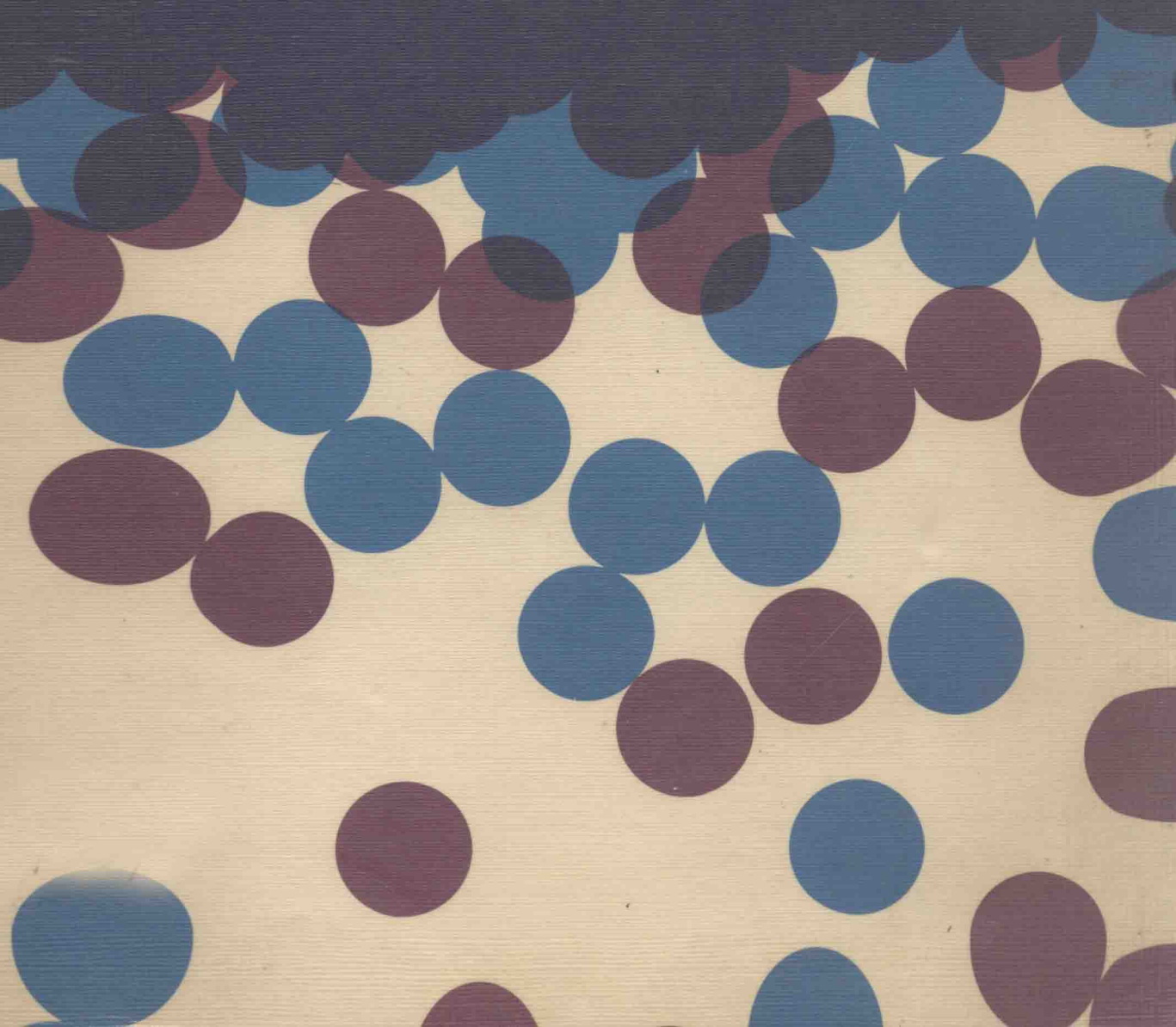


Principles of physical chemistry

David Mansfield



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David H. Mansfield, B.Sc.

*Senior Teacher and Head of the Chemistry Department,
The Harvey Grammar School, Folkestone, Kent*



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Preface

MODERN chemistry syllabus reforms at all levels place an increasing emphasis on Physical Chemistry to provide a conceptual framework within which the more factual material of Organic and Inorganic Chemistry can be systematized. This book is intended primarily to meet the needs of students preparing for G.C.E. A and S level examinations and equivalent qualifications, such as Ordinary National Certificates and Diplomas. It also covers the work required for the entrance and award papers of the Oxford, Cambridge, and London colleges. Students on introductory courses at University and other Colleges of Higher Education should also find the text useful.

There is considerably more material than is likely to be required for any particular examination syllabus and the student must make an appropriate selection under the guidance of his teacher. There is now greater divergence than ever before between individual syllabuses at intermediate level, and some traditional topics have necessarily been truncated or abandoned to make way for relevant new material. Novelty itself has not been the criterion for selection, however, and sufficient traditional material is retained here to emphasize the historical development of the subject and the debt each generation of innovators owes to workers of the past. Where appropriate this material has been restated in present-day terms to assist understanding. In addition to the historical perspective, the international nature of scientific research is stressed so that the development of important concepts can be seen to result from the combined efforts of many workers in different lands and times. Every effort has been made to show the relevance of physical chemistry in a wide range of other disciplines such as biology, engineering, geology, archaeology, food science, and in everyday life.

The mathematical demands have been carefully considered. It is recognized that many students whose interest is mainly in the biological sciences will not be studying mathematics as a main subject. The great majority of these, however, will be taking a 'mathematics for science' course. In those sections of the book covering the basic A and S level material, only mathematics familiar to such students has been employed. The use of some elementary calculus has not been avoided in the chapters on Chemical Kinetics and Chemical Thermodynamics as its use can add so enormously to understanding, even at intermediate level. The student on a modern biology course in Higher Education is certain to encounter these concepts and it is thus advantageous that a satisfactory treatment is given here.

