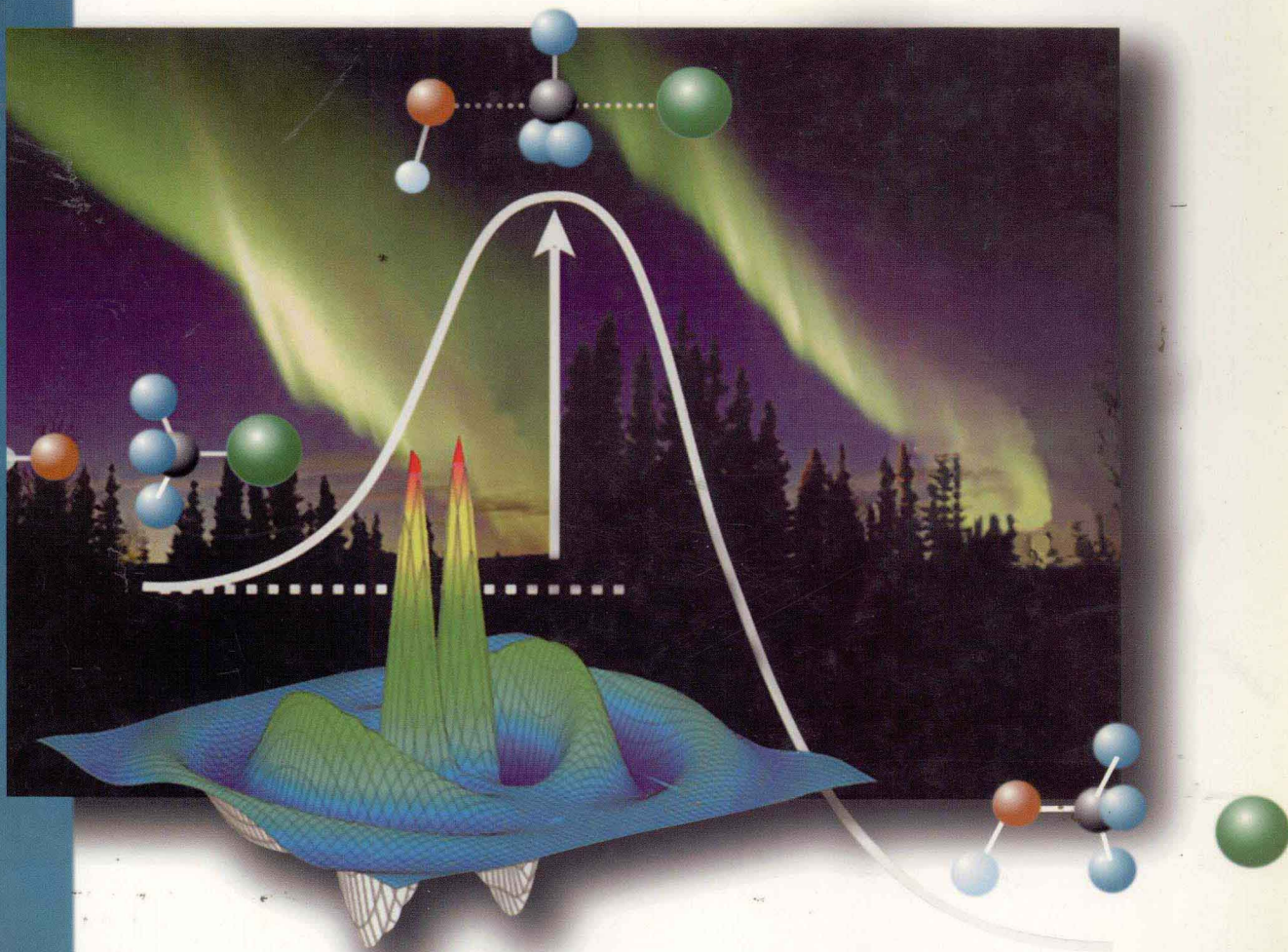


精要速览系列 (影印版)

