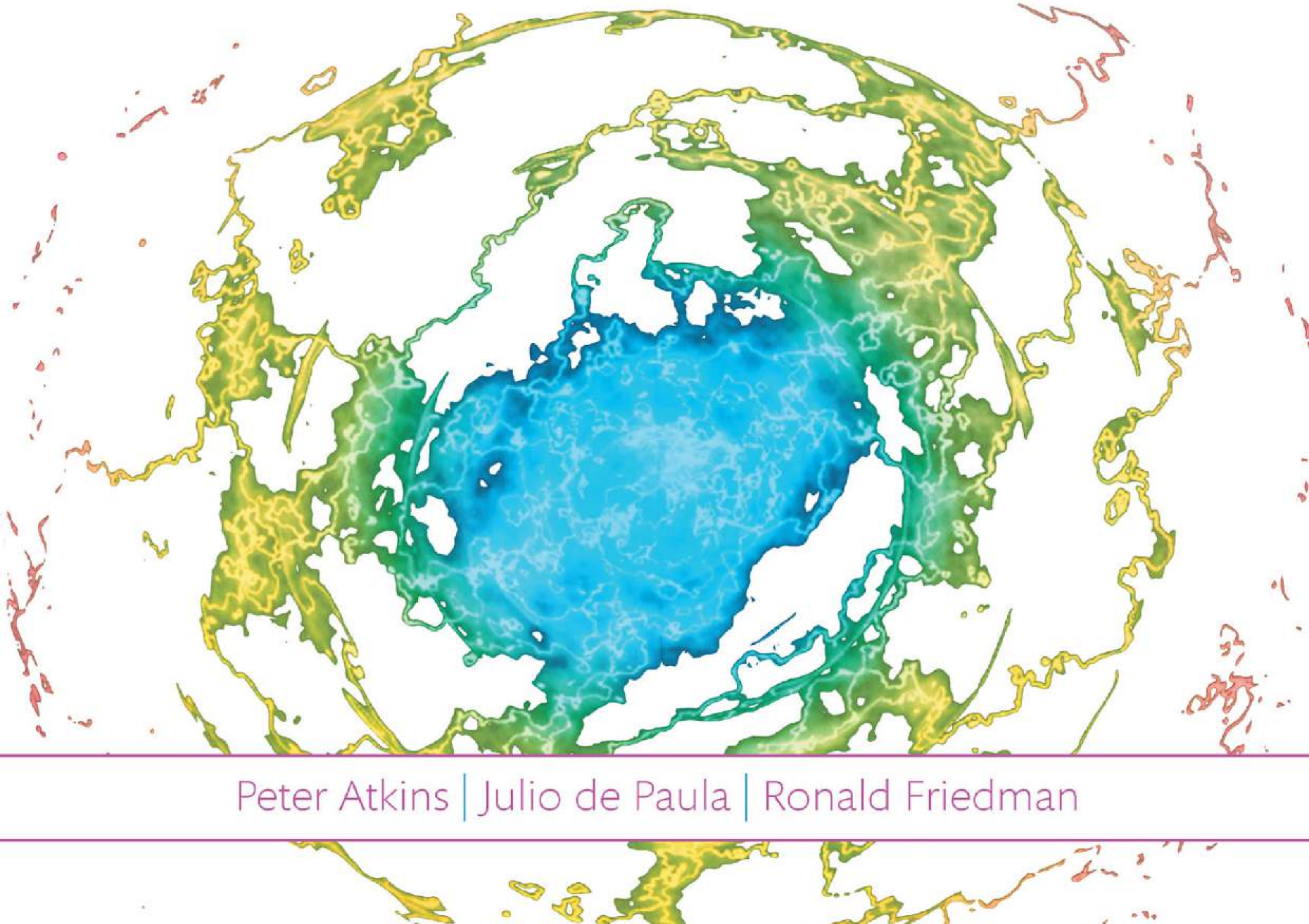
Physical Chemistry

Quanta, Matter, and Change

Second Edition



Peter Atkins | Julio de Paula | Ronald Friedman

FUNDAMENTAL CONSTANTS

Constant	Symbol	Value		
			Power of 10	Units
Speed of light	c	2.997 924 58*	10^{8}	$\mathrm{m\ s^{-1}}$
Elementary charge	e	1.602 176 565	10^{-19}	C
Planck's constant	h	6.626 069 57	10^{-34}	J s
	$\hbar=h/2\pi$	1.054 571 726	10^{-34}	J s
Boltzmann's constant	k	1.380 6488	10^{-23}	$\mathrm{J\ K^{-1}}$
Avogadro's constant	N_{A}	6.022 141 29	10^{23}	$\mathrm{mol^{-1}}$
Gas constant	$R=N_{\mathrm{A}}k$	8.314 4621		$\mathrm{J\ K^{-1}\ mol^{-1}}$
Faraday's constant	$F=N_{\mathrm{A}}e$	9.648 533 65	10^{4}	$\mathrm{C\ mol^{-1}}$
Mass				
electron	m_{e}	9.109 382 91	10^{-31}	kg
proton	m_{p}	1.672 621 777	10^{-27}	kg
neutron	m_{n}	1.674 927 351	10^{-27}	kg
atomic mass constant	m_{u}	1.660 538 921	10^{-27}	kg
Vacuum permeability	μ_0	4π*	10^{-7}	$\mathrm{J\ s^{2}\ C^{-2}\ m^{-1}}$
Vacuum permittivity	$\varepsilon_0=1/\mu_0c^2$	8.854 187 817	10^{-12}	$\mathrm{J^{-1}\ C^{2}\ m^{-1}}$
	$4\pi\varepsilon_0$	1.112 650 056	10^{-10}	$\mathrm{J^{-1}\ C^{2}\ m^{-1}}$
Bohr magneton	$\mu_{\mathrm{B}}=e\hbar/2m_{\mathrm{e}}$	9.274 009 68	10^{-24}	$\mathrm{J\ T^{-1}}$
Nuclear magneton	$\mu_{\mathrm{N}}=e\hbar/2m_{\mathrm{p}}$	5.050 783 53	10^{-27}	$\mathrm{J\ T^{-1}}$
Proton magnetic moment	μ_{p}	1.410 606 743	10^{-26}	$\mathrm{J\ T^{-1}}$
g-Value of electron	g_{e}	2.002 319 304		
Magnetogyric ratio				
electron	$\gamma_{\mathrm{e}}=-g_{\mathrm{e}}e/2m_{\mathrm{e}}$	−1.001 159 652	10^{10}	$\mathrm{C\ kg^{-1}}$
proton	$\gamma_{\mathrm{p}}=2\mu_{\mathrm{p}}/\hbar$	2.675 222 004	10^{8}	$\mathrm{C\ kg^{-1}}$
Bohr radius	$a_0=4\pi\varepsilon_0\hbar^2/e^2m_{\mathrm{e}}$	5.291 772 109	10^{-11}	m
Rydberg constant	$\tilde{R}_\infty=m_{\mathrm{e}}e^4/8h^3c\varepsilon_0^2$	1.097 373 157	10^{5}	$\mathrm{cm^{-1}}$
	$hc\tilde{R}_\infty/e$	13.605 692 53		eV
Fine-structure constant	$\alpha=\mu_0e^2c/2h$	7.297 352 5698	10^{-3}	
	α^{-1}	1.370 359 990 74	10^{2}	
Second radiation constant	$c_2=hc/k$	1.438 777 0	10^{-2}	m K
Stefan–Boltzmann constant	$\sigma=2\pi^5k^4/15h^3c^2$	5.670 373	10^{-8}	$\mathrm{W\ m^{-2}\ K^{-4}}$
Standard acceleration of free fall	g	9.806 65*		$\mathrm{m\ s^{-2}}$
Gravitational constant	G	6.673 84	10^{-11}	$\mathrm{N\ m^{2}\ kg^{-2}}$

* Exact value. For current values of the constants, see the National Institute of Standards and Technology (NIST) website.

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PHYSICAL CHEMISTRY

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Second edition

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ABOUT THE BOOK

This new edition follows the approach of the first edition in so far as it puts quantum theory in the forefront of the development, but we have transformed the presentation. Instead of the chapters of conventional texts, we have presented the material as a series of short *Topics* arranged into thematic groups we call *Focuses*. Our aim is to present reader and instructor with maximum flexibility. Although we had in mind a particular sequence when writing the book, we acknowledge that instructors might have different ideas. The division into many Topics will allow the instructor to tailor the text within the time constraints of the course as omissions will be much easier to make. The student should also find the Topics easier to assimilate and review. No longer is it necessary to take a linear path through chapters. Instead, students and instructors can match the choice of Topics to their learning objectives. Indeed, we have carefully avoided language that suggests the Topics have been read in the order they appear in the book.

We did consider avoiding any implication of structure, but came to the view that because the Topics do fall into thematic groups it would be sensible to acknowledge that fact. Moreover, we wanted the student, if not the instructor, to appreciate the intellectual coherence of the subject and to understand the context of each Topic. Each Focus therefore begins with a brief discussion of how its Topics cover a shared theme and how that theme links to others in the book. This contextual relationship is also captured by the 'Road Map' that lies at the head of each Focus. These maps also indicate not only how the Topics relate to each other but how certain Topics can be discarded and how each one draws on and feeds into other Focus groups. We wanted to convey the intellectual structure of the subject without imposing our will on its order of presentation.