This is not a practical book, but the results of many experiments are discussed to provide evidence for the ideas and concepts introduced. Wherever possible, experiments that can be performed in teaching laboratories at intermediate level have been chosen and sufficient experimental detail given to permit their reconstruction. Many of the results quoted have been obtained by my students. Suitable experimental work is contained in the *Heinemann Experimental Chemistry Series*. A selection of problems, some from recent public examinations, are given at the end of each chapter together with a short bibliography where this is appropriate.

I would like to thank the staff of Heinemann Educational Books, particularly Hamish MacGibbon and Graham Taylor, for their help, advice, and encouragement. I would welcome constructive criticism and suggestions to improve the text in future editions.

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To my students at Slough, Braintree, and Folkestone, whose enthusiasm and skill in probing into difficult areas has sustained and encouraged my interest and enthusiasm for continued enquiry into the difficult but rewarding search for a consistent and coherent systematization of the physical world.

Contents

PREFACE	v
ACKNOWLEDGEMENTS	ix
<i>Chapter</i>	
1 Gases and the Kinetic Theory of Matter	1
2 Atomic Structure	15
3 Spectroscopy and Analysis	34
4 Thermochemistry	45
5 Structure and Bonding	60
6 The Equilibrium Law	82
7 Vapour Pressure	94
8 The Ionic Theory	108
9 Ionic Equilibria	124
10 Rates of Reaction—Chemical Kinetics	145
11 Chemical Thermodynamics	167
12 The Periodic Classification	184
13 Surface Chemistry and Colloidal Systems	194
14 Nuclear and Radiochemistry	201
TABLE OF RELATIVE ATOMIC MASSES	219
UNITS AND SYMBOLS	220
INDEX	223

1. Gases and the Kinetic Theory of Matter

TRADITIONALLY, matter has been recognized to exist in three states: gaseous, liquid, and solid. Although some systems (such as helium at temperatures close to the absolute zero of temperature, and the so-called 'liquid-crystals') seem to demand the recognition of additional states of matter, it is possible to interpret the vast majority of observations made on material systems in terms of this traditional tripartite division. In this chapter we shall be concerned with the gaseous state and in particular with the development of the Kinetic Theory of Matter which grew mainly out of the investigations made on the behaviour and properties of gases.

The effect of pressure on the volume of gases

This effect can be conveniently studied in the apparatus illustrated in Figure 1.1. By altering the relative heights of the two limbs of the apparatus the volume of the fixed mass of gas trapped in the left-hand tube of the assembly can be recorded

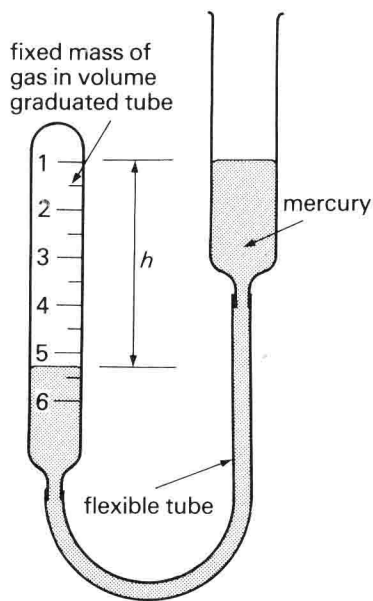


Figure 1.1 Apparatus to investigate the effect of pressure on the volume of a gas at constant temperature

under a range of pressures. It will be observed that the temperature is kept constant throughout the experiment.

$$\begin{aligned} \text{Pressure of gas/mmHg} \\ = \text{atmospheric pressure/mmHg} + h/\text{mmHg} \end{aligned}$$

If the results are plotted graphically, the results shown in Figure 1.2 are obtained. Investigations of this type were carried out by Robert Boyle who published his results in 1662. His conclusions are stated in *Boyle's Law*:

The volume of a fixed mass of gas (V) is inversely proportional to the pressure (p), provided the temperature remains constant. Stated mathematically:

$$V \propto 1/p \quad \text{or} \quad pV = \text{constant}$$

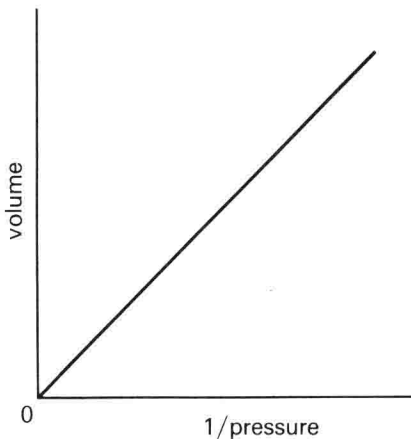


Figure 1.2 Variation of volume with pressure of a gas at constant temperature

The effect of temperature on the volume of gases

The apparatus illustrated in Figure 1.3 can be used to investigate this effect. Corresponding values of volume and temperature are noted as the water is heated electrically. The height of the right-hand limb of the apparatus is adjusted so that the mercury level is identical in both sides of the apparatus, so ensuring that all the volume measurements are made under atmospheric pressure. The results are plotted graphically as in Figure 1.4.