*Instant Notes*

PHYSICAL CHEMISTRY

# 物理化学



A.G. Whittaker, A.R. Mount & M.R. Heal 科学出版社

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# PHYSICAL CHEMISTRY

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*A. G. Whittaker, A. R. Mount & M. R. Heal*

Department of Chemistry,  
University of Edinburgh, Edinburgh, UK



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## 内 容 简 介

本书是国外优秀教材畅销榜的上榜教材,面向大学本科生,由英国著名大学具有丰富教学经验的一流教授编写,它以一种风格独特的方式,全面、系统地概括了有机化学的核心内容和前沿动态,并以一种便于学习、利于复习的编写形式,使学生能快速、准确的掌握知识,很好地指导学习和考试。书中英文使用最为自然、易懂的语句,是提高专业外语的最佳用书。

A. G. Whittaker, A. R. Mount & M. R. Heal

Instant Notes in Physical Chemistry

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# ABBREVIATIONS

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amu	atomic mass unit	LH	left hand
Bq	Becquerel	LHS	left hand side
Ci	Curie	NMR	nuclear magnetic resonance
D	debye	ppm	parts per million
emf	electromotive force	RH	right hand
ES	enzyme-substrate complex	RHS	right hand side
ESR	electron spin resonance	rms	root mean square
g	gerade	TMS	tetramethylsilane
Gy	gray	u	ungerade
LCAO	linear combination of atomic orbitals		

# PREFACE

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Physical chemistry is an unexpected shock to many university students. From the semi-empirical approaches of the school laboratory, first year undergraduates suddenly find themselves propelled into an unexpected quagmire of definitions and equations. Worse still, although the applicability of the subject is sometimes obvious, studying the behavior of a particle in an infinitely deep well can seem nothing short of farcical on first approach.

In any scientific discipline, a fundamental understanding is more important than learning lists, but this is probably more true in physical chemistry than in other branches of chemistry. Let's be clear from the outset – understanding *is* the key to physical chemistry, but the maelstrom of mathematics often clouds the student's ability to create a comprehensible mental model of the subject.

As the authors of this text, we therefore found ourselves in a paradoxical situation – writing a book containing lists of facts on a subject which isn't primarily about lists of facts. So although this book is primarily a revision text we did not wish it to be merely an encyclopedia of equations and definitions. In order that the conceptual content of the book is given sufficient weight to aid understanding, we have limited the extent of the mathematical treatments to the minimum required of a student. The rigorous arguments which underpin much of physical chemistry are left for other authors to tackle, with our own recommendations for further reading included in the bibliography.

Since our primary aim has been to produce a quick reference and revision text for all first and second year degree students whose studies include physical chemistry, we have recognized that different aspects of the subject are useful in different fields of study. As NMR spectroscopy is to a biochemist's protein study, so is band theory to the solid state chemist, and thermodynamics to the chemical engineer. With this in mind, we have drawn not just on our own teaching experiences, but have consulted with colleagues in the life sciences and in other physical sciences. The rigor of the central themes has not been diluted, but the content hopefully reflects the range of scientists for whom physical chemistry is an important supplement to their main interests.

In organizing the layout of the book, we have aimed to introduce the various aspects of physical chemistry in an order that gives the opportunity for continuous reading from front to back with the minimum of cross-referencing. Thus we start with the basic properties of matter which allows us then to discuss thermodynamics. Thermodynamics leads naturally into equilibria, solutions and then kinetics. The final sections on bonding and spectroscopy likewise follow on from the foundations laid down in the section on quantum mechanics. The background to a range of important techniques is included in the appropriate sections, and once again this reflects the wide application of the subject matter as with, for example, electrophoresis and electro-osmosis.

Whatever your background in coming to this book, our objective has been to use our own perspectives of physical chemistry to aid *your* insight of the subject. Physical chemistry is not the monster that it seems at first, if for no other reason than because a little understanding goes a long way.

We hope that this text contributes to helping you reach the level of understanding you need. Understanding the world around you really is one of the thrills of science.

Finally, we thank Kate, Sue and Janet for all their patience during the preparation of this book.