We have focused on helping students master this sometimes daunting material. Thus, each Topic opens with three questions a student typically asks: 'Why do you need to know this material?', 'What is the key idea?', and 'What do you need to know already?'. The answers to the third question point to other Topics that we consider appropriate to have studied or at least to refer to as background to the current Topic.

This edition has more *Examples,* which require readers to collect and organize their thoughts about how to proceed, and more *Brief illustrations*, which show how to use an equation in a straightforward way. Both have *Self-tests* to enable the reader to assess their grasp of the material. In response to requests from students and reviewers, we have added more steps to many of the derivations of equations and solutions of Examples and have added hints about how to go from one expression to the next. Furthermore, we bring to this edition a new feature: *The chemist's toolkit*, which offers quick and immediate help on a concept from mathematics or physics. The *Mathematical background* sections provide more support and appear where we judge they are most needed. We have structured the end-of-Focus *Discussion questions*, *Exercises*, and *Problems* to match the grouping of the Topics, but have added Topic- and Focus-crossing *Integrated activities* to emphasize that no Topic is an island. We have added new material throughout the text and have incorporated as Topics sections that were previously 'Further information' sections.

Teaching and learning are being transformed by technology, and this edition of the text incorporates several web-based resources that enhance learning: they are identified in the *How to use this book* section that follows this preface.

We hope that you will enjoy using this text as much as we have enjoyed writing it. As ever, we hope that you will contact us with your suggestions for its continued improvement.

PWA
JdeP
RSF

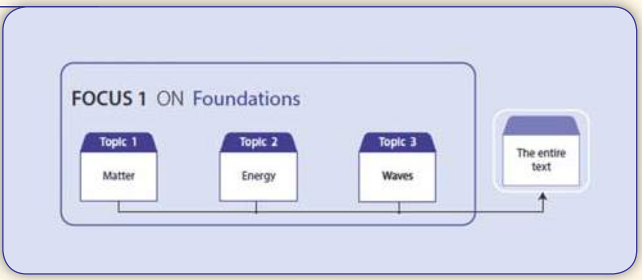
USING THE BOOK

For the second edition of *Physical Chemistry: Quanta, Matter, and Change* we have tailored the text even more closely to meet the needs of students. First, it has been radically reorganized to improve its accessibility, clarity, and flexibility. Second, in addition to the variety of learning features already present in the first edition, we have significantly enhanced the mathematics support by adding new 'Chemist's toolkit' boxes, equation annotations and labels, and checklists of key equations at the end of each Topic.

Organizing the information

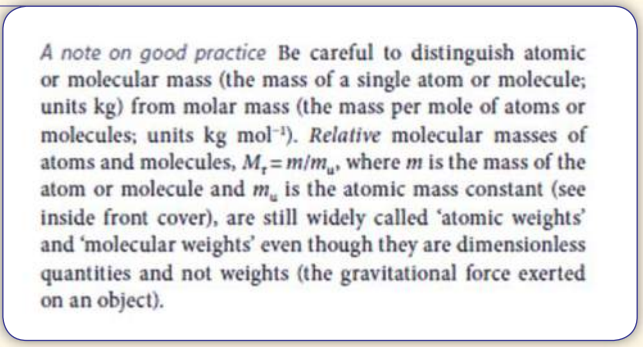
➤ Innovative new structure

Instead of being organized into chapters, the material is presented as 97 short Topics grouped into 20 Focus sections. The Roadmaps at the beginning of each Focus group show you the connections between the different Topics. Then each Topic opens with a comment on why it is important, a statement of the key idea, and a short summary of the background needed.



➤ Notes on good practice

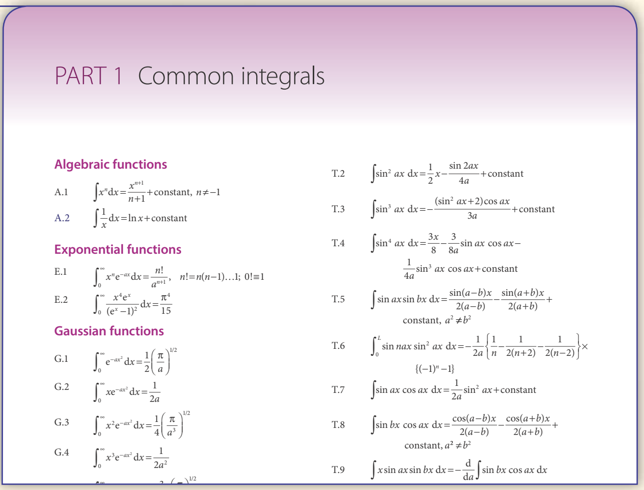
Our Notes on good practice will help you avoid making common mistakes. They encourage conformity to the international language of science by setting out the language and procedures adopted by the International Union of Pure and Applied Chemistry (IUPAC).



A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol^{-1}). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

➤ Resource section

The comprehensive 'Resource section' at the end of the book contains a table of integrals, operators, quantum numbers, and data, a summary of conventions about units, and character tables. Short extracts of these tables often appear in the Topics themselves principally to give an idea of the typical values of the physical quantities we are introducing.



PART 1 Common integrals

Algebraic functions

A.1 $\int x^n \mathrm{d}x = \frac{x^{n+1}}{n+1} + \text{constant},\ n \neq -1$

A.2 $\int \frac{1}{x} \mathrm{d}x = \ln x + \text{constant}$

Exponential functions

E.1 $\int_0^\infty x^n \mathrm{e}^{-ax} \mathrm{d}x = \frac{n!}{a^{n+1}},\quad n! = n(n-1)\ldots 1;\ 0! \equiv 1$

E.2 $\int_0^\infty \frac{x^4 \mathrm{e}^x}{(\mathrm{e}^x - 1)^2} \mathrm{d}x = \frac{\pi^4}{15}$

Gaussian functions

G.1 $\int_0^\infty \mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$

G.2 $\int_0^\infty x\mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2a}$

G.3 $\int_0^\infty x^2\mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$

G.4 $\int_0^\infty x^3\mathrm{e}^{-ax^2} \mathrm{d}x = \frac{1}{2a^2}$

T.2 $\int \sin^2 ax\ \mathrm{d}x = \frac{1}{2}x - \frac{\sin 2ax}{4a} + \text{constant}$

T.3 $\int \sin^3 ax\ \mathrm{d}x = -\frac{(\sin^2 ax + 2)\cos ax}{3a} + \text{constant}$

T.4 $\int \sin^4 ax\ \mathrm{d}x = \frac{3x}{8} - \frac{3}{8a}\sin ax \cos ax - \frac{1}{4a}\sin^3 ax \cos ax + \text{constant}$

T.5 $\int \sin ax \sin bx\ \mathrm{d}x = \frac{\sin(a-b)x}{2(a-b)} - \frac{\sin(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$

T.6 $\int_0^L \sin nax \sin^2 ax\ \mathrm{d}x = -\frac{1}{2a}\left\{\frac{1}{n} - \frac{1}{2(n+2)} - \frac{1}{2(n-2)}\right\} \times \{(-1)^n - 1\}$

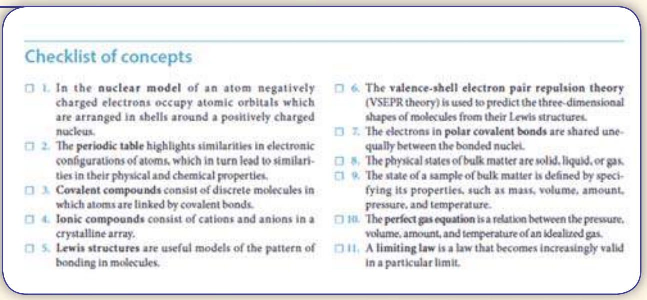
T.7 $\int \sin ax \cos ax\ \mathrm{d}x = \frac{1}{2a}\sin^2 ax + \text{constant}$

T.8 $\int \sin bx \cos ax\ \mathrm{d}x = \frac{\cos(a-b)x}{2(a-b)} - \frac{\cos(a+b)x}{2(a+b)} + \text{constant},\ a^2 \neq b^2$

T.9 $\int x \sin ax \sin bx\ \mathrm{d}x = -\frac{\mathrm{d}}{\mathrm{d}a}\int \sin bx \cos ax\ \mathrm{d}x$

➤ Checklist of concepts

A checklist of key concepts is provided at the end of each Topic, so that you can tick off those concepts which you feel you have mastered.