2 Principles of Physical Chemistry

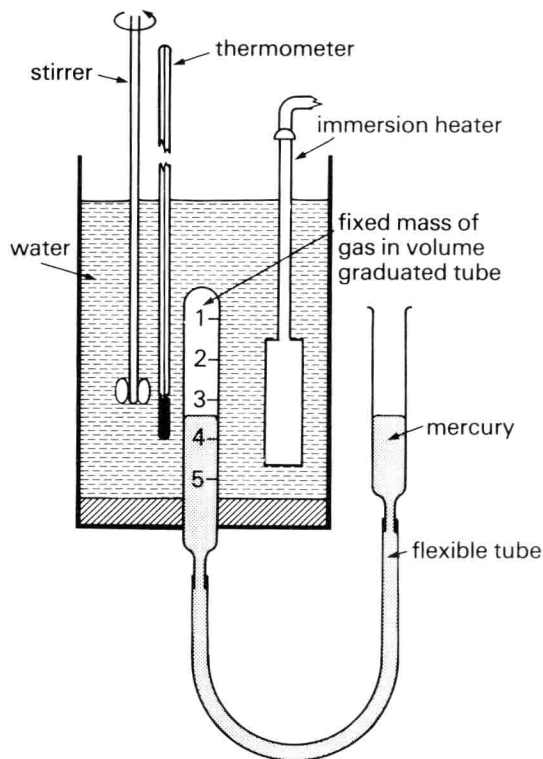


Figure 1.3 Apparatus to investigate the effect of temperature on the volume of a gas at constant pressure

If the graph is extrapolated to find the temperature at which the volume would be zero, this is found to be -273.2°C . This finding is independent of the nature and quantity of the gas employed. It is convenient to define a new temperature scale on which this temperature is taken as zero, each unit of the scale being identical with the Celsius scale. It is known as the Kelvin scale and its unit is the Kelvin. When the experimental results are replotted with the temperatures in Kelvin, the graph in Figure 1.5 is obtained. This effect was investigated by Jacques Charles in 1787 and his conclusion, in modern wording, is contained in the following statement of *Charles' Law*:

The volume of a fixed mass of gas (V) is directly proportional to its Kelvin temperature (T), provided the pressure remains constant. Stated mathematically:

$$V \propto T \quad \text{or} \quad V/T = \text{constant}$$

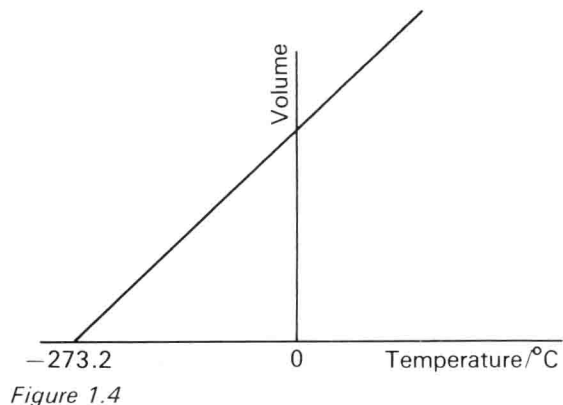


Figure 1.4

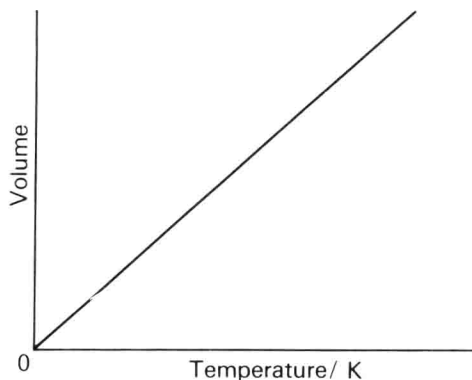


Figure 1.5

Ideal and real gases

More accurate measurements of these effects show that real gases obey the laws of Boyle and Charles with only limited accuracy. The importance of these deviations from the gas laws will be discussed later in this chapter. A useful concept is that of the 'ideal gas'. Such a gas is one that obeys the gas laws with complete accuracy.

The general gas equation

This can be obtained by combining the mathematical statements of Boyle's and Charles' laws:

$$\frac{pV}{T} = k \quad \text{or} \quad pV = kT \quad (\text{where } k \text{ is a constant})$$

The value of k depends on the amount of gas considered, and for the special case of 1 mole

of gas the symbol R is employed for the constant, i.e.

$$pV = RT \text{ (for 1 mole of gas)}$$

Hence for n moles of gas:

$$pV = nRT$$

or
$$pV = \frac{m}{M}RT$$

(where m is the mass and M the molar mass).

This can be transposed to give:

$$\begin{aligned} M &= \frac{m}{V} \times \frac{RT}{p} \\ &= \rho \times \frac{RT}{p} \end{aligned}$$

(where ρ is the density of the gas)

Thus, given a value for the Gas Constant, R , if the density of a gas is known under stated conditions of temperature and pressure, its molar mass can be calculated.

Standard temperature and pressure (s.t.p.)

It is convenient to define a standard temperature and pressure for use when quoting the volumes and densities of gases. The pressure of 1 atmosphere (760 mmHg; 101.3 kPa) and the temperature of 0°C (273.2 K) have been accepted for this purpose.

The determination of gas densities

The classical methods of gas density determination associated with the names of Victor Meyer, Regnault, and Dumas have now been superseded by the direct weighing technique described below, the use of gas syringes heated in a suitable furnace, and the gas micro-balance which will be discussed later in this chapter. Details of the older methods will be found in more traditional textbooks, such as *Physical Chemistry* by A. J. Mee (London: Heinemann Educational Books, 1962), or *Advanced Level Physical Chemistry* by A. Holderness (revised by J. Lazonby) (London: Heinemann Educational Books, 1976).