M.R. Heal, A.R. Mount, A.G. Whittaker



# CONTENTS

---

Abbreviations	vii
Preface	ix
<b>Section A – States of matter</b>	<b>1</b>
A1 Perfect gases	1
A2 Molecular behavior in perfect gases	4
A3 Non-ideal gases	8
A4 Liquids	12
A5 Crystalline solids	17
A6 Diffraction by solids	22
<b>Section B – Thermodynamics</b>	<b>27</b>
B1 The first law	27
B2 Enthalpy	32
B3 Thermochemistry	35
B4 Entropy	40
B5 Entropy and change	44
B6 Free energy	47
<b>Section C – Equilibria</b>	<b>51</b>
C1 Fundamentals of equilibria	51
C2 Fundamentals of acids and bases	58
C3 Further acids and bases	61
C4 Acid-base titrations	65
C5 Solubility	70
<b>Section D – Solutions</b>	<b>73</b>
D1 Non-electrolyte solutions	73
D2 Solutions	76
D3 Colligative properties	78
D4 Phase equilibria	82
D5 Phase diagrams of mixtures	86
<b>Section E – Ionic solutions</b>	<b>95</b>
E1 Ions in aqueous solution	95
E2 Thermodynamics of ions in solution	99
E3 Electrochemical cells	102
E4 Electrochemical thermodynamics	105
E5 Electrochemistry and ion concentration	110
E6 Macroscopic aspects of ionic motion	114
E7 Molecular aspects of ionic motion	118
E8 The motion of larger ions	120
<b>Section F – Kinetics</b>	<b>123</b>
F1 Empirical approaches to kinetics	123
F2 Rate law determination	129
F3 Energetics and mechanisms	136
F4 Formulation of rate laws	142

---

F5	Rate laws in action	146
F6	The kinetics of real systems	152
<b>Section G</b>	<b>– Quantum nature of the physical world</b>	<b>159</b>
G1	Nuclear structure	159
G2	Applications of nuclear structure	163
G3	Quantization of energy and particle-wave duality	168
G4	The wave nature of matter	174
G5	The structure of the hydrogen atom	183
G6	Many-electron atoms	189
G7	Chemical and structural effects of quantization	194
G8	Statistical thermodynamics	199
<b>Section H</b>	<b>– Bonding</b>	<b>205</b>
H1	Elementary valence theory	205
H2	Valence bond theory	209
H3	Molecular orbital theory of diatomic molecules I	213
H4	Molecular orbital theory of diatomic molecules II	218
H5	Strong solid phase interactions	225
H6	Weak intermolecular interactions	231
<b>Section I</b>	<b>– Spectroscopy</b>	<b>237</b>
I1	General features of spectroscopy	237
I2	Practical aspects of spectroscopy	241
I3	Rotational spectroscopy	246
I4	Vibrational spectroscopy	251
I5	Applied vibrational spectroscopy	255
I6	Electronic spectroscopy	259
I7	Photochemistry in the real world	264
I8	Magnetic resonance spectroscopy	268
<b>Appendix</b>	<b>– mathematical relations</b>	<b>275</b>
<b>Further reading</b>		<b>277</b>
<b>Index</b>		<b>281</b>



# A1 PERFECT GASES

## Key Notes

### Gases

A gas is a fluid which has no intrinsic shape, and which expands indefinitely to fill any container in which it is held.

### The perfect gas equations

The physical properties of a perfect gas are completely described by the amount of substance of which it is comprised, its temperature, its pressure and the volume which it occupies. These four parameters are not independent, and the relations between them are expressed in the gas laws. The three historical gas laws – Boyle's law, Charles' law and Avogadro's principle – are specific cases of the perfect gas equation of state, which is usually quoted in the form  $pV = nRT$ , where  $R$  is the gas constant.

