p_2}{\rho_2(273 + \theta_3)} = \frac{760}{273\rho_0}.$$

The cylinder temperature  $\theta_3$  is kept constant by the water bath  $W$ .

#### CHANGES OF PRESSURE, VOLUME AND TEMPERATURE

In, for example, a steam engine or motor, gases expand and are compressed, cool and are heated, in ways more complicated than those which we have already described. We shall now consider some of these ways.

#### Isothermal Changes

We have seen that the pressure  $p$ , and volume  $V$  of a given mass of gas are related by the equation

$$pV = RT,$$

where  $T$  is the absolute temperature of the gas, and  $R$  is a constant.

If the temperature is constant the curve of pressure against volume is a rectangular hyperbola,

$$pV = \text{constant},$$

representing Boyle's law. Such a curve is called an *isothermal* for the given mass of the given gas, at the temperature  $T$ . Fig. 10.19 shows a family of isothermals, for 1 g of air at different temperatures. When a gas expands, or is compressed, at *constant temperature*, its pressure and volume vary along the appropriate isothermal, and the gas is said to undergo an *isothermal compression or expansion*.

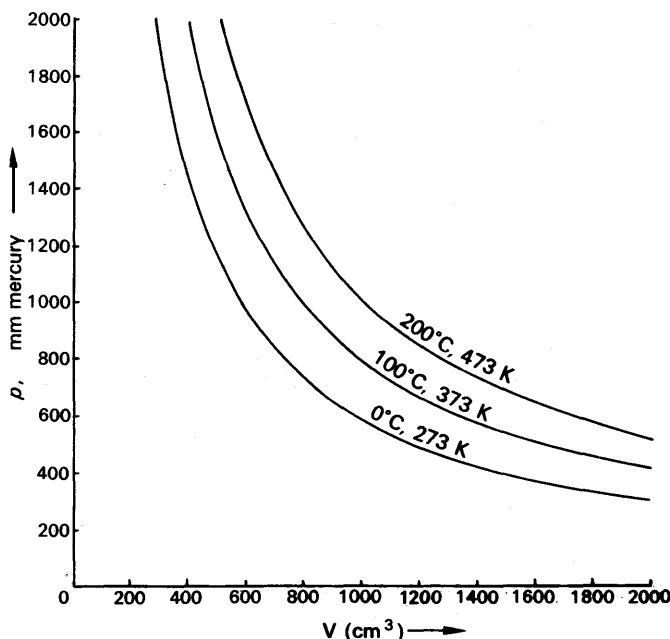


FIG. 10.19. Isothermals for 1 g air.

When a gas expands, it does work—for example, in driving a piston (Fig. 10.9, p. 229). The molecules of the gas bombard the piston, and if the piston moves they give up some of their kinetic energy to it; when a molecule bounces off a *moving* piston, it does so with a velocity less in magnitude than that with which it struck. The change in velocity is small, because the piston moves much more slowly than the molecule; but there are many molecules striking the piston at any instant, and their total loss of kinetic energy is equal to the work done in driving the piston forward.

The work done by a gas in expanding, therefore, is done at the expense of its internal energy. The temperature of the gas will consequently fall during expansion, unless heat is supplied to it. For an isothermal expansion, the gas must be held in a thin-walled, highly conducting vessel, surrounded by a constant temperature bath. And the expansion must take place slowly, so that heat can pass into the gas to maintain its temperature at every instant during the expansion.

**External Work done in Expansion**

The heat taken in when a gas expands isothermally is the heat equivalent of the mechanical work done. If the volume of the gas increases by a small amount  $\delta V$ , at the pressure  $p$ , then the work done is

$$\delta W = p\delta V \text{ (equation (11), p. 229).}$$

In an expansion from  $V_1$  to  $V_2$ , therefore, the work done is

$$W = \int dW = \int_{V_1}^{V_2} p dV.$$

By the gas equation,  $p = \frac{RT}{V}$ ,

whence 
$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} RT \frac{dV}{V}$$

or 
$$W = RT \log_e \left( \frac{V_2}{V_1} \right).$$

The heat required,  $Q$ , is therefore

$$Q = W = RT \log_e \left( \frac{V_2}{V_1} \right),$$

where  $W$  is in joules if  $R$  is in  $\text{J kg}^{-1} \text{K}^{-1}$ .

Now let us consider an isothermal compression. When a gas is compressed, work is done on it by the compressing agent. To keep its temperature constant, therefore, heat must be withdrawn from the gas, to prevent the work done from increasing its internal energy. The gas must again be held in a thin well-conducting vessel, surrounded by a constant-temperature bath; and it must be compressed slowly.

The conditions for an isothermal compression or expansion of a gas are difficult to realize; heat cannot flow through the walls of the vessel unless there is at least a small difference of temperature across them, and therefore the temperature of the gas is bound to rise a little in compression, or to fall a little in expansion.

**Reversible isothermal change**

Suppose a gas expands isothermally from  $p_1, V_1, T$  to  $p_2, V_2, T$ . If the change can be reversed so that the state of the gas is returned from  $p_2, V_2, T$  to  $p_1, V_1, T$  through exactly the same values of pressure and volume at every stage, then the isothermal change is said to be *reversible*. A reversible isothermal change is an ideal one. It requires conditions such as a light frictionless piston, so that the pressure inside and outside the gas can always be equalised and no work is done against friction; very slow expansion, so that no eddies are produced in the gas to dissipate the energy; and a constant temperature reservoir with very thin good-conducting walls, as we have seen. In a reversible isothermal change,  $pV = \text{constant} = RT$ .



### Equation for Reversible Adiabatic change

Let us now consider a change of volume in which the conditions are at the opposite extreme from isothermal; no heat is allowed to enter or leave the gas.

An expansion or contraction in which *no heat* enters or leaves the gas is called an *adiabatic expansion or contraction*. In an adiabatic expansion, the external work is done wholly at the expense of the internal energy of the gas, and the gas therefore cools. In an adiabatic compression, all the work done on the gas by the compressing agent appears as an increase in its internal energy and therefore as a rise in its temperature. We have already discussed a reversible isothermal change. A *reversible adiabatic change* is an adiabatic change which can be exactly reversed in the sense explained on p. 251. As noted there, a reversible change is an ideal case.