Gas densities by direct weighing

The gas-tight flask with fittings as illustrated in Figure 1.6 is connected via tap B to a vacuum system and exhausted with tap A closed and tap B

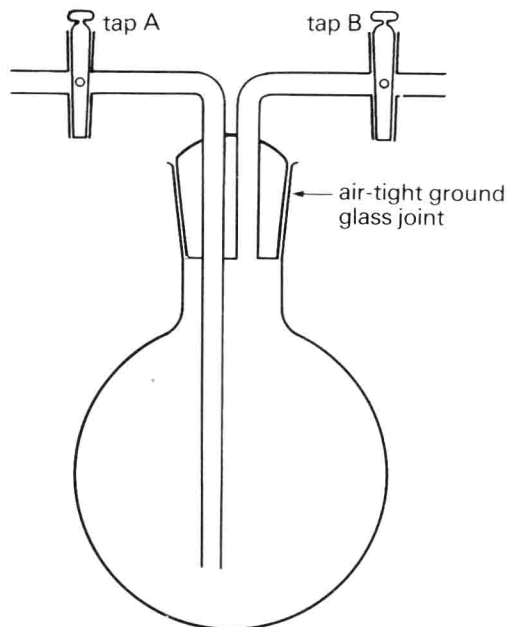


Figure 1.6 Apparatus for the direct weighing of gases

open. Tap B is closed, the flask is disconnected and weighed. A suitable source of dry gas is connected to tap A and the flask filled with both taps open. The taps are closed and the flask is disconnected and weighed. The difference in weighings gives the mass of gas contained in the flask. The flask is filled with water and weighed once more. The mass of water it will hold is found by subtraction and, knowing that 1 cm^3 of water has a mass of 1 g, the volume capacity of the flask obtained. Dividing the mass of gas by its volume gives the density under the laboratory conditions of temperature and pressure. If the density of gas at s.t.p. is required, the volume can be corrected to its value under these conditions by applying the laws of Boyle and Charles.

From the results of such experiments, if the relative molar mass of the gas is known, the volume occupied by one mole of gas can be calculated. This quantity is known as the molar volume of the gas.

It will be seen that the molar volumes of these real gases, at s.t.p., is almost constant. The accepted value for this constant for an ideal gas is $22.41\text{ dm}^3\text{ mol}^{-1}$ and it will be seen that real gases have constants approaching this value with reasonable accuracy. A further discussion of deviation from ideality will be given later in the chapter.

4 Principles of Physical Chemistry

Table 1.1 The molar volumes of some gases

Gas	Relative molar mass	Density at s.t.p./g dm ⁻³	Molar volume at s.t.p./dm ³ mol ⁻¹
Carbon monoxide	28.01	1.251	22.40
Carbon dioxide	44.01	1.977	22.26
Chlorine	70.90	3.215	22.06
Helium	4.00	0.178	22.46
Hydrogen	2.02	0.090	22.42
Nitrogen	28.01	1.251	22.40
Oxygen	32.00	1.429	22.39
Sulphur dioxide	64.06	2.927	21.89

It has been shown previously that for 1 mole of gas

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

Substituting suitable values in this equation enables us to evaluate the constant, R :

$$R = \frac{(1 \text{ atmosphere}) \times (22.41 \text{ dm}^3)}{(273.2 \text{ K})} \\ = 0.08205 \text{ atmosphere dm}^{-3} \text{ K}^{-1}$$

As discussed in the introduction, the atmosphere is not the SI unit of pressure and thus this value of R is not in SI units. It is a form of expressing R , however, which is convenient for calculations using the gas equation.

The determination of relative molecular masses (formerly called molecular weights)

The relative molecular masses of gases can be determined by the direct weighing method described earlier. An elegant technique to supplement this was developed in 1910 by W. Ramsey and R. Whytlaw-Gray to determine the relative molecular mass of radon gas. This is suitable for use when very small quantities of gas are available; the apparatus can be as small as 2 × 8 cm and is known as the microbalance. A diagrammatic illustration of the apparatus is shown in Figure 1.7. The balance is first evacuated and the quartz bulb falls as the buoyancy force of the air displaced no longer applies. A gas of known density is then slowly admitted until the pointer reaches a predetermined position on the scale and the pressure noted on the manometer. The apparatus is evacuated again and

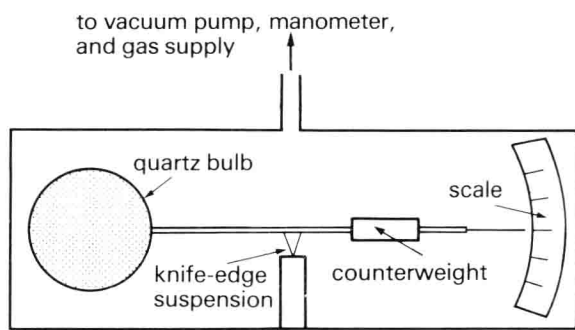


Figure 1.7 The microbalance

the gas of unknown density is admitted slowly until the pointer reaches the same position on the scale; the pressure is again noted.

Now for the standard gas of known density:

$$M(s) = \rho(s) \times \frac{RT}{p_s}$$

and for the gas of unknown density:

$$M(u) = \rho(u) \times \frac{RT}{p_u}$$

When the two pressures were recorded, the buoyancy force on the quartz bulb was equal and hence $\rho(u) = \rho(s)$ we can thus combine these two equations:

$$\frac{M(s)}{M(u)} = \frac{p_u}{p_s}$$

Hence as $M(s)$, p_u and p_s are known, substitution allows the calculation of $M(u)$.