### Partial pressure

The pressure exerted by each component in a gaseous mixture is known as the partial pressure, and is the pressure which that component would exert were it alone in that volume. For a perfect gas, the partial pressure,  $p_x$ , for  $n_x$  moles of each component  $x$  is given by  $p_x = n_x R T / V$ . Dalton's law states that 'the total pressure exerted by a mixture of ideal gases in a volume is equal to the arithmetic sum of the partial pressures'. The quantity  $n_x / n_{\text{total}}$  is known as the mole fraction of component  $A$ , and denoted  $x_A$ . It directly relates the partial pressure,  $p_A$ , of a component  $A$ , to the total pressure through the expression  $p_A = x_A p_{\text{total}}$ .

### Related topics

Molecular behavior in perfect gases (A2)

Non-ideal gases (A3)

## Gases

A gas is a fluid which has no resistance to change of shape, and will expand indefinitely to fill any container in which it is held. The molecules or atoms which make up a gas interact only weakly with one another. They move rapidly, and collide randomly and chaotically with one another.

The physical properties of an ideal gas are completely described by four parameters which, with their respective SI units are:

- the amount of substance of which it is comprised,  $n$ , in moles;
- the temperature of the gas,  $T$ , in Kelvin;
- the pressure of the gas,  $p$ , in Pascal;
- the volume occupied by the gas,  $V$ , in  $\text{m}^3$ .

The four parameters are not independent, and the relations between them are expressed in the **gas laws**. The gas laws are unified into a single **equation of state** for a gas which fully expresses the relationships between all four properties. These relationships, however, are based on approximations to experimental observations, and only apply to a **perfect gas**. In what might be deemed a circular argument, a perfect gas is defined as one which obeys the perfect gas equation of state. In practical terms, however, adherence to the perfect gas

equation of state requires that the particles which make up the gas are infinitesimally small, and that they interact only as if they were hard spheres, and so perfect gases do not exist. Fortunately, it is found that the behavior of most gases approximates to that of a perfect gas at sufficiently low pressure, with the lighter noble gases (He, Ne) showing the most ideal behavior. The greatest deviations are observed where strong intermolecular interactions exist, such as water and ammonia. The behavior of non-ideal gases is explored in topic A3.

### The perfect gas equations

Historically, several separate gas laws were independently developed:

**Boyle's law;**  $p \cdot V = \text{constant}$  at constant temperature;  
**Charles' law;**  $V \propto T$  at constant pressure;  
**Avogadro's principle;**  $V \propto n$  at constant pressure and temperature.

These three laws are combined in the **perfect gas equation of state** (also known as the **ideal gas law** or the **perfect gas equation**) which is usually quoted in the form

$$pV = nRT$$

As written, both sides of the ideal gas equation have the dimensions of energy where  $R$  is the **gas constant**, with a value of  $8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$ . The perfect gas equation may also be expressed in the form  $pV_m = RT$ , where  $V_m$  is the **molar gas volume**, that is, the volume occupied by one mole of gas at the temperature and pressure of interest. The gas laws are illustrated graphically in Fig. 1, with lines representing Boyle's and Charles' laws indicated on the perfect gas equation surface.

The gas constant appears frequently in chemistry, as it is often possible to substitute for temperature, pressure or volume in an expression using the perfect gas equation – and hence the gas constant – when developing mathematical expressions.

### Partial pressure

When two or more gases are mixed, it is often important to know the relationship between the quantity of each gas, the pressure of each gas, and the overall pressure of the mixture. If the ideal gas mixture occupies a volume,  $V$ , then the pressure exerted by each component equals the pressure which that component would exert if it were alone in that volume. This pressure is called the **partial pressure**, and is denoted as  $p_A$  for component A,  $p_B$  for component B, etc. With this definition, it follows from the perfect gas equation that the partial pressure for each component is given by:

$$p_x = n_x R T / V$$

where  $p_x$  is the partial pressure of  $n_x$  moles of component  $x$ .

The total pressure exerted by a mixture of ideal gases is related to the partial pressures through **Dalton's law**, which may be stated as,

*'the total pressure exerted by a mixture of ideal gases in a volume is equal to the arithmetic sum of the partial pressures'.*

If a gas mixture is comprised of, for example,  $n_A$ ,  $n_B$ , and  $n_C$  moles of three ideal gases, A, B, and C, then the total pressure is given by:

$$\begin{aligned} P_{\text{total}} &= p_A + p_B + p_C = n_A R T / V + n_B R T / V + n_C R T / V = (n_A + n_B + n_C) R T / V \\ &= n_{\text{total}} R T / V \end{aligned}$$

where  $n_{\text{total}}$  is the total number of moles of gas, making this a simple restatement of the **ideal gas law**.