The curve relating pressure and volume for a given mass of a given gas for adiabatic changes is called an 'adiabatic'. In Fig. 10.20, the heavy curve is an adiabatic for 1 g of air; it is steeper, at any point, than the isothermal through that point. The curve AB is the isothermal for the temperature  $T_0 = 373$  K, which cuts the adiabatic at the point  $p_0 V_0$ . If the gas is adiabatically compressed from  $V_0$  to  $V_1$ , its

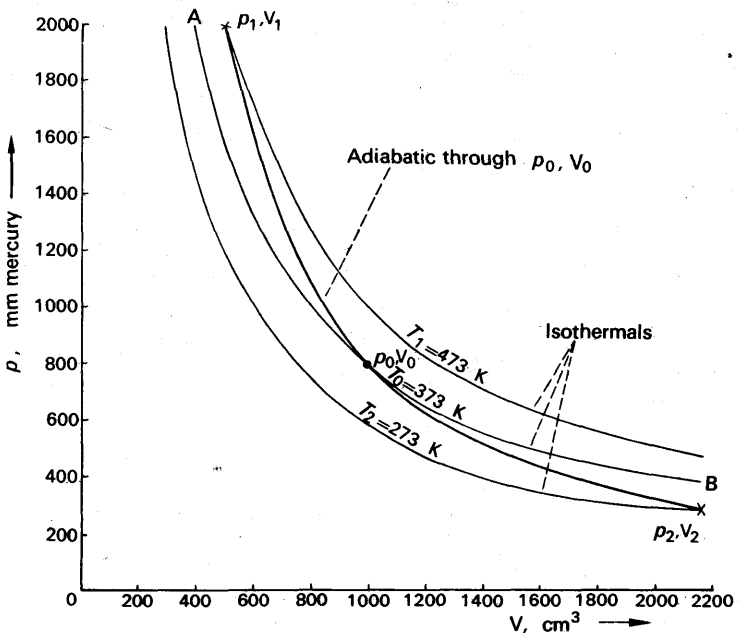


FIG. 10.20. Relationship between adiabatic and isothermals.

temperature rises to some value  $T_1$ . Its representative point  $p_1, V_1$  now lies on the isothermal for  $T_1$ , since  $p_1 V_1 = RT_1$ . Similarly, if the gas is expanded adiabatically to  $V_2$ , it cools to  $T_2$  and its representative point  $p_2, V_2$  lies on the isothermal for  $T_2$ . Thus the adiabatic through

any point—such as  $p_0, V_0$ —is steeper than the isothermal. We will find its equation shortly.

The condition for an adiabatic change is that no heat must enter or leave the gas. The gas must therefore be held in a thick-walled, badly conducting vessel; and the change of volume must take place rapidly, to give as little time as possible for heat to escape. However, in a rapid compression, for example, eddies may be formed, so that some of the work done appears as kinetic energy of the gas in bulk, instead of as random kinetic energy of its molecules. All the work done then does not go to increase the internal energy of the gas, and the temperature rise is less than in a truly adiabatic compression. If the compression is made slowly, then more heat leaks out, since no vessel has perfectly insulating walls:

Perfectly adiabatic changes are therefore impossible; and so, we have seen, are perfectly isothermal ones. Any practical expansion or compression of a gas must lie between isothermal and adiabatic. It may lie anywhere between them, but if it approximates to isothermal, the curve representing it will always be a little steeper than the ideal (Fig. 10.21); if it approximates to adiabatic, the curve representing it will never be quite as steep as the ideal.

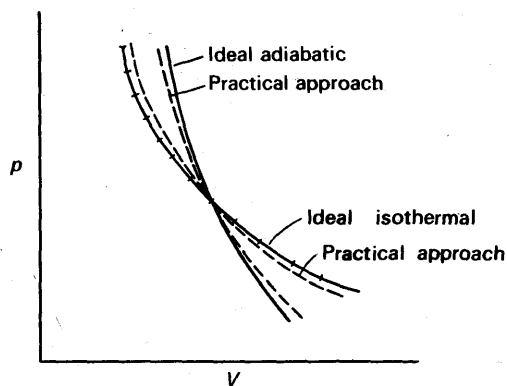


FIG. 10.21. Ideal and real  $p$ - $V$  curves for a gas.

### Equation of Reversible Adiabatic

Before considering adiabatic changes in particular, let us first consider a change of volume and temperature which takes place in an arbitrary manner. For simplicity, we consider unit mass of the gas, and we suppose that its volume expands from  $V$  to  $V + \delta V$ , and that an amount of heat  $\delta Q$  is supplied to it. In general, the internal energy of the gas will increase by an amount  $\delta U$ . And the gas will do an amount of external work equal to  $p\delta V$ , where  $p$  is its pressure. The heat supplied is equal to the increase in internal energy, plus the external work done:

$$\delta Q = \delta U + p\delta V \quad (29)$$

The increase in internal energy represents a temperature rise,  $\delta T$ . We have seen already that the internal energy is independent of the volume,

and is related to the temperature by the specific heat capacity at constant volume,  $c_v$  (p. 244). Therefore

$$\delta U = c_v \delta T.$$

Equation (29) becomes

$$\delta Q = c_v \delta T + p \delta V \quad (30)$$

Equation (30) is the fundamental equation for any change in the state of unit mass of a gas.

For a reversible isothermal change,  $\delta T = 0$ , and  $\delta Q = p \delta V$ .

For a reversible adiabatic change,  $\delta Q = 0$  and therefore

$$c_v \delta T + p \delta V = 0 \quad (31)$$

To eliminate  $\delta T$  we use the general equation, relating pressure, volume and temperature:

$$pV = RT,$$

where  $R$  is the gas constant for unit mass. Since both pressure and volume may change, when we differentiate this to find  $\delta T$  we must write

$$p \delta V + V \delta p = R \delta T,$$

whence

$$\delta T = \frac{p \delta V + V \delta p}{R}.$$

Therefore, by equation (31),

$$c_v \frac{p \delta V + V \delta p}{R} + p \delta V = 0$$

or

$$c_v(p \delta V + V \delta p) + R p \delta V = 0.$$

Now we have seen, on p. 245, that

$$R = c_p - c_v;$$

therefore

$$c_v(p \delta V + V \delta p) + (c_p - c_v)p \delta V = 0.$$

Hence

$$c_v V \delta p + c_p p \delta V = 0$$

or

$$V \delta p + \frac{c_p}{c_v} p \delta V = 0$$

or

$$V \delta p + \gamma p \delta V = 0 \quad \left( \text{where } \gamma = \frac{c_p}{c_v} \right).$$

Therefore

$$\frac{\delta p}{p} + \gamma \frac{\delta V}{V} = 0.$$

Integrating, we find

$$\int \frac{dp}{p} + \gamma \int \frac{dV}{V} = 0$$

or

$$\log_e p + \gamma \log_e V = A,$$

where  $A$  is a constant.

Therefore,

$$pV^\gamma = C,$$

where  $C$  is also a constant. This is the equation of a reversible adiabatic; the value of  $C$  can be found from the initial pressure and volume of the gas.