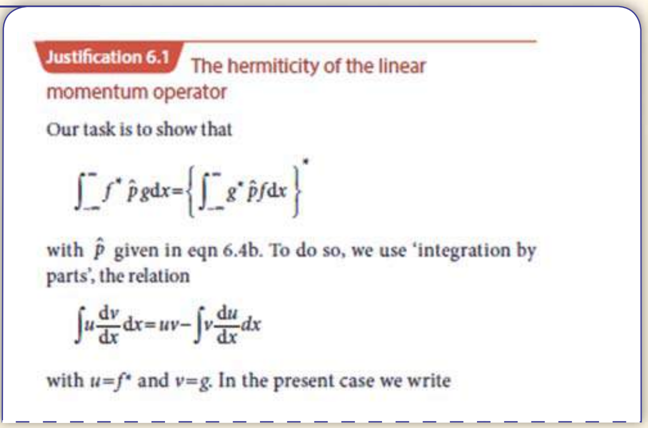
Checklist of concepts

☐ 1. In the **nuclear model** of an atom negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.
☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.
☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.
☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.
☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.
☐ 6. The **valence-shell electron pair repulsion theory** (VSEPR theory) is used to predict the three-dimensional shapes of molecules from their Lewis structures.
☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.
☐ 8. The physical states of bulk matter are solid, liquid, or gas.
☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.
☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.
☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Presenting the mathematics

➤ Justifications

Mathematical development is an intrinsic part of physical chemistry, and to achieve full understanding you need to see how a particular expression is obtained and if any assumptions have been made. The Justifications are set off from the text to let you adjust the level of detail that you require to your current needs and make it easier to review material.



Justification 6.1 The hermiticity of the linear momentum operator

Our task is to show that

$$\int_{-\infty}^{\infty} f^{*}\hat{p}g\,\mathrm{d}x=\left\{\int_{-\infty}^{\infty} g^{*}\hat{p}f\,\mathrm{d}x\right\}^{*}$$

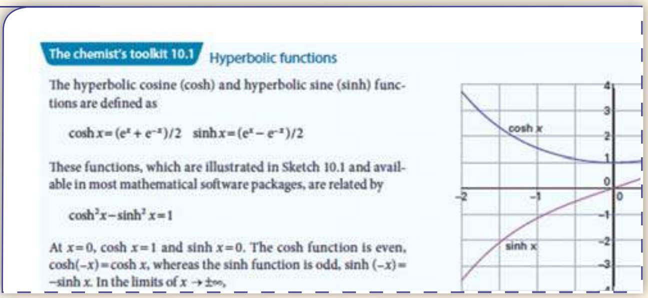
with $\hat{p}$ given in eqn 6.4b. To do so, we use ‘integration by parts’, the relation

$$\int u\frac{\mathrm{d}v}{\mathrm{d}x}\mathrm{d}x=uv-\int v\frac{\mathrm{d}u}{\mathrm{d}x}dx$$

with $u=f^{*}$ and $v=g$. In the present case we write

➤ Chemist’s toolkits

New to this edition, the Chemist’s toolkits are succinct reminders of the mathematical concepts and techniques that you will need in order to understand a particular derivation being described in the main text.



The chemist’s toolkit 10.1 Hyperbolic functions

The hyperbolic cosine (cosh) and hyperbolic sine (sinh) functions are defined as

$$\cosh x=(e^{x}+e^{-x})/2 \quad \sinh x=(e^{x}-e^{-x})/2$$

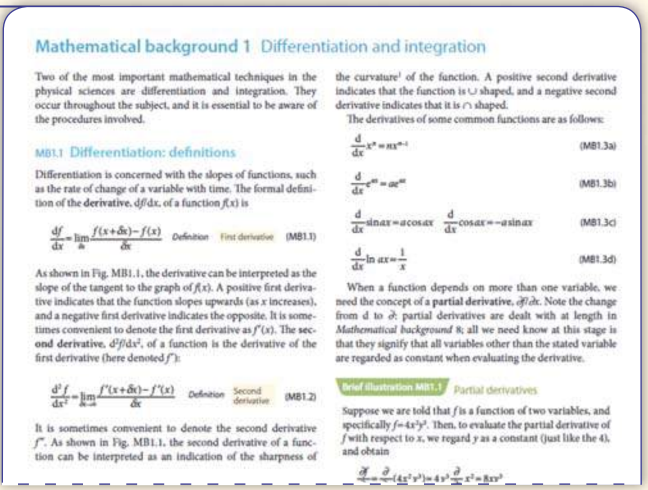
These functions, which are illustrated in Sketch 10.1 and available in most mathematical software packages, are related by

$$\cosh^{2}x-\sinh^{2}x=1$$

At $x=0$, $\cosh x=1$ and $\sinh x=0$. The cosh function is even, $\cosh(-x)=\cosh x$, whereas the sinh function is odd, $\sinh(-x)=-\sinh x$. In the limits of $x\to\pm\infty$,

➤ Mathematical backgrounds

There are eight Mathematical background sections dispersed throughout the text. They cover in detail the main mathematical concepts that you need to understand in order to be able to master physical chemistry. Each one is located at the end of the Focus where it is first needed.



Mathematical background 1 Differentiation and integration

Two of the most important mathematical techniques in the physical sciences are differentiation and integration. They occur throughout the subject, and it is essential to be aware of the procedures involved.

MB1.1 Differentiation: definitions

Differentiation is concerned with the slopes of functions, such as the rate of change of a variable with time. The formal definition of the **derivative**, d*f*/d*x*, of a function *f*(*x*) is

$$\frac{\mathrm{d}f}{\mathrm{d}x}=\lim_{\delta x\to 0}\frac{f(x+\delta x)-f(x)}{\delta x} \quad \text{Definition} \quad \text{First derivative} \quad \text{(MB1.1)}$$

As shown in Fig. MB1.1, the derivative can be interpreted as the slope of the tangent to the graph of *f*(*x*). A positive first derivative indicates that the function slopes upwards (as *x* increases), and a negative first derivative indicates the opposite. It is sometimes convenient to denote the first derivative as *f*′(*x*). The **second derivative**, d²*f*/d*x*², of a function is the derivative of the first derivative (here denoted *f*′):

$$\frac{\mathrm{d}^{2}f}{\mathrm{d}x^{2}}=\lim_{\delta x\to 0}\frac{f'(x+\delta x)-f'(x)}{\delta x} \quad \text{Definition} \quad \text{Second derivative} \quad \text{(MB1.2)}$$

It is sometimes convenient to denote the second derivative *f*″. As shown in Fig. MB1.1, the second derivative of a function can be interpreted as an indication of the sharpness of the curvature[1] of the function. A positive second derivative indicates that the function is ∪ shaped, and a negative second derivative indicates that it is ∩ shaped.

The derivatives of some common functions are as follows:

$$\frac{\mathrm{d}}{\mathrm{d}x}x^{n}=nx^{n-1} \quad \text{(MB1.3a)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}e^{ax}=ae^{ax} \quad \text{(MB1.3b)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\sin ax=a\cos ax \quad \frac{\mathrm{d}}{\mathrm{d}x}\cos ax=-a\sin ax \quad \text{(MB1.3c)}$$

$$\frac{\mathrm{d}}{\mathrm{d}x}\ln ax=\frac{1}{x} \quad \text{(MB1.3d)}$$

When a function depends on more than one variable, we need the concept of a **partial derivative**, ∂*f*/∂*x*. Note the change from d to ∂: partial derivatives are dealt with at length in *Mathematical background 8*; all we need know at this stage is that they signify that all variables other than the stated variable are regarded as constant when evaluating the derivative.

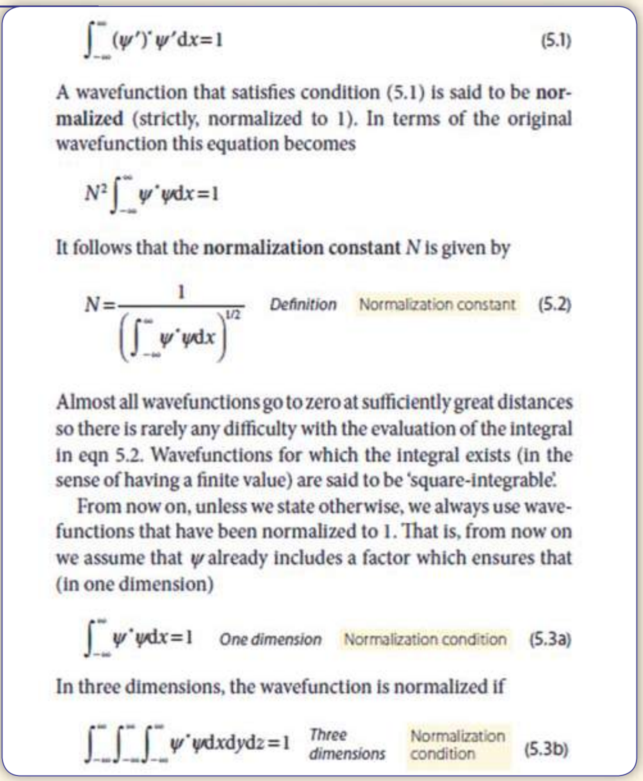
Brief illustration MB1.1 Partial derivatives

Suppose we are told that *f* is a function of two variables, and specifically $f=4x^{2}y^{3}$. Then, to evaluate the partial derivative of *f* with respect to *x*, we regard *y* as a constant (just like the 4), and obtain

$$\frac{\partial f}{\partial x}=\frac{\partial}{\partial x}(4x^{2}y^{3})=4y^{3}\frac{\partial}{\partial x}x^{2}=8xy^{3}$$

➤ Annotated equations and equation labels

We have annotated many equations to help you follow how they are developed. An annotation can take you across the equals sign: it is a reminder of the substitution used, an approximation made, the terms that have been assumed constant, the integral used, and so on. An annotation can also be a reminder of the significance of an individual term in an expression. We sometimes color a collection of numbers or symbols to show how they carry from one line to the next. Many of the equations are labeled to highlight their significance.



$$\int_{-\infty}^{\infty}(\psi')^{*}\psi'\mathrm{d}x=1 \qquad (5.1)$$

A wavefunction that satisfies condition (5.1) is said to be **normalized** (strictly, normalized to 1). In terms of the original wavefunction this equation becomes

$$N^2\int_{-\infty}^{\infty}\psi^{*}\psi\mathrm{d}x=1$$

It follows that the **normalization constant** N is given by

$$N=\frac{1}{\left(\int_{-\infty}^{\infty}\psi^{*}\psi\mathrm{d}x\right)^{1/2}} \qquad \textit{Definition} \quad \text{Normalization constant} \qquad (5.2)$$

Almost all wavefunctions go to zero at sufficiently great distances so there is rarely any difficulty with the evaluation of the integral in eqn 5.2. Wavefunctions for which the integral exists (in the sense of having a finite value) are said to be 'square-integrable.'