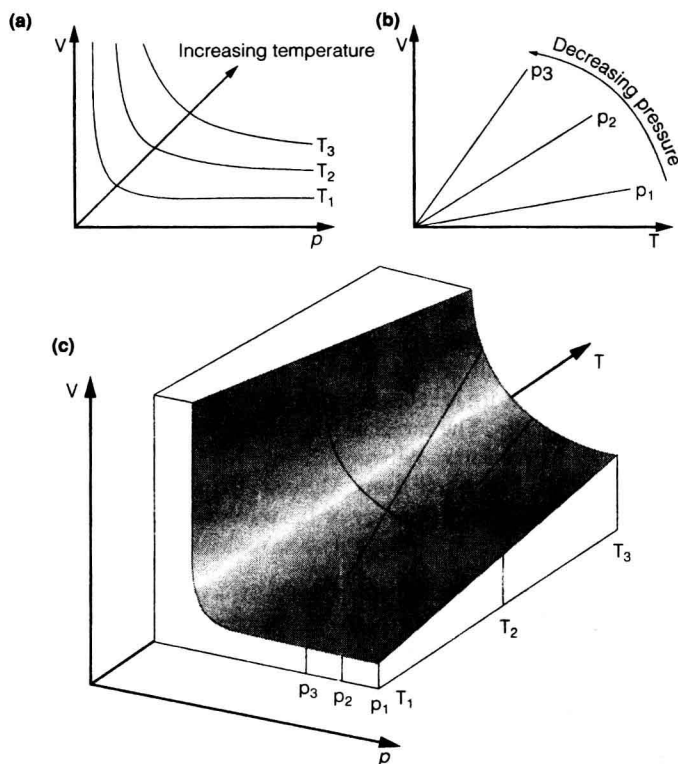


Fig. 1. Graphical representations of the ideal gas equations. (a) Boyle's law; (b) Charles' law; (c) The surface representing the perfect gas equation. The locations of the lines from (a) and (b) are indicated on the surface.

The partial pressure of component A divided by the total pressure is given by:

$$p_A/p_{\text{total}} = (n_A R T/V)/(n_{\text{total}} R T/V) = n_A/n_{\text{total}}$$

The quantity  $n_A / n_{\text{total}}$  is known as the **mole fraction** of component A, and is denoted  $x_A$  (Topic D1). The advantage of this quantity is that it is easily calculated, and allows ready calculation of partial pressures through the relation:

$$p_A = x_A p_{\text{total}}$$

# A2 MOLECULAR BEHAVIOR IN PERFECT GASES

## Key Notes

### The kinetic theory of gases

The kinetic theory of gases is an attempt to describe the macroscopic properties of a gas in terms of molecular behavior. Pressure is regarded as the result of molecular impacts with the walls of the container, and temperature is related to the average translational energy of the molecules. The molecules are considered to be of negligible size, with no attractive forces between them, travelling in straight lines, except during the course of collisions. Molecules undergo perfectly elastic collisions, with the kinetic energy of the molecules being conserved in all collisions, but being transferred between molecules.

### The speed of molecules in gases

The range of molecular speeds for a gas follows the Maxwell distribution. At low temperatures, the distribution comprises a narrow peak centered at low speed, with the peak broadening and moving to higher speeds as the temperature increases. A useful average, the root mean square (rms) speed,  $c$ , is given by  $c = (3RT/M)^{1/2}$  where  $M$  is the molar mass.

### The molecular origin of pressure

According to the kinetic theory of gases, the pressure which a gas exerts is attributed to collisions of the gas molecules with the walls of the vessel within which they are contained. The pressure from these collisions is given by  $p = (nMc^2)/3V$ , where  $n$  is the number of moles of gas in a volume  $V$ . Substitution for  $c$ , yields the ideal gas law.