If we have a mass  $M$  of the gas, its volume at any temperature and pressure is

$$V = MV,$$

where  $V$  is the volume of unit mass at the same temperature and pressure. Therefore for any mass of gas, the equation of an adiabatic change is

$$pV^\gamma = \text{constant} \quad (32)$$

**Equation for Temperature Change in an Adiabatic**

If we wish to introduce the temperature,  $T$ , into equation (32), we use the general gas equation

$$pV = RT.$$

Thus

$$p = \frac{RT}{V}$$

and

$$pV^\gamma = \frac{RT}{V} \cdot V^\gamma = RTV^{\gamma-1}.$$

Thus equation (32) becomes

$$RTV^{\gamma-1} = \text{constant},$$

and since  $R$  is a constant for a given mass of gas, the equation for an adiabatic temperature change becomes

$$TV^{\gamma-1} = \text{constant}.$$

**Measurement of  $\gamma$ .**

In books on Sound, it is shown that sound waves are propagated through a gas by rapid compressions and rarefactions; these changes in pressure and volume are adiabatic. In consequence, the velocity of sound in a gas depends upon the ratio of the specific heat capacities of the gas,  $\gamma$ ; and the value of  $\gamma$  can be found from measurements of the velocity of sound in the gas. This is the most convenient way of measuring  $\gamma$ .

A direct measurement of  $\gamma$  can be made by the method of Clément and Désormes (1819). A large vessel—such as a carboy—contains the gas, which in a teaching experiment is usually air (Fig. 10.22). The

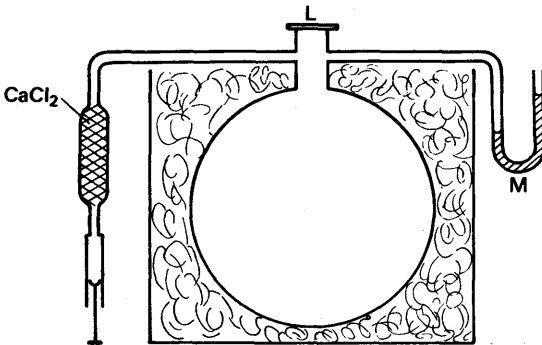


FIG. 10.22. Clément and Désormes experiment.

carboy is well lagged to minimize the exchange of heat with its surroundings. It is attached to a manometer M, and, via a drying-tube, to a bicycle pump. Its mouth has a large and well-fitting, flap-like, lid, L. Air is blown in until its pressure is a little above atmospheric, and time is allowed for the gas to settle down to room temperature. When it has done so the manometer reading becomes steady, and the pressure  $p_1$  of the gas is recorded. The flap-valve is now sharply opened and closed. The gas makes an adiabatic expansion, and its pressure  $p_2$  is immediately read. With the flap still closed, the gas is then left; it

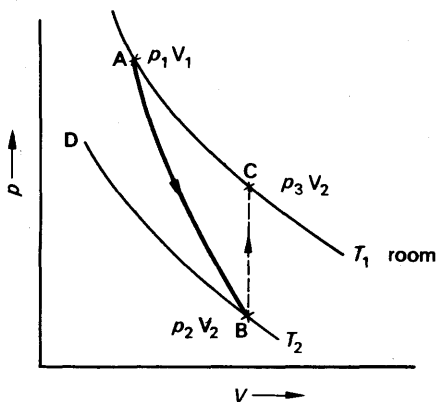


FIG. 10.23. Theory of Clément and Désormes.

gradually returns to room temperature, absolute temperature  $T_1$ , at constant volume, and its pressure rises to  $p_3$ . These changes are shown in Fig. 10.23. Since some gas escapes in the expansion, we must consider unit mass. Its state at the start of the experiment is represented by the point A on the isothermal for  $T_1$ , its volume being  $V_1$ . B represents the end of the adiabatic, when the gas has cooled to  $T_2$ , and expanded to  $V_2$  per unit mass. DB is the isothermal for  $T_2$ . BC represents the return to room temperature. For the adiabatic AB, we have

$$p_1 V_1^\gamma = p_2 V_2^\gamma,$$

or

$$\frac{p_1}{p_2} = \left(\frac{V_2}{V_1}\right)^\gamma \quad (33)$$

After the gas has returned to room temperature, its representative point C lies on the same isothermal as A; therefore

$$p_3 V_2 = p_1 V_1,$$

or

$$\frac{p_1}{p_3} = \frac{V_2}{V_1}.$$

From equation (33), therefore,

$$\frac{p_1}{p_2} = \left(\frac{p_1}{p_3}\right)^\gamma$$

whence  $\log_e p_1 - \log_e p_2 = \gamma(\log_e p_1 - \log_e p_3)$

and  $\gamma = \frac{\log_e p_1 - \log_e p_2}{\log_e p_1 - \log_e p_3}$

If  $h_1$  is the difference in levels of M corresponding to the pressure

$p_1$ , and  $h_2$  is the final difference in levels, corresponding to the pressure  $p_3$ , it can be shown that, to a good approximation, the formula for  $\gamma$  reduces to

$$\gamma = \frac{h_1}{h_1 - h_2}$$

A light oil is used in the manometer M.

VACUUM PUMPS AND GAUGES

**The Filter Pump**

The simplest pump for evacuating a vessel is the filter pump, so-called because it is used for speeding-up filtration (Fig. 10.24). It consists of a nozzle N surrounded by a chamber C; water rushes from the nozzle and out of the chamber at the bottom. The layer of air around the jet is dragged along with it, and carried out of the chamber. The lowest pressure which this pump can produce is the saturation vapour-pressure of water, about 15 mm mercury at 18°C. (Chapter 14). It cannot produce what we would nowadays call a 'good vacuum'.

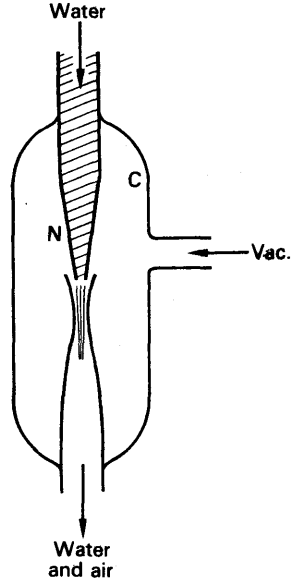


Fig. 10.24. Filter pump.

**The Piston Pump**

A piston-type air pump is similar to the common water pump, but more accurately made. Its plunger has a greased leather washer, W in Fig. 10.25, and its valves  $F_1$  and  $F_2$  are flaps of oiled silk.

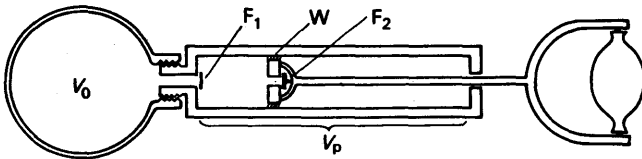


Fig. 10.25. Piston-type vacuum pump.