Relative molecular masses of liquids

The relative molecular masses of liquids can be determined if a known mass is vaporized and its volume determined under known conditions of temperature and pressure. A convenient apparatus for this purpose is shown in Figure 1.8. A gas syringe is contained in a suitable furnace which maintains it at a steady temperature at least 10°C above the boiling point of the liquid under test. This furnace may be electrically heated or the vapour of a suitable liquid, usually water, may be passed continuously through it. The nozzle of the gas syringe is fitted with a self-sealing rubber cap. The apparatus is left until thermal equilibrium is reached between the furnace interior and the 15 cm^3 or so of air the syringe contains initially. A smaller syringe fitted with a hypodermic needle is filled with the liquid under test, some of which is injected into the gas syringe and the small syringe is reweighed to give the mass of liquid injected. The liquid vaporizes in the gas syringe and its volume at the temperature of the furnace and under laboratory pressure can be recorded. This procedure is repeated using different masses of liquid and the results plotted graphically. Graphs of the type shown in Figure 1.9 are obtained. These results were obtained at a temperature of 100°C (373 K) and 756 mmHg ($756/760$ atmosphere).

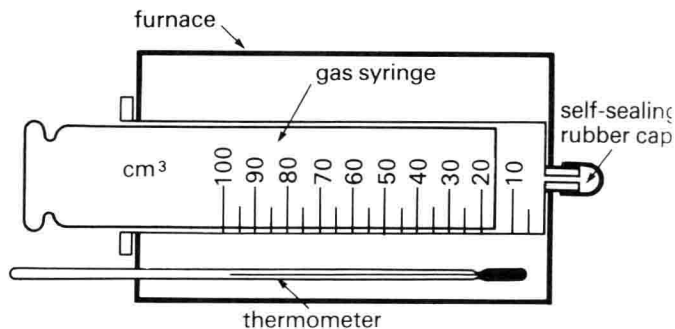
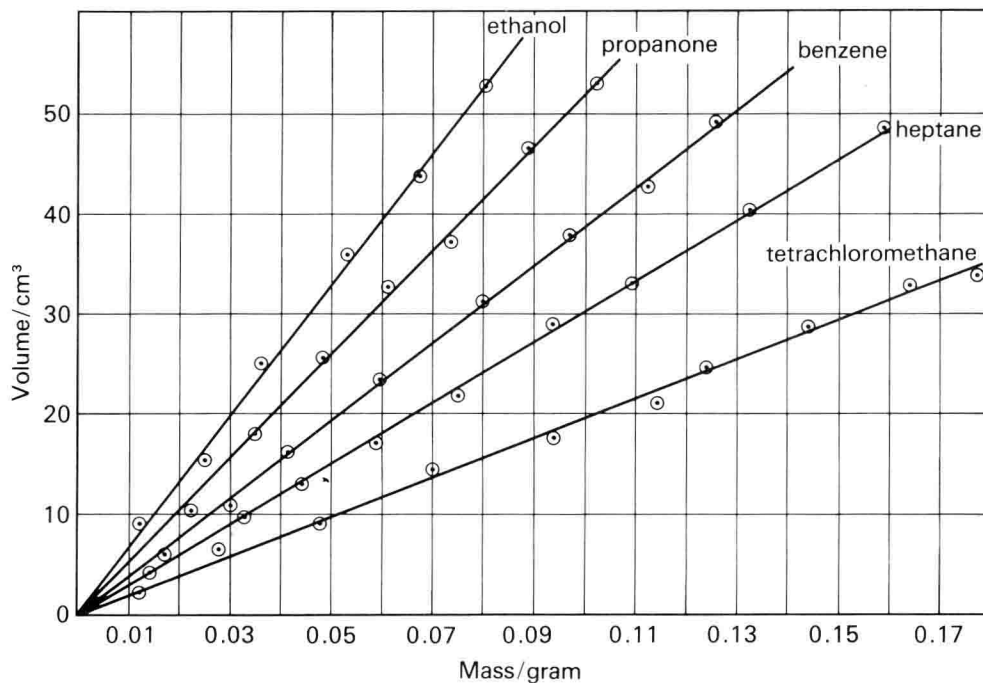


Figure 1.8 Apparatus to determine relative molecular masses of liquids

The reciprocal of the slope of each curve is the density of the vapour under the temperature and pressure at which the measurements were made. Hence the density of propanone vapour under these conditions is 0.0019 g cm^{-3} , or 1.9 g dm^{-3} . We can substitute this value in the equation:

$$M = \rho \times \frac{RT}{p}$$

Figure 1.9 Graph from which the densities of vapours can be deduced



6 Principles of Physical Chemistry

remembering that the units used for other quantities are consistent with those for R .

$$\begin{aligned}M &= (1.9 \text{ g dm}^{-3}) \times \frac{(0.082 \text{ atm dm}^3 \text{ K}^{-1}) \times (373 \text{ K})}{(756/760 \text{ atm})} \\ &= 1.9 \times 0.082 \times 373 \times 760/756 \text{ g} \\ &= 58 \text{ g}\end{aligned}$$

thus $M_r = 58$

Alternatively, the SI value of R can be used. When this is done, it is not necessary to insert units as they will be consistent by definition. If the SI value is used, however, the pressure and the density must be inserted in their basic SI units.

$$760 \text{ mmHg} = 101\,300 \text{ Pa}$$

$$\text{thus } 756 \text{ mmHg} = 100\,800 \text{ Pa} = 1.01 \times 10^5 \text{ Pa}$$

$$\begin{aligned}1.90 \text{ g dm}^{-3} &= 1.90 \text{ g dm}^{-3} \times \\ &\quad 10^{-3} \text{ kg g}^{-1} \times 10^6 \text{ dm}^3 \text{ m}^{-3} \\ &= 1.90 \times 10^3 \text{ kg m}^{-3}\end{aligned}$$

Substitution in the general gas equation gives:

$$\begin{aligned}M &= \frac{1.90 \times 10^3 \times 8.31 \times 373}{1.01 \times 10^5} \\ &= 58\end{aligned}$$

If such a series of results is not available an individual pair of values of mass and volume may be substituted in the equation; however, the averaging of errors available by using the graphical method is lost. An alternative method of carrying out these calculations is to correct the volume of vapour to s.t.p. and then find the mass of vapour that would occupy 22.4 dm^3 under these conditions. This mass is, of course, the relative molar mass.