From now on, unless we state otherwise, we always use wavefunctions that have been normalized to 1. That is, from now on we assume that ψ already includes a factor which ensures that (in one dimension)

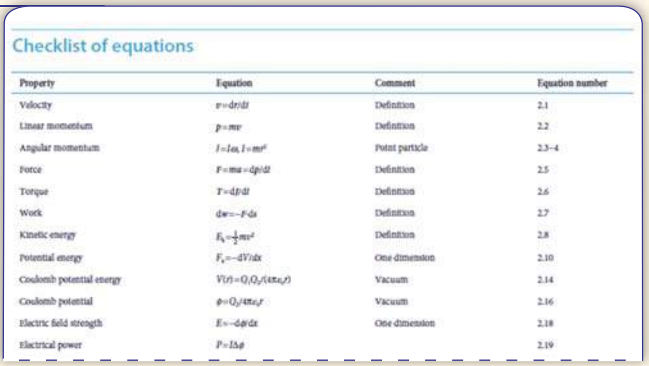
$$\int_{-\infty}^{\infty}\psi^{*}\psi\mathrm{d}x=1 \qquad \textit{One dimension} \quad \text{Normalization condition} \qquad (5.3a)$$

In three dimensions, the wavefunction is normalized if

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\psi^{*}\psi\mathrm{d}x\mathrm{d}y\mathrm{d}z=1 \qquad \textit{Three dimensions} \quad \text{Normalization condition} \qquad (5.3b)$$

➤ Checklists of equations

You don't have to memorize every equation in the text. A checklist at the end of each Topic summarizes the most important equations and the conditions under which they apply.



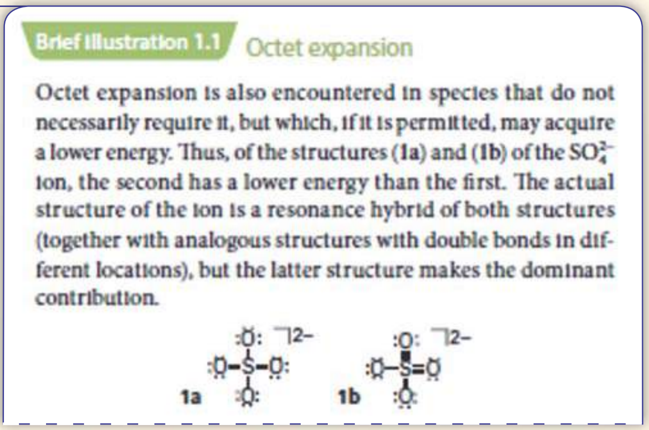
Checklist of equations

Property	Equation	Comment	Equation number
Velocity	$v=\mathrm{d}r/\mathrm{d}t$	Definition	2.1
Linear momentum	$p=mv$	Definition	2.2
Angular momentum	$J=I\omega$, $I=mr^2$	Point particle	2.3–4
Force	$F=ma=\mathrm{d}p/\mathrm{d}t$	Definition	2.5
Torque	$T=\mathrm{d}J/\mathrm{d}t$	Definition	2.6
Work	$\mathrm{d}w=-F\cdot\mathrm{d}s$	Definition	2.7
Kinetic energy	$E_k=\frac{1}{2}mv^2$	Definition	2.8
Potential energy	$F_x=-\mathrm{d}V/\mathrm{d}x$	One dimension	2.10
Coulomb potential energy	$V(r)=Q_1Q_2/(4\pi\varepsilon_0 r)$	Vacuum	2.14
Coulomb potential	$\phi=Q_2/4\pi\varepsilon_0 r$	Vacuum	2.16
Electric field strength	$E=-\mathrm{d}\phi/\mathrm{d}x$	One dimension	2.18
Electrical power	$P=I\Delta\phi$		2.19

Setting up and solving problems

➤ Brief illustrations

A Brief illustration shows you how to use equations or concepts that have just been introduced in the text. They will help you to learn how to use data, manipulate units correctly, and become familiar with the magnitudes of properties. They are all accompanied by a Self-test which you can use to monitor your progress.

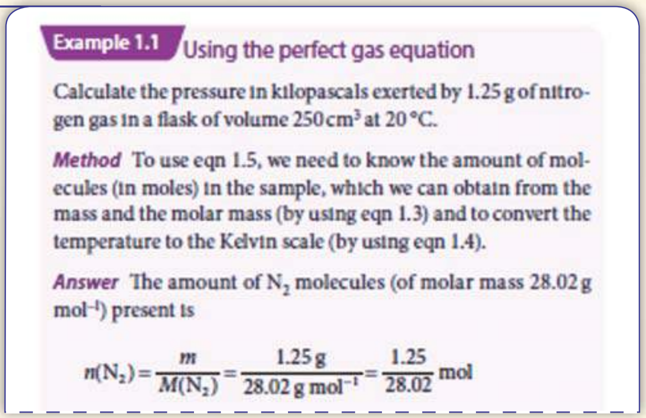


Brief illustration 1.1 Octet expansion

Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (**1a**) and (**1b**) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.

➤ Worked examples

Worked examples are more detailed illustrations of the application of the material, which require you to assemble and develop concepts and equations. We provide a suggested method for solving the problem and then implement it to reach the answer. Worked examples are also accompanied by Self-tests.



Example 1.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm³ at 20 °C.

Method To use eqn 1.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn 1.3) and to convert the temperature to the Kelvin scale (by using eqn 1.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol^{-1}) present is

$$n(N_2)=\frac{m}{M(N_2)}=\frac{1.25\,\text{g}}{28.02\,\text{g mol}^{-1}}=\frac{1.25}{28.02}\,\text{mol}$$

➤ Discussion questions

Discussion questions appear at the end of every Focus, where they are organized by Topic. These questions are designed to encourage you to reflect on the material you have just read, and to view it conceptually.

➤ Exercises and problems

Exercises and problems are also provided at the end of every Focus and organized by Topic. They prompt you to test your understanding of the Topics in that Focus group. Exercises are designed as relatively straightforward numerical tests whereas the problems are more challenging. The Integrated activities, which are problems that cross several Topics, also appear at the end of each Focus.

Discussion questions

1.1 Summarize the features of the nuclear model of the atom. Define the terms atomic number, nucleon number, mass number.

1.2 Where in the periodic table are metals, non-metals, transition metals, lanthanoids, and actinoids found?

1.3 Summarize what is meant by a single and a multiple bond.

1.4 Summarize the principal concepts of the VSEPR theory of molecular shape.

1.5 Compare and contrast the properties of (a) the solid, liquid, and gas states of matter, (b) the condensed and gaseous states of matter.

Exercises

1.1(a) Express the typical ground-state electron configuration of an atom of an element in (a) Group 2, (b) Group 7, (c) Group 15 of the periodic table.
1.1(b) Express the typical ground-state electron configuration of an atom of an element in (a) Group 3, (b) Group 5, (c) Group 13 of the periodic table.

1.2(a) Identify the oxidation numbers of the elements in (a) $MgCl_2$, (b) FeO, (c) Hg_2Cl_2.
1.2(b) Identify the oxidation numbers of the elements in (a) CaH_2, (b) CaC_2, (c) LiN_3.

1.3(a) Identify a molecule with a (a) single, (b) double, (c) triple bond between a carbon and a nitrogen atom.
1.3(b) Identify a molecule with (a) one, (b) two, (c) three lone pairs on the central atom.

1.4(a) Draw the Lewis (electron dot) structures of (a) SO_3^{2-}, (b) XeF_4, (c) P_4.
1.4(b) Draw the Lewis (electron dot) structures of (a) O_3, (b) ClF_3^+, (c) N_3^-.

1.5(a) Identify three compounds with an incomplete octet.
1.5(b) Identify four hypervalent compounds.

1.6(a) Use VSEPR theory to predict the structures of (a) PCl_3, (b) PCl_5, (c) XeF_2, (d) XeF_4.
1.6(b) Use VSEPR theory to predict the structures of (a) H_2O_2, (b) FSO_3^-, (c) KrF_2, (d) PCl_4^+.

1.7(a) Identify the polarities (by attaching partial charges δ+ and δ–) of the bonds (a) C–Cl, (b) P–H, (c) N–O.
1.7(b) Identify the polarities (by attaching partial charges δ+ and δ–) of the bonds (a) C–H, (b) P–S, (c) N–Cl.