To develop a simple theory of the pump, we first assume that, when the piston is pushed right in, there is no space between it and the bottom of the barrel. We suppose that the pump is connected to a vessel of volume  $V_0$ , that the piston displaces a volume  $V_p$ , and that the pressure in the vessel is  $p_0$  when the piston is right in, at the start of the evacuation. When the piston is pulled right out, the volume of the air originally in the vessel increases to  $V_0 + V_p$ . Since the action

is slow, we may assume that the expansion is isothermal; the pressure  $p_1$  after expansion is therefore given by

$$p_1(V_0 + V_P) = p_0 V_0,$$

whence

$$p_1 = \left( \frac{V_0}{V_0 + V_P} \right) p_0.$$

When the piston is pushed in again, the valve  $F_1$  closes, and the air in the vessel remains at the pressure  $p_1$ . The second out-stroke then reduces the pressure to

$$p_2 = \left( \frac{V_0}{V_0 + V_P} \right) p_1 = \left( \frac{V_0}{V_0 + V_P} \right)^2 p_0.$$

Similarly, after  $n$  strokes, the pressure is reduced to

$$p_n = \left( \frac{V_0}{V_0 + V_P} \right)^n p_0.$$

According to this theory, the final pressure tends to zero as the number of strokes tends to infinity. In practice, however, a pump has a limiting pressure. This is due to the fact that the piston can never in practice be brought right down to the valve  $F_1$ , so that there is a residual volume, or dead-space,  $v$ , between the piston and the bottom of the barrel. Air can escape through the valve  $F_2$  only when the pressure in the volume  $v$  is greater than atmospheric. And air can pass from the vessel through  $F_1$  only when the pressure in the barrel is less than the pressure in the vessel. Thus the limiting pressure,  $p_\infty$ , is the pressure which  $v$  cm<sup>3</sup> of gas, at atmospheric pressure, exert when expanded to  $V_P$  cm<sup>3</sup>. That is to say

$$p_\infty V_P = p_{atmos.} v,$$

whence

$$p_\infty = \frac{v}{V_P} p_{atmos.}$$

The ratio  $v/V_P$  may be about 1/1000, so that  $p_\infty$  is about 1 mm mercury. Piston pumps of more elaborate designs can give better vacua than this, about 0.01 mm mercury; they have all been made obsolete, however, by the rotary pump.

### Rotary Pumps

Fig. 10.26 illustrates one form of rotary vacuum pump. It consists of a rotor, R, which turns eccentrically in a casing, C, being a close fit at the ends and along the line A. The rotor carries two scraping blades  $B_1$ ,  $B_2$ , separated by a strong spring. The vessel to be evacuated is connected to the inlet port I, and the outlet port O is fitted with a valve N. As the rotor turns, the volume  $V_1$  increases, so that air expands from the vessel into the pump. When the blades are in the positions shown, the air in the space  $V_2$  is being compressed; when its pressure rises to atmospheric, the valve N opens, and the air passes out through O. As the blade  $B_2$  crosses the seat of the valve N, the valve closes

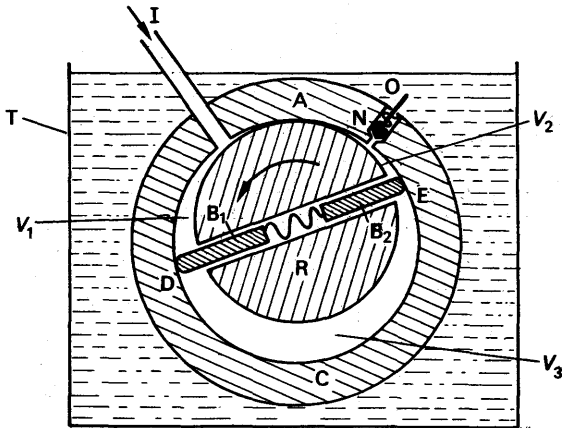


FIG. 10.26. Rotary vacuum pump.

because the air in  $V_3$  is below atmospheric pressure. Thus atmospheric air cannot blow back into the pump. The lines of contact, A, D, E are made airtight by a film of oil. All the working parts of the pump are enclosed in a tank T containing oil. When the pump is at rest, the oil seeps back through the outlet valve and fills the working space; but the first revolutions of the pump sweep out the excess oil, and leave just the necessary film over the metal surfaces.

A single rotary pump will give an ultimate pressure of about 0.01 mm mercury. Very often two pumps are housed in the same tank of oil, and driven off the same shaft; they are connected in cascade, and may give an ultimate pressure of less than 0.001 mm mercury.

### The MacLeod Gauge

The MacLeod Gauge is a gauge used for measuring pressures below a few mm mercury; these are pressures which cannot be measured accurately on a U-tube manometer. It consists of a bulb B, connected to a mercury reservoir M and terminated in a capillary tube T (Fig. 10.27 (a)); just below the bulb a branch-tube, P, leads to the vacuum system under test. It also carries a branch-tube, D, which is a capillary of the same bore as T. A millimetre scale, S, lies underneath T and D.

To measure the pressure in a vacuum system, the reservoir M is lowered until the mercury falls below the branch-point C. The air in B is then at the unknown pressure,  $p$ . The reservoir is now slowly raised. As soon as the mercury closes the branch at C, the air in B starts to be compressed. M is raised until the mercury in B just reaches the foot of the capillary T. The height  $h$  of the mercury in D, above that in B, is then measured. The purpose of having equal bores for T and D is to equalize surface tension effects in each.

If the pressure  $p$  is expressed in mm mercury then the pressure of the air trapped in T is  $p+h$ . The volume of this air is the volume  $v$  of the capillary T. At the moment when the mercury passed the point C, this air had the pressure  $p$ , and the volume  $V+v$ , where  $V$  is the



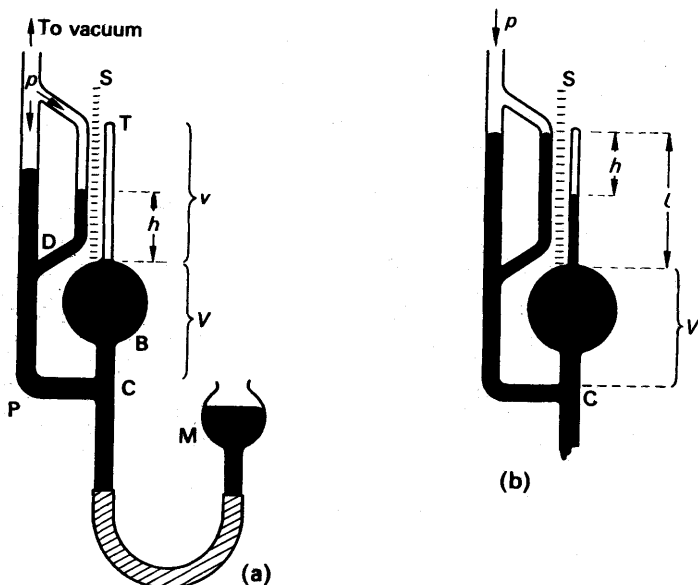


FIG. 10.27. MacLeod gauge.