### Effusion

Effusion is the escape of a gas through an orifice. The rate of escape of the gas will be directly related to the root mean square speed of the molecules. Graham's law of effusion relates the rates of effusion and molecular mass or density of any two gases at constant temperatures:

$$\frac{c_1}{c_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{\rho_2}{\rho_1}}$$

### Mean free path

The mean free path,  $\lambda$ , is the mean distance travelled by a gas molecule between collisions given by

$$\lambda = \frac{RT}{\sqrt{2}N_A\sigma p}$$

where  $\sigma$  is the collision cross-section of the gas molecules.

### The collision frequency

The collision frequency,  $z$ , is the mean number of collisions which a molecule undergoes per second, and is given by:

$$z = \frac{\sqrt{2}N_A\sigma p c}{RT}$$

## Related topics

Perfect gases (A1)

Non-ideal gases (A3)

### The kinetic theory of gases

The gas laws (see Topic A1) were empirically developed from experimental observations. The **kinetic theory of gases** attempts to reach this same result from a model of the molecular nature of gases. A gas is described as a collection of particles in motion, with the macroscopic physical properties of the gas following from this premise. Pressure is regarded as the result of molecular impacts with the walls of the container, and temperature is related to the average translational energy of the molecules.

Three basic assumptions underpin the theory, and these are considered to be true of real systems at low pressure:

1. the size of the molecules which make up the gas is negligible compared to the distance between them;
2. there are no attractive forces between the molecules;
3. the molecules travel in straight lines, except during the course of collisions. Molecules undergo perfectly elastic collisions; i.e. the kinetic energy of the molecules is conserved in all collisions, but may be transferred between them.

### The speed of molecules in gases

Although the third premise means that the mean molecular energy is constant at constant temperature, the energies, and hence the velocities of the molecules, will be distributed over a wide range. The distribution of molecular speeds follows the **Maxwell distribution of speeds**. Mathematically, the distribution is given by:

$$\frac{dn_s}{N} = f(s)ds = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{M}{RT}\right)^{3/2} s^2 e^{-ms^2/2RT} ds$$

where  $f(s)ds$  is the probability of a molecule having a velocity in the range from  $s$  to  $s + ds$ ,  $N$  is the number and  $M$  is the molar mass of the gaseous molecules. At low temperatures, the distribution is narrow with a peak at low speeds, but as the temperature increases, the peak moves to higher speeds and distribution broadens out (Fig. 1).

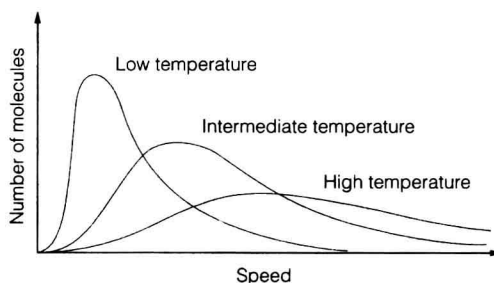


Fig. 1. The Maxwell distribution of speeds for a gas, illustrating the shift in peak position and distribution broadening as the temperature increases.

The **most probable speed** of a gas molecule is simply the maximum in the Maxwell distribution curve, and may be obtained by differentiation of the previous expression to give:

$$\text{most probable } s = \left(\frac{2RT}{M}\right)^{1/2}$$

A more useful quantity in the analysis of the properties of gases is the **root mean square (rms) speed**,  $c$ . This is the square root of the arithmetic mean of the squares of the molecular speeds given by:

$$c = \left( \frac{3RT}{M} \right)^{\frac{1}{2}}$$

$$\text{where } c = \sqrt{\frac{s_1^2 + s_2^2 + \dots + s_N^2}{N}} = \sqrt{\frac{\sum_{i=1}^N s_i^2}{N}}$$

The rms speed is always greater than the most probable speed. For oxygen molecules at standard temperature, the most probable speed is  $393 \text{ m s}^{-1}$  and the root mean square speed is  $482 \text{ m s}^{-1}$ .