1.8(a) State whether you expect the following molecules to be polar or nonpolar: (a) CO_2, (b) SO_2, (c) N_2O, (d) SF_4.
1.8(b) State whether you expect the following molecules to be polar or nonpolar: (a) O_3, (b) XeF_2, (c) NO_2, (d) C_6H_{14}.

1.9(a) Arrange the molecules in Exercise 1.8(a) by increasing dipole moment.
1.9(b) Arrange the molecules in Exercise 1.8(b) by increasing dipole moment.

1.10(a) Classify the following properties as extensive or intensive: (a) mass, (b) mass density, (c) temperature, (d) number density.
1.10(b) Classify the following properties as extensive or intensive: (a) pressure, (b) specific heat capacity, (c) weight, (d) molality.

1.11(a) Calculate (a) the amount of C_2H_5OH (in moles) and (b) the number of molecules present in 25.0 g of ethanol.
1.11(b) Calculate (a) the amount of $C_6H_{22}O_{11}$ (in moles) and (b) the number of molecules present in 5.0 g of glucose.

1.12(a) Calculate (a) the mass, (b) the weight on the surface of the Earth (where $g=9.81\,\text{m s}^{-2}$) of 10.0 mol $H_2O(l)$.
1.12(b) Calculate (a) the mass, (b) the weight on the surface of Mars (where $g=3.72\,\text{m s}^{-2}$) of 10.0 mol $C_6H_6(l)$.

1.13(a) Calculate the pressure exerted by a person of mass 65 kg standing (on the surface of the Earth) on shoes with soles of area 150 cm².
1.13(b) Calculate the pressure exerted by a person of mass 60 kg standing (on the surface of the Earth) on shoes with stiletto heels of area 2 cm² (assume that the weight is entirely on the heels).

1.14(a) Express the pressure calculated in Exercise 1.13(a) in atmospheres.
1.14(b) Express the pressure calculated in Exercise 1.13(b) in atmospheres.

1.15(a) Express a pressure of 1.45 atm in (a) pascal, (b) bar.
1.15(b) Express a pressure of 222 atm in (a) pascal, (b) bar.

1.16(a) Convert blood temperature, 37.0 °C, to the Kelvin scale.
1.16(b) Convert the boiling point of oxygen, 90.18 K, to the Celsius scale.

1.17(a) Equation 1.4 is a relation between the Kelvin and Celsius scales. Devise the corresponding equation relating the Fahrenheit and Celsius scales and use it to express the boiling point of ethanol (78.5 °C) in degrees Fahrenheit.
1.17(b) The Rankine scale is a version of the thermodynamic temperature scale in which the degrees (°R) are the same size as degrees Fahrenheit. Derive an expression relating the Rankine and Kelvin scales and express the freezing point of water in degrees Rankine.

1.18(a) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0 °C. What can its pressure be expected to be when the temperature is 7.0 °C?
1.18(b) A sample of 325 mg of neon occupies 2.00 dm³ at 20.0 °C. Use the perfect gas law to calculate the pressure of the gas.

1.19(a) At 500 °C and 93.2 kPa, the mass density of sulfur vapour is 3.710 kg m⁻³. What is the molecular formula of sulfur under these conditions?
1.19(b) At 100 °C and 1.60 kPa, the mass density of phosphorus vapour is 0.6388 kg m⁻³. What is the molecular formula of phosphorus under these conditions?

1.20(a) Calculate the pressure exerted by 22 g of ethane behaving as a perfect gas when confined to 1000 cm³ at 25.0 °C.
1.20(b) Calculate the pressure exerted by 7.05 g of oxygen behaving as a perfect gas when confined to 100 cm³ at 100.0 °C.

1.21(a) A vessel of volume 10.0 dm³ contains 2.0 mol H_2 and 1.0 mol N_2 at 5.0 °C. Calculate the partial pressure of each component and their total pressure.
1.21(b) A vessel of volume 100 cm³ contains 0.25 mol O_2 and 0.034 mol CO_2 at 10.0 °C. Calculate the partial pressure of each component and their total pressure.

➤ Integrated activities

At the end of most Focus sections, you will find questions designed to help you use your knowledge creatively in a variety of ways. Some of the questions refer to the 'Living graphs' on the Book Companion Site, which you will find helpful for answering them.

➤ Solutions manuals

Two solutions manuals have been written by Charles Trapp, Marshall Cady, and Carmen Giunta to accompany this book.

The *Student Solutions Manual* (ISBN 1-4641-2442-6) provides full solutions to the 'a' exercises and to the odd-numbered problems.

The *Instructor's Solutions Manual* provides full solutions to the 'b' exercises and to the even-numbered problems (available to registered adopters of the book only). The Instructor's Solutions Manual is available online only and can be accessed on the Book Companion Site.

THE BOOK COMPANION SITE

The Book Companion Site to accompany *Physical Chemistry: Quanta, Matter, and Change*, second edition provides a number of useful teaching and learning resources for students and instructors.

The Book Companion Site can be accessed by visiting:

www.whfreeman.com/qmc2e

Instructor resources are available only to regisered adopters of the textbook. To register, simply visit www.whfreeman.com/qmc2e and follow the appropriate links.

Student resources are openly available to all, without registration.

Materials on the Book Companion Site include:

Online Impact sections

Impact sections place the subject of physical chemistry in context by showing how it has been applied in a variety of modern contexts. New for this edition, the Impacts are linked from the text by QR codes. Alternatively, visit the URL displayed next to the QR code.

Group theory tables

Comprehensive group theory tables are available to download.

Figures and tables from the book

Instructors can find the artwork and tables from the book online in ready-to-download format. These may be used for lectures without charge (but not for commercial purposes without specific permission).

Molecular modelling problems

PDFs containing molecular modelling problems can be downloaded, designed for use with the Spartan Student™ software. However they can also be completed using any modeling software program that allows Hartree–Fock, density functional, and MP2 calculations.

Living graphs

These interactive graphs can be used to explore how a property changes as various parameters are changed. Living graphs are sometimes referred to in the 'Integrated activities' section of a Focus group.

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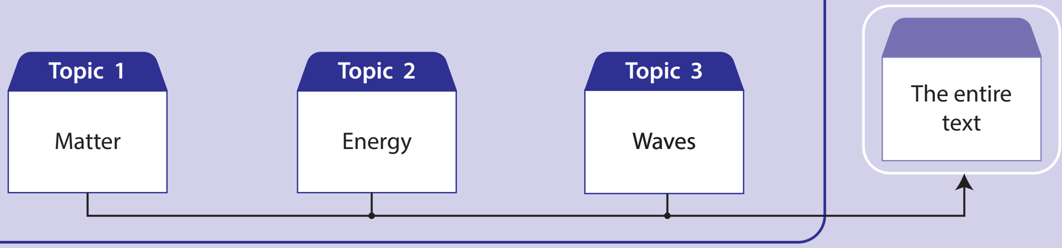
FOCUS 1 ON Foundations



Chemistry is the science of matter and the changes it can undergo. Physical chemistry is the branch of chemistry that establishes and develops the principles of the subject in terms of the underlying concepts of physics and the language of mathematics. It provides the basis for developing new spectroscopic techniques and their interpretation, for understanding the structures of molecules and the details of their electron distributions, and for relating the bulk properties of matter to their constituent atoms. Physical chemistry also provides a window on to the world of chemical reactions, and allows us to understand in detail how they take place.

Throughout the text we draw on a number of concepts that should already be familiar from introductory chemistry, such as the 'nuclear model' of the atom, 'Lewis structures' of molecules, and the 'perfect gas equation'. **Topic 1** reviews these and other concepts of chemistry that appear at many stages of the presentation.

Because physical chemistry lies at the interface between physics and chemistry, we also need to review some of the concepts from elementary physics that we need to draw on in the text. **Topic 2** begins with a brief summary of 'classical mechanics', our starting point for discussion of the motion and energy of particles. Then it reviews concepts of 'thermodynamics' that should already be part of your chemical vocabulary. Finally, we introduce the 'Boltzmann distribution' and the 'equipartition theorem', which help to establish connections between the bulk and molecular properties of matter.

Topic 3 describes waves, with a focus on 'harmonic waves', which form the basis for the classical description of electromagnetic radiation. The classical ideas of motion, energy, and waves in **Topics 2** and **3** are then expanded with *The principles of quantum mechanics*, setting the stage for the treatment of electrons, atoms, and molecules. From quantum mechanics we develop through the text principles of chemical structure and change, and the basis of many techniques of investigation.

TOPIC 1

Matter

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➤ Why do you need to know this material?

Because chemistry is about matter and the changes that it can undergo, both physically and chemically, the properties of matter underlie the entire discussion in this book.

➤ What is the key idea?

The bulk properties of matter are related to the identities and arrangements of atoms and molecules in a sample.

➤ What do you need to know already?

This Topic reviews material commonly covered in introductory chemistry.

The presentation of physical chemistry in this text is based on the experimentally verified fact that matter consists of atoms. In this Topic, which is a review of elementary concepts and language widely used in chemistry, we begin to make connections between atomic, molecular, and bulk properties. Most of the material is developed in greater detail later in the text.