volume between C and the base of T. The compression is slow enough to be isothermal, so that

$$p(V+v) = (p+h)v$$

Hence

$$pV = hv,$$

and

$$p = \frac{v}{V}h.$$

Another way of using the gauge is to raise the reservoir M until the mercury in D is level with the top of T (Fig. 10.27 (b)). Then if  $s$  is the cross-section of T, the volume of trapped air is  $hs$ . And if  $l$  is the whole length of T, its volume is  $ls$ . Therefore, as before,

$$p(V+ls) = (p+h)hs,$$

or

$$p(V+ls-hs) = h^2s,$$

whence

$$p = \frac{h^2s}{V+(l-h)s}.$$

The term  $(l-h)s$  in the denominator is usually negligible compared with  $V$ , so that

$$p \simeq \frac{h^2s}{V}.$$

Because  $p$  is proportional to  $h^2$ , the gauge can cover a wider range of pressures when it is used in this way, than when it is used in the way first described. But for the same reason it is less accurate. In practice

the second way is generally chosen, and the scale  $S$  is calibrated to read the pressure  $p$  directly.

### EXAMPLES

1. The density of a gas is  $10775 \text{ kg m}^{-3}$  at  $27^\circ\text{C}$  and  $10^5 \text{ N m}^{-2}$  pressure and its specific heat capacity at constant pressure is  $0.846 \text{ kJ kg}^{-1} \text{ K}^{-1}$ . Find the ratio of its specific heat capacity at constant pressure to that at constant volume.

The gas constant per kg of gas is given by

$$R = \frac{pV}{T} = \frac{10^5 \times 1}{1.775 \times 300} \text{ J kg}^{-1} \text{ K}^{-1}$$

since  $V = 1 \text{ m}^3/1.775$ ,  $T = 273 + 27 = 300 \text{ K}$ . Converting  $\text{J}$  to  $\text{kJ}$ ,

$$\therefore R = \frac{10^5 \times 1}{1.775 \times 300 \times 1000} \text{ kJ kg}^{-1} \text{ K}^{-1}.$$

Now

$$c_p - c_v = R$$

$$\therefore 0.846 - c_v = \frac{10^5 \times 1}{1.775 \times 300 \times 1000} = 0.188$$

$$\therefore c_v = 0.846 - 0.188 = 0.658 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

$$\therefore \gamma = \frac{c_p}{c_v} = \frac{0.846}{0.658} = 1.29.$$

This value for  $\gamma$  suggests that the gas is polyatomic (see p. 246).

2. An ideal gas at  $17^\circ\text{C}$  has a pressure of  $760 \text{ mm}$  mercury, and is compressed (i) isothermally, (ii) adiabatically until its volume is halved, in each case reversibly. Calculate in each case the final pressure and temperature of the gas, assuming  $c_p = 2.1$ ,  $c_v = 1.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$ .

(i) Isothermally,  $pV = \text{constant}$ .

$$\therefore p \times \frac{V}{2} = 760 \times V$$

$$\therefore p = 1520 \text{ mm mercury.}$$

The temperature is constant at  $17^\circ\text{C}$ .

(ii) Adiabatically,  $pV^\gamma = \text{constant}$ , and  $\gamma = 2.1/1.5 = 1.4$ .

$$\therefore p \times \left(\frac{V}{2}\right)^{1.4} = 760 \times V^{1.4}$$

$$\therefore p = 760 \times 2^{1.4} = 2010 \text{ mm mercury.}$$

Since  $TV^{\gamma-1} = \text{constant}$ ,

$$\therefore T \times \left(\frac{V}{2}\right)^{0.4} = (273 + 17) \times V^{0.4}$$

$$\therefore T = 290 \times 2^{0.4} = 383 \text{ K.}$$

$$\therefore \text{temperature} = 110^\circ\text{C.}$$

3. State the laws of gases usually associated with the names of Boyle, Charles, Dalton and Graham. Two gas containers with volumes of  $100 \text{ cm}^3$  and  $1000 \text{ cm}^3$  respectively are connected by a tube of negligible volume, and contain air at a

pressure of 1000 mm mercury. If the temperature of both vessels is originally  $0^{\circ}\text{C}$ , how much air will pass through the connecting tube when the temperature of the smaller is raised to  $100^{\circ}\text{C}$ ? Give your answer in  $\text{cm}^3$  measured at  $0^{\circ}\text{C}$  and 760 mm mercury. (L.)

*First part.* Boyle, Charles, Dalton, Graham, see text.

*Second part.* The pressure is 1000 mm mercury when the temperature is  $0^{\circ}\text{C}$  (273 K). Let the density of air under these conditions be  $\rho_1$ . Let the volumes of the large and small vessels be  $V$  and  $V^1$ ; then the mass of air in the two vessels is

$$M = (V + V^1)\rho_1 = (1000 + 100)\rho_1 = 1100\rho_1 \quad \dots \quad (\text{i})$$

When the smaller vessel is heated, the pressure throughout the system rises to  $p$ , say. Let  $\rho_2$  be the density of the air in the smaller vessel; then, by equation (9), p. 227:

$$\frac{p}{\rho_2} = R \times 373; \quad \frac{1000}{\rho_1} = R \times 273 \quad \dots \quad (\text{ii})$$

$$\therefore \frac{\rho_2}{\rho_1} = \frac{273}{373} \times \frac{p}{1000}$$

$$\therefore \rho_2 = \frac{273}{373} \times \frac{p}{1000} \rho_1$$

In the larger vessel, the temperature of the air does not change; therefore the density of the air in the larger vessel,  $\rho_3$ , is

$$\rho_3 = \frac{p}{1000} \rho_1$$

The total mass of air, which is unchanged, is therefore

$$\begin{aligned} M &= V\rho_3 + V^1\rho_2 = 1000\rho_3 + 100\rho_2 \\ &= 1000 \frac{p\rho_1}{1000} + 100 \frac{273}{373} \frac{p\rho_1}{1000} \\ &= 1 + \left( \frac{273}{3730} \right) p\rho_1 \end{aligned}$$

Hence, by equation (i),

$$1100\rho_1 = \left( 1 + \frac{273}{3730} \right) p\rho_1,$$

and 
$$p = \frac{3730 \times 1100}{4003} = 1025 \text{ mm mercury.}$$

The mass which flows out of the smaller vessel is

$$\begin{aligned} m &= V^1(\rho_1 - \rho_2) = 100\rho_1 \left( 1 - \frac{\rho_2}{\rho_1} \right) \\ &= 100\rho_1 \left( 1 - \frac{273}{373} \times \frac{p}{1000} \right) \\ m &= 100\rho_1 \left( 1 - \frac{273}{373} \times \frac{1025}{1000} \right) \quad \dots \quad (\text{iii}) \end{aligned}$$

The volume of this mass, at  $0^{\circ}\text{C}$  and 760 mm mercury, is

$$V = \frac{m}{\rho_4}$$

where  $\rho_4$  is the density of air at this temperature and pressure.