The composition of water

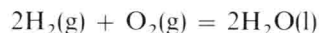
Water was regarded as an element until towards the end of the eighteenth century when Joseph Priestley observed the formation of water when mixtures of air and hydrogen were exploded by electrical detonation in a closed vessel. Henry Cavendish, in 1781, measured the volume proportions in which hydrogen and oxygen combine during the formation of water and found them to be 201 : 100.

Jean Dumas, in 1842, investigated the gravimetric composition of water by passing carefully purified hydrogen over heated black copper oxide and measuring the loss of mass of the copper oxide due to removal of oxygen and the mass of the water formed. He found that the gravimetric proportions in which hydrogen and oxygen combined to form water was 7.98 : 1. Little was known at that

time about the proportions in which atoms combined either with themselves in pure elements or with the atoms of other elements in compounds. Hence it was assumed that, in terms of John Dalton's Atomic Theory of 1802, that one atom of hydrogen combined with one atom of oxygen to form one 'compound-atom' (in modern language one molecule) of water. The formula of water was thus declared to be HO and the atomic mass of oxygen (on the scale $H = 1$) to be 8.

It was difficult to reconcile these conclusions with the volumetric investigations made earlier; particularly as Dalton, in an extension of his Atomic Theory, postulated that the volumes occupied by the atoms of all gases are equal when measured under the same conditions of temperature and pressure. A modification to Dalton's postulate by Amadeo Avogadro of Italy brought the solution to such problems.

Avogadro's hypothesis states: *equal volumes of all gases, measured under the same conditions of temperature and pressure, contain the same number of molecules*. Thus the observed facts of both the volumetric and gravimetric composition of water could be explained. We would nowadays write the equation for the formation of water as:



The difficulty of applying Dalton's theory disappears when instead of having to consider the ultimate particles in gaseous elements to be *atoms*, Avogadro's interpretation allows us to regard the ultimate particles in such gaseous elements as hydrogen and oxygen to be *diatomic molecules*. Avogadro's hypothesis is also consistent with the observation that one mole of gases have a volume of about 22.4 dm^3 at s.t.p., for one mole of any gas contains the same number of molecules. This number is known as the Avogadro or Loschmidt number, and given the symbol L . Methods for determining the Avogadro number will be discussed in later chapters.

The volume proportions in which gases react

This aspect of reactions between gases was studied by many investigators in the eighteenth and nineteenth centuries. It is possible to duplicate their experiments today, using gas-syringe techniques, with an ease that these investigators would envy.

Ammonia gas is known to be composed of nitrogen and hydrogen. If a fixed volume of ammonia is passed between two gas syringes over a heated

iron catalyst, it is virtually decomposed into its elements. The volume of the nitrogen/hydrogen mixture so formed is double that of the original ammonia. If this mixture is passed over heated copper oxide, the hydrogen in it combines with oxygen from the solid to form water which on cooling occupies negligible volume. The residual gas, which is nitrogen, is found to have a volume of one-third that of the nitrogen/hydrogen mixture. Thus

two volumes of ammonia → one volume of nitrogen + three volumes of hydrogen

Assuming the diatomicity of nitrogen and hydrogen, this is consistent with the equation:



From a study of the results obtained by his own investigations and those of others, the French chemist Joseph Gay-Lussac published his Law of Volume Combinations in Gases. This can be stated in the form: *when gases combine, the volume proportions in which they do so are in simple numerical ratios to each other and to those of any gaseous products. All volumes must be measured under the same conditions of temperature and pressure.*

Determination of relative atomic masses (formerly called atomic weights)

In 1858 the Italian chemist Stanislao Cannizzaro demonstrated how the work of Avogadro particularly could form the basis of a powerful method of deducing relative atomic masses. His method can be applied only to those elements that form a reasonably wide range of volatile compounds and was most useful in fixing the relative atomic masses of the non-metallic elements such as carbon. Examination of the data in Table 1.2 will make his method clear.

Table 1.2 Cannizzaro's method applied to carbon

Compound	Relative molar mass	% carbon	Mass of carbon in one mole/g
Carbon dioxide	44	23.7	12
Carbon monoxide	28	42.9	12
Cyanogen	52	46.2	24
Ethane	30	80	24
Ethene	28	85.7	24
Ethyne	26	92.3	24
Methane	16	75	12
Propane	44	81.8	36
Benzene	78	92.3	72
Butane	58	82.7	48
Trichloromethane	119.5	10	12

Since the smallest mass of carbon in one mole of any of the above compounds is 12 and the other masses of carbon per mole are whole number multiples of this, the relative atomic mass of carbon is likely to be 12.

The use of the mass spectrometer has, in recent years, rendered these classical methods of determining relative molar masses and atomic masses obsolete. The principle of the mass spectrometer is discussed in the next chapter.

The kinetic theory of matter

In 1827, the English botanist Robert Brown was observing a suspension of pollen grains in water through a microscope. He was interested to note that the pollen grains exhibited constant and random motion. This type of motion, now known as Brownian motion, was also observed when other relatively small particles were suspended in a liquid or a gas. An explanation of this effect was suggested in 1863 by Wiener. He explained the random motion as due to the continual bombardment of the particles by the molecules of the material in which they were suspended. The motion of the invisible molecules is thus made manifest by its effect on the suspended particles.