### The molecular origin of pressure

In the kinetic theory of gases, the pressure which a gas exerts is attributed to collisions of the gas molecules with the walls of the vessel within which they are contained. A molecule colliding with the wall of the vessel will change its direction of travel, with a corresponding change in its momentum (the product of the mass and velocity of the particle). The force from the walls is equal to the rate of change of momentum, and so the faster and heavier and more dense the gas molecules, the greater the force will be. The equation resulting from mathematical treatment of this model may be written as:

$$p = \frac{nMc^2}{3V}$$

where  $n$  is the number of moles of gas in a volume  $V$  (i.e. the density). This equation may be rearranged to a similar form to that of the ideal gas law:  $PV = nMc^2/3$ .

Substituting for  $c$ , yields  $PV = n m(3RT/m)/3 = nRT$ , i.e. the ideal gas law.

Alternatively, we may recognize that the value  $\frac{1}{2}Mc^2$  represents the rms kinetic energy of the gas,  $E_{\text{kinetic}}$  and rewrite the equation to obtain the **kinetic equation for gases**:

$$pV = \frac{2nE_{\text{kinetic}}}{3}$$

### Effusion

Effusion is the escape of a gas through an orifice. The rate of escape of the gas is directly related to  $c$ :

$$c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3pV}{nM}} = \sqrt{\frac{3p}{\rho}}$$

where  $\rho$  is the density of the gas. For two gases at the same temperature and pressure, for example nitrogen and hydrogen, it follows that the ratio of the velocities is given by:

$$\frac{c_{H_2}}{c_{N_2}} = \sqrt{\frac{M_{N_2}}{M_{H_2}}} = \sqrt{\frac{\rho_{N_2}}{\rho_{H_2}}}$$

This is **Graham's law of effusion**.

**Mean free path**

Gas particles undergo collisions with other gas particles in addition to colliding with the walls. The mean distance travelled by a gas molecule between these random collisions is referred to as the **mean free path**,  $\lambda$ . If two molecules are regarded as hard spheres of radii  $r_A$  and  $r_B$ , then they will collide if they come within a distance  $d$  of one another where  $d = r_A + r_B$ . (see Topic F3, Fig. 2). The area circumscribed by this radius, given by  $\pi d^2$ , is the **collision cross-section**,  $\sigma$ , of the molecule. As molecules are not hard spheres, the collision cross-section will deviate markedly from this idealized picture, but  $\sigma$  still represents the effective physical cross-sectional area within which a collision may occur as the molecule travels through the gas. The mean free path decreases with increasing value of  $\sigma$ , and with increasing pressure, and is given by:

$$\lambda = \frac{RT}{\sqrt{2}N_A\sigma p} = \frac{k_B T}{\sqrt{2}\sigma p}$$

where **Avogadro's constant**,  $N_A$ , converts between molar and molecular units ( $R = N_A k_B$ , where  $k_B$  is the **Boltzmann Constant**).

**The collision frequency**

The **collision frequency**,  $z$ , of molecules in a gas is the mean number of collisions which a molecule will undergo per second. The collision frequency is inversely related to the time between collisions and it therefore follows that  $z$  is inversely proportional to the **mean free path** and directly proportional to the speed of the molecule i.e.  $z = c / \lambda$ ,

$$z = \frac{\sqrt{2}N_A\sigma p c}{RT}$$



## A3 NON-IDEAL GASES

### Key Notes

#### Non-ideal gases

Real gases at moderate and high pressures do not conform to the ideal gas equation of state, as intermolecular interactions become important. At intermediate pressures, attractive forces dominate the molecular interactions, and the volume of the gas becomes lower than the ideal gas laws would predict. At higher pressures, repulsive forces dominate the intermolecular interactions. At high pressure, the volume of all gases is larger than the ideal gas law predicts, and they are also much less compressible.

#### The virial equation

The virial equation is a mathematical approach to describing the deviation of real gases from ideal behavior by expanding the ideal gas equation using powers of the molar volume,  $V_m$ :

$$pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots\right)$$

The virial coefficients B, C, D, etc. are specific to a particular gas, but have no simple physical significance. A gas at low pressure has a large molar volume, making the second and subsequent terms very small, and reduces the equation to that of the perfect gas equation of state.