From the equation of state,

$$\frac{760}{\rho_4} = R \times 273;$$

therefore 
$$\frac{\rho_1}{\rho_4} = \frac{1000}{760},$$

or 
$$\frac{1}{\rho_4} = \frac{100}{76\rho_1}.$$

Hence, by (iii), 
$$V = \frac{m}{\rho_4} = \frac{100 \times 100}{76} \left( 1 - \frac{273}{373} \times \frac{1025}{1000} \right)$$

$$= 33 \text{ cm}^3.$$

4. Distinguish between *isothermal* and *adiabatic* changes. Show that for an ideal gas the curves relating pressure and volume for an adiabatic change have a greater slope than those for an isothermal change, at the same pressure.

A quantity of oxygen is compressed isothermally until its pressure is doubled. It is then allowed to expand adiabatically until its original volume is restored. Find the final pressure in terms of the initial pressure. (The ratio of the specific heat capacities of oxygen is to be taken at 1.40.) (L.)

*First part.* An isothermal change is one made at constant temperature; an adiabatic change is one made at constant heat, that is, no heat enters or leaves the system concerned.

For a reversible isothermal change,  $pV = \kappa$ , or  $p = \kappa/V$ . By differentiation, the slope,  $dp/dV$ ,  $= -\kappa/V^2 = -pV/V^2 = -p/V$ .

For a reversible adiabatic change,  $pV^\gamma = c$ , or  $p = c/V^\gamma$ . By differentiation, we find the slope,  $dp/dV$ ,  $= -\gamma p/V$ .

$$\therefore \text{ratio of adiabatic slope to isothermal slope} = \gamma.$$

Since  $\gamma$  is always greater than 1, the adiabatic slope is greater than the isothermal slope.

*Second part.* Let  $p_0, V_0$  = the original pressure and volume of the oxygen.

Since  $pV = \text{constant}$  for an isothermal change,

$$\therefore \text{new volume} = \frac{V_0}{2} \text{ when new pressure is } 2p_0.$$

Suppose the gas expands adiabatically to its volume  $V_0$ , when the pressure is  $p$ .

Then 
$$p \times V_0^{1.4} = 2p_0 \times \left( \frac{V_0}{2} \right)^{1.4}$$

$$\therefore p = 2p_0 \times \left( \frac{1}{2} \right)^{1.4} = 0.8 p_0.$$

5. Derive an expression for the difference between the specific heat capacities of an ideal gas and discuss the significance of the ratio of these two specific heat capacities for real gases.

Assuming that the ratio of the specific heat capacities of hydrogen is 1.41 and that its density at s.t.p. is  $0.0900 \text{ kg m}^{-3}$ , find a value for its specific heat capacity at constant volume in  $\text{J kg}^{-1} \text{K}^{-1}$ .

What explanation can you suggest for the small difference between the specific heat capacities of a solid? (Standard atmospheric pressure  $= 1.013 \times 10^5 \text{ N m}^{-2}$ .) (N.)

*First part.* The expression required is  $c_p - c_v = R$ , discussed on p. 245. The

ratio,  $\gamma$ , of these two specific heats =  $1 + \frac{2}{n}$  on the kinetic theory of gases, where  $n$  is the number of degrees of freedom of the molecules. For a monatomic gas  $n = 3$ , so that  $\gamma = 1.66$ ; for a diatomic gas  $n = 5$  usually, so that  $\gamma = 1.4$ ; for triatomic gases  $\gamma$  is less than 1.4, e.g. 1.29. Thus  $\gamma$  gives information about the number of atoms in the molecule of the gas.

*Second part.*  $c_p - c_v = R$ , where  $R$  may be in  $\text{J kg}^{-1} \text{K}^{-1}$  and  $c_p, c_v$  are in the same units. Since  $0.09 \text{ kg}$  occupies  $1 \text{ m}^3$  and  $p = 1.013 \times 10^5 \text{ newton m}^{-2}$ , then, from  $pV = RT$ ,

$$R = \frac{pV}{T} = \frac{(1.013 \times 10^5) \times 1}{273 \times 0.09} \text{ J kg}^{-1} \text{K}^{-1}$$

$$= 4.12 \text{ kJ kg}^{-1} \text{K}^{-1}$$

$$\therefore c_p - c_v = 4.12 \quad \dots \dots \dots (i)$$

But  $\frac{c_p}{c_v} = 1.41 \quad \dots \dots \dots (ii)$

$$\therefore c_p = 1.41 c_v. \text{ Substituting for } c_p \text{ in (i),}$$

$$\therefore 1.41 c_v - c_v = 4.12 = 0.41 c_v.$$

$$\therefore c_v = \frac{4.12}{0.41} = 10.0 \text{ kJ kg}^{-1} \text{K}^{-1}.$$

*Third part.* The difference in the specific heat capacities of a solid is proportional to the external work done in expansion. But the expansion of a solid is small. Consequently the difference in specific heat capacities of the solid is small.

## EXERCISES 10

### Gas Laws—Specific Heat Capacities of Gases

1. State *Boyle's law* and *Charles' law*, and show how they lead to the gas equation  $PV = RT$ . Describe an experiment you would perform to measure the thermal expansion coefficient of dry air.

What volume of liquid oxygen (density  $1140 \text{ kg m}^{-3}$ ) may be made by liquefying completely the contents of a cylinder of gaseous oxygen containing 100 litres of oxygen at 120 atmospheres pressure and  $20^\circ\text{C}$ ? Assume that oxygen behaves as an ideal gas in this latter region of pressure and temperature.

[1 atmosphere =  $1.01 \times 10^5 \text{ newton metre}^{-2}$ ; gas constant =  $8.31 \text{ joule mol}^{-1} \text{K}^{-1}$ ; molecular weight of oxygen = 32.0.] (*O. & C.*)

2. Give brief accounts of experiments which illustrate the relationship between the volume of a fixed mass of gas and (a) the pressure it exerts at a fixed temperature, (b) the temperature on a centigrade mercury thermometer at a fixed pressure. State the two 'laws' which summarise the results.

A gas cylinder contains 6400 g of oxygen at a pressure of 5 atmospheres. An exactly similar cylinder contains 4200 g of nitrogen at the same temperature. What is the pressure on the nitrogen? (Molecular weights: oxygen = 32, nitrogen = 28; assume that each behaves as a perfect gas.) (*O. & C.*)

3. State *Boyle's Law*.

Describe how you would verify the law for dry air over a range of pressures from 0.5 to 1.5 atmospheres. Would the form of the apparatus you describe be suitable if the working range of pressure was 0.5 to 10 atmospheres? Give reasons for your answer.