Out of such observations the Kinetic Theory, the theory of molecules in motion, gradually emerged. The postulates on which the quantitative interpretation of the Kinetic Theory is based are:

- gases consist of large assemblies of molecules in which the distance between the molecules is very much greater than their diameters;
- there are no attractive or repulsive forces between the molecules;
- the molecules are in a rapid state of random motion in all directions;
- the temperature of the gas is a function of the average kinetic energy of the molecules.

8 Principles of Physical Chemistry

It is possible to apply the principles of Newtonian mechanics to these postulates to obtain an equation relating the motion of the molecules to the measurable parameters volume, pressure, and temperature.

In mechanics a distinction is made between speed and velocity. The speed of a body is the rate of change of position with time without specification of direction; it is said to be a *scalar* quantity. Velocity is the rate of change of position in a specific direction; it is said to be a *vector* quantity. Hence the average velocity of the molecules in a sample of gas is zero. (If they are regarded as travelling in every possible direction, the velocity of any one molecule being balanced on average by that of another molecule travelling at the same speed and in a direction 180° to it.) For this reason it is necessary to define the quantity *root mean square velocity*, given the symbol \bar{c}^2 . Consider n molecules which at a given instant have velocities $c_1, c_2, c_3, \dots, c_n$. The root mean square velocity is given by:

$$\bar{c}^2 = \sqrt{[c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2] \times \frac{1}{n}}$$

This device makes all the velocity values positive by squaring the negative values, and hence the average is not zero.

Let these n molecules be contained in a cubic vessel of side l metres and let the mass of each molecule be m grams. The root mean square velocity will be in m s^{-1} . Consider one of these molecules, of velocity c_1 , whose motion and velocity is represented by the line OA on Figure 1.10. Its velocity can be resolved into the three components x , y , and z represented by the lines Ox, Oy, and Oz which are parallel to the walls of the container.

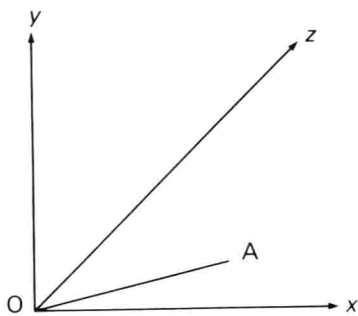


Figure 1.10 The motion of a molecule in a cubical container

Thus

$$c_1^2 = x^2 + y^2 + z^2$$

Consider the component of the motion of the molecule along the axis Ox. On collision with one wall of the containing vessel, which it strikes normally, it is reflected in a direction 180° to its original motion by this collision and it suffers a change of momentum:

$$mx - (-mx) = 2mx$$

Travelling x metres in one second, the molecule makes one impact with a wall for each distance of l metres travelled, and it suffers x/l changes of direction per second. The change of momentum per second is therefore:

$$\frac{x}{l} \times 2mx = \frac{2mx^2}{l}$$

Similarly its change of momentum per second along the y and z axes is given by $2my^2/l$ and $2mz^2/l$. Thus the total change of momentum per second of the molecule is:

$$\frac{2m}{l}(x^2 + y^2 + z^2) = \frac{2mc_1^2}{l}$$

According to Newton's second law of motion, the force exerted by the impact of a body on a surface is equal to the rate of change of momentum of that body. Thus the force exerted on the walls of the containing cube by our molecule is $2mc_1^2/l$. The total force exerted by the n molecules is:

$$\frac{2m}{l}(c_1^2 + c_2^2 + c_3^2 + \dots + c_n^2) = \frac{2nm\bar{c}^2}{l}$$

(Collisions between molecules do not result in change of total momentum and so can be neglected in this argument.)

Pressure is force per unit area and the total area of the six faces of our cube is $6l^2$, hence the total pressure of the gas is:

$$\frac{2nm\bar{c}^2}{l} \times \frac{1}{6l^2} = \frac{2nm\bar{c}^2}{6l^3}$$

and as l^3 is the volume of the container, this becomes:

$$pV = \frac{1}{3} nm\bar{c}^2$$

or for one mole of gas containing Avogadro's number of molecules (L),

$$pV = RT = \frac{1}{3} Lm\bar{c}^2$$

We can use this relationship to demonstrate the connection between the temperature and the kinetic energy of the molecules,

$$RT = \frac{1}{3} Lm\bar{c}^2 = \frac{2}{3} \times \frac{Lm\bar{c}^2}{2}$$

But $Lm\bar{c}^2/2$ is the total kinetic energy (K.E.) of the molecules.

Hence,

$$RT = \frac{2}{3} \text{ K.E.}$$

$$T = \frac{2}{3} \text{ K.E.} \times \frac{1}{R}$$

Thus the total, and therefore the average, kinetic energy of the molecules is directly proportional to the temperature.

Root mean square velocities of gaseous molecules

We can use the equation $RT = \frac{1}{3} Lm\bar{c}^2$ to calculate the root mean square velocities of gases under known temperature conditions.

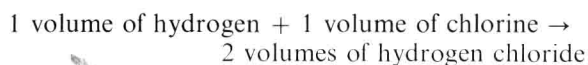
Table 1.3 Root mean square velocities of some gases at 0 °C

Gas	Root mean square velocity at 0 °C/m s ⁻¹
Argon	410
Carbon dioxide	390
Hydrogen	1838
Nitrogen	493
Oxygen	460

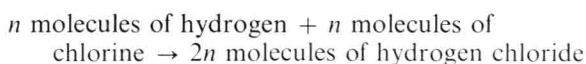
The atomicities of gases

In earlier work in this chapter the diatomicity of many common elemental gases has been assumed. It is now possible to present evidence in support of this assumption.