1.1 Atoms

The atom of an element is characterized by its **atomic number**, Z, which is the number of protons in its nucleus. The number of neutrons in a nucleus is variable to a small extent, and the **nucleon number** (which is also commonly called the *mass number*), A, is the total number of protons and neutrons in the nucleus. Protons and neutrons are collectively called **nucleons**. Atoms of the same atomic number but different nucleon number are the **isotopes** of the element.

(a) The nuclear model

According to the **nuclear model**, an atom of atomic number Z consists of a nucleus of charge $+Ze$ surrounded by Z electrons each of charge $-e$ (e is the fundamental charge: see inside the front cover for its value and the values of the other fundamental constants). These electrons occupy **atomic orbitals**, which are regions of space where they are most likely to be found, with no more than two electrons in any one orbital. The atomic orbitals are arranged in **shells** around the nucleus, each shell being characterized by the **principal quantum number**, $n = 1, 2, \ldots$. A shell consists of n^2 individual orbitals, which are grouped together into n **subshells**; these subshells, and the orbitals they contain, are denoted s, p, d, and f. For all neutral atoms other than hydrogen, the subshells of a given shell have slightly different energies.

(b) The periodic table

The sequential occupation of the orbitals in successive shells results in periodic similarities in the **electronic configurations**, the specification of the occupied orbitals, of atoms when they are arranged in order of their atomic number. This periodicity of structure accounts for the formulation of the **periodic table** (see inside the back cover). The vertical columns of the periodic table are called **groups** and (in the modern convention) numbered from 1 to 18. Successive rows of the periodic table are called **periods**, the number of the period being equal to the principal quantum number of the **valence shell**, the outermost shell of the atom.

Some of the groups also have familiar names: Group 1 consists of the **alkali metals**, Group 2 (more specifically, calcium, strontium, and barium) of the **alkaline earth metals**, Group 17 of the **halogens**, and Group 18 of the **noble gases.** Broadly speaking, the elements towards the left of the periodic table are **metals** and those towards the right are **non-metals**; the two classes of substance meet at a diagonal line running from boron to polonium, which constitute the **metalloids**, with properties intermediate between those of metals and non-metals.

The periodic table is divided into s, p, d, and f **blocks**, according to the subshell that is last to be occupied in the formulation of the electronic configuration of the atom. The members of the d block (specifically the members of Groups 3–11 in the d block) are also known as the **transition metals**; those of the f block (which is not divided into numbered groups) are sometimes called the **inner transition metals**. The upper row of the f block (Period 6) consists of the **lanthanoids** (still commonly the 'lanthanides') and the lower row (Period 7) consists of the **actinoids** (still commonly the 'actinides').

(c) Ions

A monatomic **ion** is an electrically charged atom. When an atom gains one or more electrons it becomes a negatively charged **anion**; when it loses one or more electrons it becomes a positively charged **cation**. The charge number of an ion is called the **oxidation number** of the element in that state (thus, the oxidation number of magnesium in Mg^{2+} is +2 and that of oxygen in O^{2-} is −2). It is appropriate, but not always done, to distinguish between the oxidation number and the **oxidation state**, the latter being the physical state of the atom with a specified oxidation number. Thus, the oxidation number *of* magnesium is +2 when it is present as Mg^{2+}, and it is present *in* the oxidation state Mg^{2+}.

The elements form ions that are characteristic of their location in the periodic table: metallic elements typically form cations by losing the electrons of their outermost shell and acquiring the electronic configuration of the preceding noble gas atom. Nonmetals typically form anions by gaining electrons and attaining the electronic configuration of the following noble gas atom.

1.2 Molecules

A **chemical bond** is the link between atoms. Compounds that contain a metallic element typically, but far from universally, form **ionic compounds** that consist of cations and anions in a crystalline array. The 'chemical bonds' in an ionic compound are due to the Coulombic interactions between all the ions in the crystal, and it is inappropriate to refer to a bond between a specific pair of neighbouring ions. The smallest unit of an ionic compound is called a **formula unit**. Thus $NaNO_3$, consisting of a Na^+ cation and a NO_3^- anion, is the formula unit of sodium nitrate. Compounds that do not contain a metallic element typically form **covalent compounds** consisting of discrete molecules. In this case, the bonds between the atoms of a molecule are **covalent**, meaning that they consist of shared pairs of electrons.

A note on good practice Some chemists use the term 'molecule' to denote the smallest unit of a compound with the composition of the bulk material regardless of whether it is an ionic or covalent compound and thus speak of 'a molecule of NaCl'. We use the term 'molecule' to denote a discrete covalently bonded entity (as in H_2O); for an ionic compound we use 'formula unit'.

(a) Lewis structures

The pattern of bonds between neighbouring atoms is displayed by drawing a **Lewis structure**, in which bonds are shown as lines and **lone pairs** of electrons, pairs of valence electrons that are not used in bonding, are shown as dots. Lewis structures are constructed by allowing each atom to share electrons until it has acquired an **octet** of eight electrons (for hydrogen, a *duplet* of two electrons). A shared pair of electrons is a **single bond**, two shared pairs constitute a **double bond**, and three shared pairs constitute a **triple bond**. Atoms of elements of Period 3 and later can accommodate more than eight electrons in their valence shell and 'expand their octet' to become **hypervalent**, that is, form more bonds than the octet rule would allow (for example, SF_6), or form more bonds to a small number of atoms (see *Brief illustration* 1.1). When more than one Lewis structure can be written for a given arrangement of atoms, it is supposed that **resonance**, a blending of the structures, may occur and distribute multiple-bond character over the molecule (for example, the two Kekulé structures of benzene). Examples of these aspects of Lewis structures are shown in Fig. 1.1.

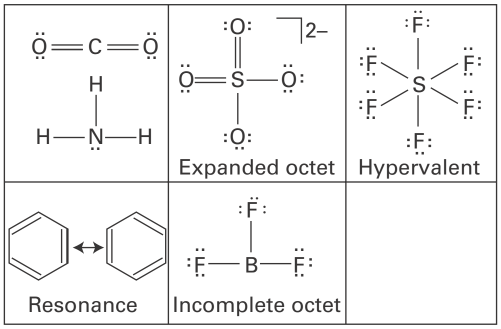
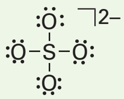
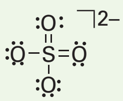


Figure 1.1 Examples of Lewis structures.

Brief illustration 1.1 Octet expansion

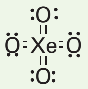
Octet expansion is also encountered in species that do not necessarily require it, but which, if it is permitted, may acquire a lower energy. Thus, of the structures (**1a**) and (**1b**) of the SO_4^{2-} ion, the second has a lower energy than the first. The actual structure of the ion is a resonance hybrid of both structures (together with analogous structures with double bonds in different locations), but the latter structure makes the dominant contribution.


1a


1b

Self-test 1.1 Draw the Lewis structure for XeO_4.

Answer: **2**



(b) VSEPR theory

Except in the simplest cases, a Lewis structure does not express the three-dimensional structure of a molecule. The simplest approach to the prediction of molecular shape is **valence-shell electron pair repulsion theory** (VSEPR theory). In this approach, the regions of high electron density, as represented by bonds—whether single or multiple—and lone pairs, take up orientations around the central atom that maximize their separations. Then the position of the attached atoms (not the lone pairs) is noted and used to classify the shape of the molecule. Thus, four regions of electron density adopt a tetrahedral arrangement; if an atom is at each of these locations (as in CH_4), then the molecule is tetrahedral; if there is an atom at only three of these locations (as in NH_3), then the molecule is trigonal pyramidal, and so on. The names of the various shapes that are commonly found are shown in Fig. 1.2. In a refinement of the theory, lone pairs are assumed to repel bonding pairs more strongly than bonding pairs repel each other. The shape a molecule then adopts, if it is not determined fully by symmetry, is such as to minimize repulsions from lone pairs.

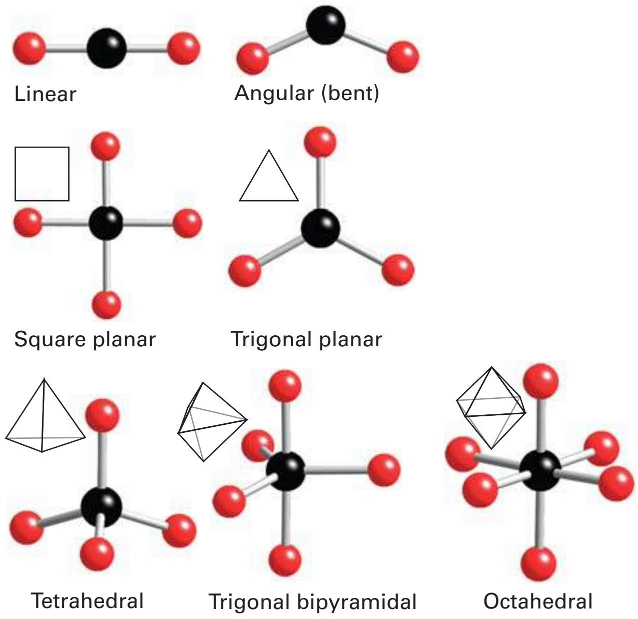


Figure 1.2 The shapes of molecules that result from application of VSEPR theory.