Two glass vessels of equal volume are joined by a tube, the volume of which may be neglected. The whole is sealed and contains air at S.T.P. If one vessel is

placed in boiling water at  $100^{\circ}\text{C}$  and the other is placed in melting ice, what will be the resultant pressure of the air? (*N.*)

4. The formula  $pv = mRT$  is often used to describe the relationship between the pressure  $p$ , volume  $v$ , and temperature  $T$  of a mass  $m$  of a gas,  $r$  being a constant. Referring in particular to the experimental evidence how do you justify (a) the use of this formula, (b) the usual method of calculating  $T$  from the temperature  $t$  of the gas on the centigrade (Celsius) scale?

Two vessels each of capacity 1.00 litre are connected by a tube of negligible volume. Together they contain 0.342 g of helium at a pressure of 80 cm of mercury and temperature  $27^{\circ}\text{C}$ . Calculate (i) a value for the constant  $r$  for helium, (ii) the pressure developed in the apparatus if one vessel is cooled to  $0^{\circ}\text{C}$  and the other heated to  $100^{\circ}\text{C}$ , assuming that the capacity of each vessel is unchanged. (*N.*)

5. State Boyle's law and Charles' law and show how they may be combined to give the equation of state of an ideal gas.

Two glass bulbs of equal volume are joined by a narrow tube and are filled with a gas at s.t.p. When one bulb is kept in melting ice and the other is placed in a hot bath, the new pressure is 87.76 cm mercury. Calculate the temperature of the bath. (*L.*)

6. Describe experiments in which the relation between the pressure and volume of a gas has been investigated at constant temperature over a wide range of pressure. Sketch the form of the isothermal curves obtained.

Explain briefly how far van der Waals' equation accounts for the form of these isothermals. (*L.*)

7. Describe, with a diagram, the essential features of an experiment to study the departure of a real gas from ideal gas behaviour.

Give freehand, labelled sketches of the graphs you would expect to obtain on plotting (a) pressure  $P$  against volume  $V$ , (b)  $PV$  against  $P$  for such a gas at its critical temperature and at one temperature above and one below the critical temperature.

Explain van der Waals' attempt to produce an equation of state which would describe the behaviour of real gases.

Show that van der Waals' equation is consistent with the statement that all gases approach ideal gas behaviour at low pressures. (*O. & C.*)

8. State Boyle's Law and describe how you would attempt to discover whether air shows any deviations from the law. Draw an approximate set of curves to show the way in which a gas deviates from Boyle's Law in the region close to where the gas liquefies.

Two one-litre flasks are joined by a closed tap and the whole is held at a constant temperature of  $50^{\circ}\text{C}$ . One flask is evacuated and the other contains air, water vapour, and a small quantity of liquid water. The total pressure in the latter flask is 200 mm Hg. The tap is then opened, and the system is allowed to reach equilibrium, when some liquid water remains. Assuming that air obeys Boyle's law, find the final pressure in the flasks.

[Vapour pressure of water at  $50^{\circ}\text{C} = 93 \text{ mmHg.}]$  (*O. & C.*)

9. Explain why the specific heat capacity of a gas is greater if it is allowed to expand while being heated than if the volume is kept constant. Discuss whether it is possible for the specific heat capacity of a gas to be zero.

When 1 g of water at  $100^{\circ}\text{C}$  is converted into steam at the same temperature 2264 J must be supplied. How much of this energy is used in forcing back the atmosphere? Explain what happens to the remainder of the energy. [1 g of water  $100^{\circ}\text{C}$  occupies  $1 \text{ cm}^3$ . 1 g of steam at  $100^{\circ}\text{C}$  and 76 cm of mercury occupies  $1601 \text{ cm}^3$ . Density of mercury =  $13600 \text{ kg m}^{-3}$ .] (*C.*)

**10.** Define *heat capacity* and *specific heat capacity*.

Describe an experiment to determine the specific heat capacity of a gas *either* at constant volume *or* at constant pressure. Point out likely sources of error and indicate how they may be minimized.

Explain why it is necessary to specify the condition of constant pressure or constant volume. (L.)

**11.** Explain why, when quoting the specific heat of a gas, it is necessary to specify the conditions under which the change of temperature occurs. What conditions are normally specified?

A vessel of capacity 10 litres contains 130 g of a gas at  $20^{\circ}\text{C}$  and 10 atmospheres pressure. 8000 joule of heat energy are suddenly released in the gas and raise the pressure to 14 atmospheres. Assuming no loss of heat to the vessel, and ideal gas behaviour, calculate the specific heat of the gas under these conditions.

In a second experiment the same mass of gas, under the same initial conditions, is heated through the same rise in temperature while it is allowed to expand slowly so that the pressure remains constant. What fraction of the heat energy supplied in this case is used in doing external work? Take 1 atmosphere =  $10^5$  newton metre $^{-2}$ . (O. & C.)

**12.** The two specific heat capacities in  $\text{kJ kg}^{-1} \text{K}^{-1}$  units for argon are 0.521 and 0.313 and for air are 1.012 and 0.722. Explain these statements and discuss their significance in relation to (a) the atomicity of the molecules of the two gases, (b) the relative values of the adiabatic elasticities of argon and air.

Describe an experiment to verify *one* of the above values of specific heat capacities. (L.)

**13.** A litre of air, initially at  $20^{\circ}\text{C}$  and at 76.0 cm of mercury pressure, is heated at constant pressure until its volume is doubled. Find (a) the final temperature, (b) the external work done by the air in expanding, (c) the quantity of heat supplied.

[Assume that the density of air at s.t.p. is  $1.293 \text{ kg m}^{-3}$  and that the specific heat capacity of air at constant volume is  $0.714 \text{ kJ kg}^{-1} \text{K}^{-1}$ .] (L.)

**14.** Describe an experiment to determine the specific heat capacity of water, at about  $15^{\circ}\text{C}$ , deriving from first principles any equations used.

Deduce an expression for the difference between the specific heat capacities of an ideal gas. If the specific heat capacity of air at constant pressure is  $1.013 \text{ kJ kg}^{-1} \text{K}^{-1}$  and the density at s.t.p. is  $1.29 \text{ kg m}^{-3}$  estimate a value for the specific heat capacity of air at constant volume. [Assume the density of mercury at  $0^{\circ}\text{C}$  to be  $13600 \text{ kg m}^{-3}$ .] (L.)

**15.** Distinguish between an *isothermal change* and an *adiabatic change*. In each instance state, for a reversible change of an ideal gas, the relation between pressure and volume.

A mass of air occupying initially a volume  $2000 \text{ cm}^3$  at a pressure of 76.0 cm of mercury and a temperature of  $20.0^{\circ}\text{C}$  is expanded adiabatically and reversibly to twice its volume, and then compressed isothermally and reversibly to a volume of  $3000 \text{ cm}^3$ . Find the final temperature and pressure, assuming the ratio of the specific heat capacities of air to be 1.40. (L.)