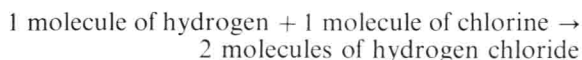
(1) *Evidence from Gay-Lussac's law and Avogadro's hypothesis* When the combination of hydrogen and chlorine to form hydrogen chloride is investigated volumetrically, it is found that:



Applying Avogadro's hypothesis,



Thus



Each molecule of hydrogen chloride must thus contain *half* a molecule of hydrogen and thus the hydrogen molecule must contain an even number of hydrogen atoms. Additional evidence that this even number is two can be deduced from the observation that hydrogen chloride dissolves in water to form a monobasic acid (i.e. each mole of acid contains one mole of replaceable hydrogen).

(2) *Evidence from the Kinetic Theory* It can be shown, as a consequence of the kinetic theory, that the ratio

$$\gamma = \frac{\text{specific heat of a gas at constant pressure}}{\text{specific heat of the gas at constant volume}}$$

is, theoretically, 1.67 for a monatomic gas and 1.40 for a diatomic gas. The measured value for this ratio for hydrogen is 1.40.

Deducing the gas laws from the kinetic theory

Boyle's law is directly deducible from the kinetic theory as $Lm\bar{c}^2$ is a constant at any one temperature and hence:

$$pV = \frac{1}{3} Lm\bar{c}^2 = \text{constant}$$

Charles' law is involved in deducing the direct relationship between the temperature of a gas and the average kinetic energy of the molecules and this demonstrates the fundamental nature of this law.

Two other gas laws, originally established on an empirical basis, can be deduced from the kinetic theory of gases.

(a) *Dalton's law of partial pressures* We have seen that, in terms of the kinetic theory, the pressure of a gas can be regarded as due to the forces exerted on the walls of the containing vessel due to their change of momentum on collision. Thus if a mixture of different types of molecule is contained in the vessel, each component of the mixture contributes its partial pressure to the total pressure independently of the contribution of the other components. Hence the total pressure (p_{total}) is equal to the sum of the partial pressures of the components ($p_1, p_2, p_3, \dots, p_n$).

$$p_{\text{total}} = p_1 + p_2 + p_3 + \dots + p_n$$

10 Principles of Physical Chemistry

(b) Graham's law of diffusion (or effusion)

Diffusion in a gas is the tendency of that gas to fill the entire space available to it. If a gas is held in a container with an outlet into an environment at lower pressure, because of diffusion the gas will pass from the container to the outside until the pressures inside and outside the container are equalized. This process is defined as effusion. Applying the quantitative statement of the kinetic theory in the form:

$$pV = \frac{1}{3} Lm\bar{c}^2$$

we see that $\bar{c}^2 \propto 1/m$ and as the rate of diffusion of a gas is proportional to the average speed of the molecules,

$$\text{rate of diffusion (or effusion)} \propto \frac{1}{\sqrt{\text{molar mass}}}$$

This relationship was first established experimentally by Thomas Graham in 1829. Experimental evidence for the law can be obtained using the apparatus shown in Figure 1.11. A supply of dry gas is attached to the apparatus via the three-way tap as shown and used to sweep air out of the gas syringe. When this has been accomplished, the tap is adjusted to connect the syringe to the lower tube and the time taken for a suitable volume of gas to effuse from the apparatus via the pin-hole aperture is noted. The experiment is then repeated for other gases.

Specimen results are shown in Figure 1.12. The linear plot, passing through the origin, shows experimental agreement with the theoretical prediction.

Real gases and deviations from the gas laws

From the mathematical statement of Boyle's law, $pV = \text{constant}$, we should expect a graph of the product of pressure and volume, for a fixed mass of gas at constant temperature, plotted against pressure to be linear and parallel to the x axis. In Figure 1.13, this plot is made for sulphur dioxide and it can be seen that considerable deviation from this expectation occurs. This is due to the fact that real gases do not show behaviour in complete accord with the postulates of the kinetic theory in two important respects:

(1) There is not zero attraction between the molecules of the gas, the bulk of the gas molecules exert forces on those on the outside of the gas having the effect of pulling these latter molecules away

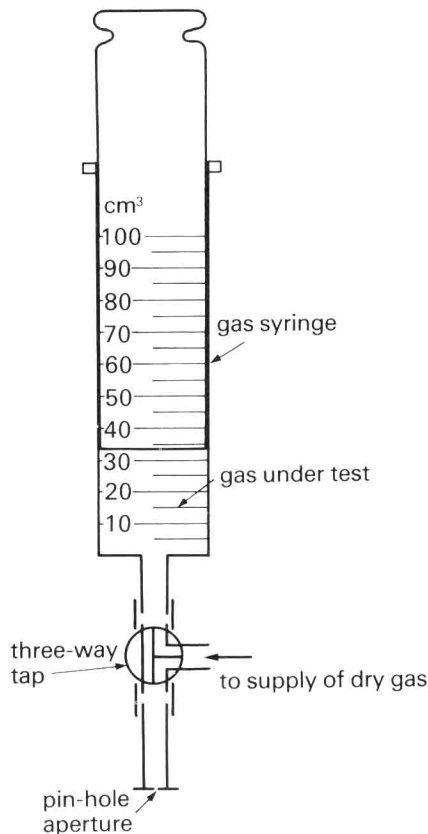


Figure 1.11 Apparatus to investigate the rates of effusion of gases

from the wall of the container. The effective pressure is thus less than the ideal pressure postulated by the kinetic theory. This 'internal pressure' demands that a correction term be added to the measured pressure. The forces responsible for the internal pressure of a gas are known as van der Waals' forces, a name whose significance will become apparent later.

(2) The volumes of the molecules are not completely negligible in comparison with the total volume of the gas. The effective volume of gas is thus the measured volume less a correction term for the volumes of the molecules.

In 1873, Johannes van der Waals proposed the following modification to the gas equation to take account of these considerations:

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