Brief illustration 1.2 Molecular shapes

In SF_4 the lone pair adopts an equatorial position and the two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule (Fig. 1.3).

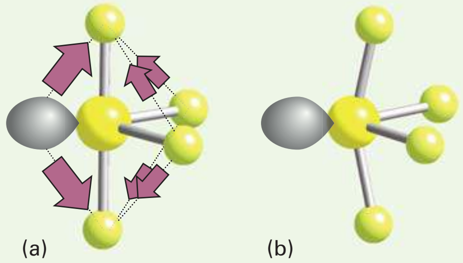


Figure 1.3 (a) In SF_4 the lone pair adopts an equatorial position. (b) The two axial S–F bonds bend away from it slightly, to give a bent see-saw shaped molecule.

Self-test 1.2 Predict the shape of the SO_3^{2-} ion.

Answer: Trigonal pyramid

(c) Polar bonds

Covalent bonds may be **polar**, or correspond to an unequal sharing of the electron pair, with the result that one atom has a partial positive charge (denoted δ+) and the other a partial negative charge (δ–). The ability of an atom to attract electrons to itself when part of a molecule is measured by the **electronegativity**, χ (chi), of the element. The juxtaposition of equal and opposite partial charges constitutes an **electric dipole**. If those charges are $+Q$ and $-Q$ and they are separated by a distance d, the magnitude of the **electric dipole moment**, μ, is

$$\mu = Qd \qquad \textit{Definition} \qquad \text{Magnitude of the electric dipole moment} \qquad (1.1)$$

Brief illustration 1.3 Nonpolar molecules with polar bonds

Whether or not a molecule as a whole is polar depends on the arrangement of its bonds, for in highly symmetrical molecules there may be no net dipole. Thus, although the linear CO_2 molecule (which is structurally OCO) has polar CO bonds, their effects cancel and the molecule as a whole is nonpolar.

Self-test 1.3 Is NH_3 polar?

Answer: Yes

1.3 Bulk matter

Bulk matter consists of large numbers of atoms, molecules, or ions. Its physical state may be solid, liquid, or gas:

A **solid** is a form of matter that adopts and maintains a shape that is independent of the container it occupies.

A **liquid** is a form of matter that adopts the shape of the part of the container it occupies (in a gravitational field, the lower part) and is separated from the unoccupied part of the container by a definite surface.

A **gas** is a form of matter that immediately fills any container it occupies.

A liquid and a solid are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter: they flow in response to forces (such as gravity) that are applied.

(a) Properties of bulk matter

The state of a bulk sample of matter is defined by specifying the values of various properties. Among them are:

The **mass**, m, a measure of the quantity of matter present (unit: 1 kilogram, 1 kg).

Brief illustration 1.4 Volume units

Volume is also expressed as submultiples of 1 m^3, such as cubic decimetres (1 $dm^3 = 10^{-3}$ m^3) or cubic centimetres (1 $cm^3 = 10^{-6}$ m^3). It is also common to encounter the non-SI unit litre (1 L = 1 dm^3) and its submultiple the millilitre (1 mL = 1 cm^3). To carry out simple unit conversions, simply replace the fraction of the unit (such as 1 cm) by its definition (in this case, 10^{-2} m). Thus, to convert 100 cm^3 to cubic decimetres (litres), use 1 cm = 10^{-1} dm, in which case 100 cm^3 = 100 $(10^{-1}\ dm)^3$, which is the same as 0.100 dm^3.

Self-test 1.4 Express a volume of 100 mm^3 in units of cm^3.

Answer: 0.100 cm^3

The **volume**, V, a measure of the quantity of space the sample occupies (unit: 1 cubic metre, 1 m^3).

The **amount of substance**, n, a measure of the number of specified entities (atoms, molecules, or formula units) present (unit: 1 mole, 1 mol).

An **extensive property** of bulk matter is a property that depends on the amount of substance present in the sample; an **intensive property** is a property that is independent of the amount of substance. The volume is extensive; the mass density, ρ (rho), with

$$\rho = \frac{m}{V} \qquad \text{Mass density} \qquad (1.2)$$

is intensive.

The amount of substance, n (colloquially, 'the number of moles'), is a measure of the number of specified entities present in the sample. 'Amount of substance' is the official name of the quantity; it is commonly simplified to 'chemical amount' or simply 'amount'. The unit 1 mol is currently defined as the number of carbon atoms in exactly 12 g of carbon-12. (In 2011 the decision was taken to replace this definition, but the change has not yet, in 2014, been implemented.) The number of entities per mole is called **Avogadro's constant**, N_A; the currently accepted value is 6.022×10^{23} mol^{-1} (note that N_A is a constant with units, not a pure number).

The **molar mass of a substance**, M (units: formally kilograms per mole but commonly grams per mole, g mol^{-1}), is the mass per mole of its atoms, its molecules, or its formula units. The amount of substance of specified entities in a sample can readily be calculated from its mass, by noting that

$$n = \frac{m}{M} \qquad \text{Amount of substance} \qquad (1.3)$$

A note on good practice Be careful to distinguish atomic or molecular mass (the mass of a single atom or molecule; units kg) from molar mass (the mass per mole of atoms or molecules; units kg mol^{-1}). *Relative* molecular masses of atoms and molecules, $M_r = m/m_u$, where m is the mass of the atom or molecule and m_u is the atomic mass constant (see inside front cover), are still widely called 'atomic weights' and 'molecular weights' even though they are dimensionless quantities and not weights (the gravitational force exerted on an object).

A sample of matter may be subjected to a **pressure**, p (unit: 1 pascal, Pa; 1 Pa = 1 kg m^{-1} s^{-2}), which is defined as the force, F, it is subjected to, divided by the area, A, to which that force is applied. A sample of gas exerts a pressure on the walls of its container because the molecules of gas are in ceaseless, random motion, and exert a force when they strike the walls. The frequency of the collisions is normally so great that the force, and therefore the pressure, is perceived as being steady.

Although 1 pascal is the SI unit of pressure (*The chemist's toolkit* 1.1), it is also common to express pressure in bar (1 bar = 10^5 Pa) or atmospheres (1 atm = 101 325 Pa exactly), both of which correspond to typical atmospheric pressure. Because many physical properties depend on the pressure acting on a sample, it is appropriate to select a certain value of the pressure to report their values. The **standard pressure** for reporting physical quantities is currently defined as $p^{\ominus} = 1$ bar exactly.

To specify the state of a sample fully it is also necessary to give its **temperature**, T. The temperature is formally a property that determines in which direction energy will flow as heat when two samples are placed in contact through thermally conducting walls: energy flows from the sample with the higher temperature to the sample with the lower temperature. The symbol T is used to denote the **thermodynamic temperature**, which is an absolute scale with $T=0$ as the lowest point. Temperatures above $T=0$ are then most commonly expressed by using the **Kelvin scale**, in which the gradations of temperature are expressed as multiples of the unit 1 kelvin (1 K). The Kelvin scale is currently defined by setting the triple point of water (the temperature at which ice, liquid water, and water vapour are in mutual equilibrium) at exactly 273.16 K (as for certain other units, a decision has been taken to revise this definition, but it has not yet, in 2014, been implemented). The freezing point of water (the melting point of ice) at 1 atm is then found experimentally to lie 0.01 K below the triple point, so the freezing point of water is 273.15 K. The Kelvin scale is unsuitable for everyday measurements of temperature, and it is common to use the **Celsius scale**, which is defined in terms of the Kelvin scale as

$$\theta/{}^{\circ}\mathrm{C} = T/\mathrm{K} - 273.15 \qquad \textit{Definition} \quad \text{Celsius scale} \qquad (1.4)$$

Thus, the freezing point of water is 0 °C and its boiling point (at 1 atm) is found to be 100 °C (more precisely 99.974 °C). Note that in this text T invariably denotes the thermodynamic (absolute) temperature and that temperatures on the Celsius scale are denoted θ (theta).

A note on good practice Note that we write $T=0$, not $T=0\,\mathrm{K}$. General statements in science should be expressed without reference to a specific set of units. Moreover, because T (unlike θ) is absolute, the lowest point is 0 regardless of the scale used to express higher temperatures (such as the Kelvin scale). Similarly, we write $m=0$, not $m=0\,\mathrm{kg}$ and $l=0$, not $l=0\,\mathrm{m}$.

The chemist's toolkit 1.1 Quantities and units

The result of a measurement is a **physical quantity** that is reported as a numerical multiple of a unit:

$$\text{physical quantity} = \text{numerical value} \times \text{unit}$$

It follows that units may be treated like algebraic quantities and may be multiplied, divided, and cancelled. Thus, the expression (physical quantity)/unit is the numerical value (a dimensionless quantity) of the measurement in the specified units. For instance, the mass m of an object could be reported as $m = 2.5\,\mathrm{kg}$ or $m/\mathrm{kg} = 2.5$. See Table 1.1 in the *Resource section* for a list of units. Although it is good practice to use only SI units, there will be occasions where accepted practice is so deeply rooted that physical quantities are expressed using other, non-SI units. By international convention, all physical quantities are represented by sloping symbols; all units are roman (upright).