**16.** Explain why the specific heat of a gas at constant pressure is different from that at constant volume.

The density of an ideal gas is  $1.60 \text{ kg m}^{-3}$  at  $27^{\circ}\text{C}$  and  $1.00 \times 10^5$  newton metre $^{-2}$  pressure and its specific heat capacity at constant volume is  $0.312 \text{ kJ kg}^{-1} \text{K}^{-1}$ . Find the ratio of the specific heat capacity at constant pressure to that at constant volume. Point out any significance to be attached to the result. (N.)

**17.** Explain the meaning of the terms *isothermal*, *adiabatic*. What is the importance of the ratio of the specific heat capacity of an ideal gas?

Air initially at  $27^{\circ}\text{C}$  and at 75 cm of mercury pressure is compressed isothermally until its volume is halved. It is then expanded adiabatically until its original volume is recovered. Assuming the changes to be reversible, find the final pressure and temperature.

[Take the ratio of the specific heat capacities of air as 1.40.] (L.)

### Kinetic Theory of Gases

18. Explain what is meant by the *root mean square velocity* of the molecules of a gas. Use the concepts of the elementary kinetic theory of gases to derive an expression for the root mean square velocity of the molecules in terms of the pressure and density of the gas.

Assuming the density of nitrogen at s.t.p. to be  $1.251\text{ kg m}^{-3}$ , find the root mean square velocity of nitrogen molecules at  $127^{\circ}\text{C}$ . (L.)

19. State the postulates on which the simple kinetic theory of gases is based. What modifications are made to the postulates in dealing with real gases? How are these modifications represented in van der Waals' equation? (N.)

20. State the assumptions that are made in the kinetic theory of gases and derive an expression for the pressure exerted by a gas which conforms to these assumptions, in terms of its density ( $\rho$ ) and the mean square velocity ( $\bar{c}^2$ ) of its molecules.

Show (a) how *temperature* may be interpreted in terms of the theory, (b) how the theory accounts for Dalton's law of partial pressures. (L.)

21. Calculate the pressure in mm of mercury exerted by hydrogen gas if the number of molecules per  $\text{cm}^3$  is  $6.80 \times 10^{15}$  and the root mean square speed of the molecules is  $1.90 \times 10^3\text{ m s}^{-1}$ . Comment on the effect of a pressure of this magnitude (a) above the mercury in a barometer tube; (b) in a cathode ray tube. (Avogadro's Number =  $6.02 \times 10^{23}$ . Molecular weight of hydrogen = 2.02.) (N.)

22. Use a simple treatment of the kinetic theory of gases, stating any assumptions you make, to derive an expression for the pressure exerted by a gas on the walls of its container. Thence deduce a value for the root mean square speed of thermal agitation of the molecules of helium in a vessel at  $0^{\circ}\text{C}$ . (Density of helium at s.t.p. =  $0.1785\text{ kg m}^{-3}$ ; 1 atmosphere =  $1.013 \times 10^5\text{ N m}^{-2}$ .)

If the total translational kinetic energy of all the molecules of helium in the vessel is  $5 \times 10^{-6}$  joule, what is the temperature in another vessel which contains twice the mass of helium and in which the total kinetic energy is  $10^{-5}$  joule? (Assume that helium behaves as a perfect gas.) (O. & C.)

23. Explain the meaning of the terms *ideal gas* and *molecule*.

What properties of a gas such as carbon dioxide distinguish it from an ideal gas and how may these differences from 'ideal' be demonstrated experimentally?

According to simple kinetic theory the pressure exerted by a gas of density  $\rho$  is  $\frac{1}{3}\rho\bar{c}^2$  where  $\bar{c}^2$  is the mean square molecular velocity. Show how this relation may be correlated with the equation of state for an ideal gas,  $PV = RT$ , explaining clearly what further assumptions you have to make. (O. & C.)

24. Derive an expression for the pressure ( $p$ ) exerted by a mass of gas in terms of its molecular velocities, stating the assumptions made. What further assumption regarding the absolute temperature ( $T$ ) of the gas is necessary to show that the expression is consistent with the equation  $pv = kT$  where  $v$  is the volume of the mass of gas and  $k$  a constant? Which of the assumptions referred to did van der Waals modify to bring the equation  $pv = kT$  more closely in agreement with the behaviour of real gases and what equation did he deduce? (L.)

25. Explain the following in terms of the simple kinetic theory without mathematical treatment:



(a) A gas fills any container in which it is placed and exerts a pressure on the walls of the container.

(b) The pressure of a gas rises if its temperature is increased without the mass and volume being changed.

(c) The temperature of a gas rises if it is compressed in a vessel from which heat cannot escape.

(d) The pressure in an oxygen cylinder falls continuously as the gas is taken from it, while the pressure in a cylinder containing chlorine remains constant until very nearly all the chlorine has been used. The contents of the cylinder are kept at room temperature in both cases.

[Critical temperature of chlorine =  $146^{\circ}\text{C}$ .] (C.)

26. (a) State the assumptions of the kinetic theory of gases. How does the theory represent the temperature of a gas, and how does it account for the fact that a gas exerts a pressure on the walls of its container? (The derivation of an expression for the pressure is NOT required.)

(b) Near 0 K the specific heat capacity of silver,  $c$ , is not constant, but obeys the relation

$$c = \alpha T^{-3} + \beta T,$$

where  $T$  is the absolute temperature and  $\alpha$  and  $\beta$  are constants typical of silver given by  $\alpha = 15.12 \times 10^{-7} \text{ kJ kg}^{-1} \text{ deg}^{-4}$  and  $\beta = 5.88 \times 10^{-6} \text{ kJ kg}^{-1} \text{ deg}^{-1}$ . By means of a graph, or otherwise, find the heat required to raise the temperature of 5.0 g of silver from 1 K to 20 K. (C.)

27. Explain in terms of the kinetic theory what happens to the energy supplied to a gas when it is heated (a) at constant volume, (b) at constant pressure.

Deduce the total kinetic energy of the molecules in 1 g of an ideal gas at  $0^{\circ}\text{C}$  if its specific heat capacity at constant volume is  $0.60 \text{ kJ kg}^{-1} \text{ K}^{-1}$ .

An iron rod 1 metre long is heated without being allowed to expand lengthwise. When the temperature has been raised by  $500^{\circ}\text{C}$  the rod exerts a force of  $1.2 \times 10^4$  newtons on the walls preventing its expansion. How much work could be obtained if it were possible to maintain it at this temperature and allow it to expand gradually until free from stress? [Linear expansivity of iron =  $1.0 \times 10^{-5} \text{ K}^{-1}$ .] (C.)