#### The van der Waals equation of state

This is a modification of the perfect gas equation which allows for the attractive and repulsive forces between molecules. The equation has the form  $(V - nb)(p + a(n/V)^2) = nRT$ . The van der Waals parameters,  $a$  and  $b$ , convey direct information about the molecular behavior. The term  $(V - nb)$  models the repulsive potential between the molecules, and the term  $(p + a(n/V)^2)$  compensates for the attractive potential. At high temperatures and low pressures, the correction terms become small compared to  $V$  and  $T$  and the equation reduces to the perfect gas equation of state.

#### Related topics

Perfect gases (A1)

Molecular behavior in perfect gases (A2)

### Non-ideal gases

Ideal gases are assumed to be comprised of infinitesimally small particles, and to interact only at the point of collision. At low pressure, the molecules in a real gas are small relative to the mean free path, and sufficiently far apart that they may be considered only to interact close to the point of collision, and so comply with this assumption. Because the intermolecular interactions become important for real gases at moderate and high pressures, they are **non-ideal gases** and they no longer conform to the ideal gas laws.

At intermediate pressures, attractive forces dominate the molecular interactions, and the volume of the gas becomes lower than the ideal gas laws would predict. As progressively higher pressures are reached, the molecules increase

their proximity to one another and repulsive forces now dominate the intermolecular interactions. At high pressures, all gases have a higher volume than the ideal gas law predicts, and are much less compressible.

The **compression factor**,  $Z$  expresses this behavior, and is commonly plotted as a function of pressure. It is defined as:

$$Z = \frac{pV_m}{RT}$$

where  $V_m$  is the **molar volume**.

$Z$  is equal to 1 at all pressures for a gas which obeys the ideal gas law, and it is found that all gases tend to this value at low pressure. For all real gases,  $Z$  is greater than 1 at high pressure, and for many gases it is less than 1 at intermediate pressures. The plot of  $Z$  as a function of  $p$  is shown in Fig. 1. Note that an equivalent plot of the product  $pV$  as a function of pressure at constant temperature is commonly used, and takes an almost identical form.

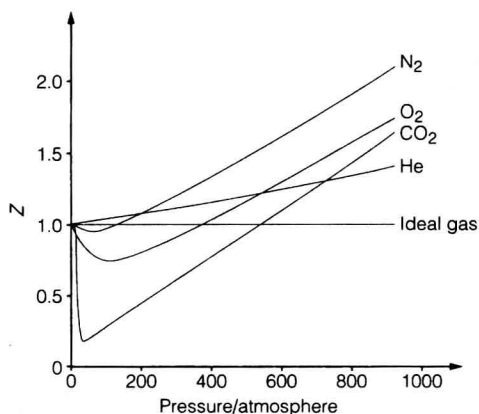


Fig. 1. Deviation of  $Z$  from ideality as a function of pressure.

Numerous attempts have been made to modify the perfect gas equation of state in order to describe real gases. The two most significant equations are the virial equation and the Van der Waals equation of state.

### The virial equation

The **virial equation** is primarily a mathematical attempt to describe the deviation from ideality in terms of powers of the molar volume,  $V_m$ . It takes the form:

$$pV_m = RT\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \dots\right)$$

The coefficients  $B$ ,  $C$ ,  $D$ , etc. are the **virial coefficients**. The expression converges very rapidly, so that  $B > C > D$ , and the expression is usually only quoted with values for  $B$  and  $C$  at best. For a gas at low pressure,  $V_m$  is large, making the second and subsequent terms very small, reducing the equation to that of the perfect gas equation of state. For an ideal gas,  $B$ ,  $C$ ,  $D$ , etc. are equal to zero, and the equation again reduces to that for an ideal gas. Although the virial equation provides an accurate description of the behavior of a real gas, the fit is empirical, and the coefficients  $B$ ,  $C$ ,  $D$ , etc., are not readily related to the molecular behavior.