Units may be modified by a prefix that denotes a factor of a power of 10. Among the most common SI prefixes are those listed in Table 1.2 in the *Resource section*. Examples of the use of these prefixes are:

$$1\,\mathrm{nm} = 10^{-9}\,\mathrm{m} \qquad 1\,\mathrm{ps} = 10^{-12}\,\mathrm{s} \qquad 1\,\mu\mathrm{mol} = 10^{-6}\,\mathrm{mol}$$

Powers of units apply to the prefix as well as the unit they modify. For example, $1\,\mathrm{cm}^3 = 1\,(\mathrm{cm})^3$, and $(10^{-2}\,\mathrm{m})^3 = 10^{-6}\,\mathrm{m}^3$. Note that $1\,\mathrm{cm}^3$ does not mean $1\,\mathrm{c}(\mathrm{m}^3)$. When carrying out numerical calculations, it is usually safest to write out the numerical value of an observable in scientific notation (as $n.nnn \times 10^n$).

There are seven SI base units, which are listed in Table 1.3 in the *Resource section*. All other physical quantities may be expressed as combinations of these base units (see Table 1.4). *Molar concentration* (more formally, but very rarely, *amount of substance concentration*), for example, which is an amount of substance divided by the volume it occupies, can be expressed using the derived units of mol dm^{-3} as a combination of the base units for amount of substance and length. A number of these derived combinations of units have special names and symbols and we highlight them as they arise.

(b) The perfect gas equation

The properties that define the state of a system are not in general independent of one another. The most important example of a relation between them is provided by the idealized fluid known as a **perfect gas** (also, commonly, an 'ideal gas'):

$$pV = nRT \qquad \text{Perfect gas equation} \qquad (1.5)$$

Here R is the **gas constant**, a universal constant (in the sense of being independent of the chemical identity of the gas) with the value 8.3145 J K^{-1} mol^{-1}. Throughout this text, equations applicable only to perfect gases (and other idealized systems) are labelled, as here, with the number in blue.

A note on good practice Although the term 'ideal gas' is almost universally used in place of 'perfect gas', there are reasons for preferring the latter term. In an ideal system the interactions between molecules in a mixture are all the same. In a perfect gas not only are the interactions all the same but they are in fact zero. Few, though, make this useful distinction.

Equation 1.5, the **perfect gas equation**, is a summary of three empirical conclusions, namely Boyle's law ($p \propto 1/V$ at constant temperature and amount), Charles's law ($p \propto T$ at constant volume and amount), and Avogadro's principle ($V \propto n$ at constant temperature and pressure).

Example 1.1 Using the perfect gas equation

Calculate the pressure in kilopascals exerted by 1.25 g of nitrogen gas in a flask of volume 250 cm^3 at 20 °C.

Method To use eqn 1.5, we need to know the amount of molecules (in moles) in the sample, which we can obtain from the mass and the molar mass (by using eqn 1.3) and to convert the temperature to the Kelvin scale (by using eqn 1.4).

Answer The amount of N_2 molecules (of molar mass 28.02 g mol^{-1}) present is

$$n(\text{N}_2)=\frac{m}{M(\text{N}_2)}=\frac{1.25\ \text{g}}{28.02\ \text{g mol}^{-1}}=\frac{1.25}{28.02}\ \text{mol}$$

The temperature of the sample is

$$T/\text{K}=20+273.15,\ \text{so}\ T=(20+273.15)\ \text{K}$$

Therefore, after rewriting eqn 1.5 as $p=nRT/V$,

$$p=\frac{\overbrace{(1.25/28.02)\,\text{mol}}^{n}\times\overbrace{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})}^{R}\times\overbrace{(20+273.15)\,\text{K}}^{T}}{\underbrace{(2.50\times10^{-4})\,\text{m}^3}_{V}}$$

$$=\frac{(1.25/28.02)\times(8.3145)\times(20+273.15)}{2.50\times10^{-4}}\,\frac{\text{J}}{\text{m}^3}$$

$$\overset{1\,\text{J m}^{-3}=1\,\text{Pa}}{=}\ 4.35\times10^{5}\,\text{Pa}=435\,\text{kPa}$$

A note on good practice It is best to postpone a numerical calculation to the last possible stage, and carry it out in a single step. This procedure avoids rounding errors. When we judge it appropriate to show an intermediate result without committing ourselves to a number of significant figures, we write it as *n.nnn*….

Self-test 1.5 Calculate the pressure exerted by 1.22 g of carbon dioxide confined to a flask of volume 500 dm^3 (5.00×10^2 dm^3) at 37 °C.

Answer: 143 Pa

All gases obey the perfect gas equation ever more closely as the pressure is reduced towards zero. That is, eqn 1.5 is an example of a **limiting law**, a law that becomes increasingly valid in a particular limit, in this case as the pressure is reduced to zero. In practice, normal atmospheric pressure at sea level (about 1 atm) is already low enough for most gases to behave almost perfectly, and, unless stated otherwise, we assume in this text that the gases we encounter behave perfectly and obey eqn 1.5.

A mixture of perfect gases behaves like a single perfect gas. According to **Dalton's law**, the total pressure of such a mixture is the sum of the pressures to which each gas would give rise if it occupied the container alone:

$$p=p_{\text{A}}+p_{\text{B}}+\ldots \qquad \text{Dalton's law} \qquad (1.6)$$

Each pressure, p_{J}, can be calculated from the perfect gas equation in the form $p_{\text{J}}=n_{\text{J}}RT/V$.

Checklist of concepts

☐ 1. In the **nuclear model** of an atom, negatively charged electrons occupy atomic orbitals which are arranged in shells around a positively charged nucleus.

☐ 2. The **periodic table** highlights similarities in electronic configurations of atoms, which in turn lead to similarities in their physical and chemical properties.

☐ 3. **Covalent compounds** consist of discrete molecules in which atoms are linked by covalent bonds.

☐ 4. **Ionic compounds** consist of cations and anions in a crystalline array.

☐ 5. **Lewis structures** are useful models of the pattern of bonding in molecules.

☐ 6. The **valence-shell electron pair repulsion theory** (VSEPR theory) is used to predict the three-dimensional shapes of molecules from their Lewis structures.

☐ 7. The electrons in **polar covalent bonds** are shared unequally between the bonded nuclei.

☐ 8. The physical states of bulk matter are solid, liquid, and gas.

☐ 9. The state of a sample of bulk matter is defined by specifying its properties, such as mass, volume, amount, pressure, and temperature.

☐ 10. The **perfect gas equation** is a relation between the pressure, volume, amount, and temperature of an idealized gas.

☐ 11. A **limiting law** is a law that becomes increasingly valid in a particular limit.

Checklist of equations

Property	Equation	Comment	Equation number
Electric dipole moment	$\mu = Qd$		1.1
Mass density	$\rho = m/V$	Intensive property	1.2
Amount of substance	$n = m/M$	Extensive property	1.3
Celsius scale	$\theta/°\mathrm{C} = T/\mathrm{K} - 273.15$	Temperature is an intensive property	1.4
Perfect gas equation	$pV = nRT$		1.5
Dalton's law	$p = p_\mathrm{A} + p_\mathrm{B} + \ldots$		1.6

TOPIC 2

Energy

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➤ Why do you need to know this material?

Energy is the central unifying concept of physical chemistry, and you need to gain insight into how electrons, atoms, and molecules gain, store, and lose energy.

➤ What is the key idea?

Energy, the capacity to do work, is restricted to discrete values in electrons, atoms, and molecules.

➤ What do you need to know already?

You need to review the laws of motion and principles of electrostatics normally covered in introductory physics, and concepts of thermodynamics normally covered in introductory chemistry.

Much of chemistry is concerned with transfers and transformations of energy, and from the outset it is appropriate to define this familiar quantity precisely. We begin here by reviewing **classical mechanics**, which was formulated by Isaac Newton in the seventeenth century, and establishes the vocabulary used to describe the motion and energy of particles. These classical ideas prepare us for **quantum mechanics**, the more fundamental theory formulated in the twentieth century for the study of small particles, such as electrons, atoms, and molecules. We develop the concepts of quantum mechanics throughout the text. Here we begin to see why it is needed as a foundation for understanding atomic and molecular structure.

2.1 Force

Molecules are built from atoms and atoms are built from subatomic particles. To understand their structures we need to know how these bodies move under the influence of the forces they experience.

(a) Momentum

‘Translation’ is the motion of a particle through space. The **velocity**, v, of a particle is the rate of change of its position $\boldsymbol{r}$:

$$\boldsymbol{v}=\frac{\mathrm{d}\boldsymbol{r}}{\mathrm{d}t} \tag{2.1}$$

Definition Velocity

For motion confined to a single dimension, we would write $v_x=\mathrm{d}x/\mathrm{d}t$. The velocity and position are vectors, with both direction and magnitude (vectors and their manipulation are treated in detail in *Mathematical background* 4). The magnitude of the velocity is the **speed**, v. The **linear momentum**, $\boldsymbol{p}$, of a particle of mass m is related to its velocity, $\boldsymbol{v}$, by

$$\boldsymbol{p}=m\boldsymbol{v} \tag{2.2}$$

Definition Linear momentum

Like the velocity vector, the linear momentum vector points in the direction of travel of the particle (Fig. 2.1); its magnitude is denoted p.