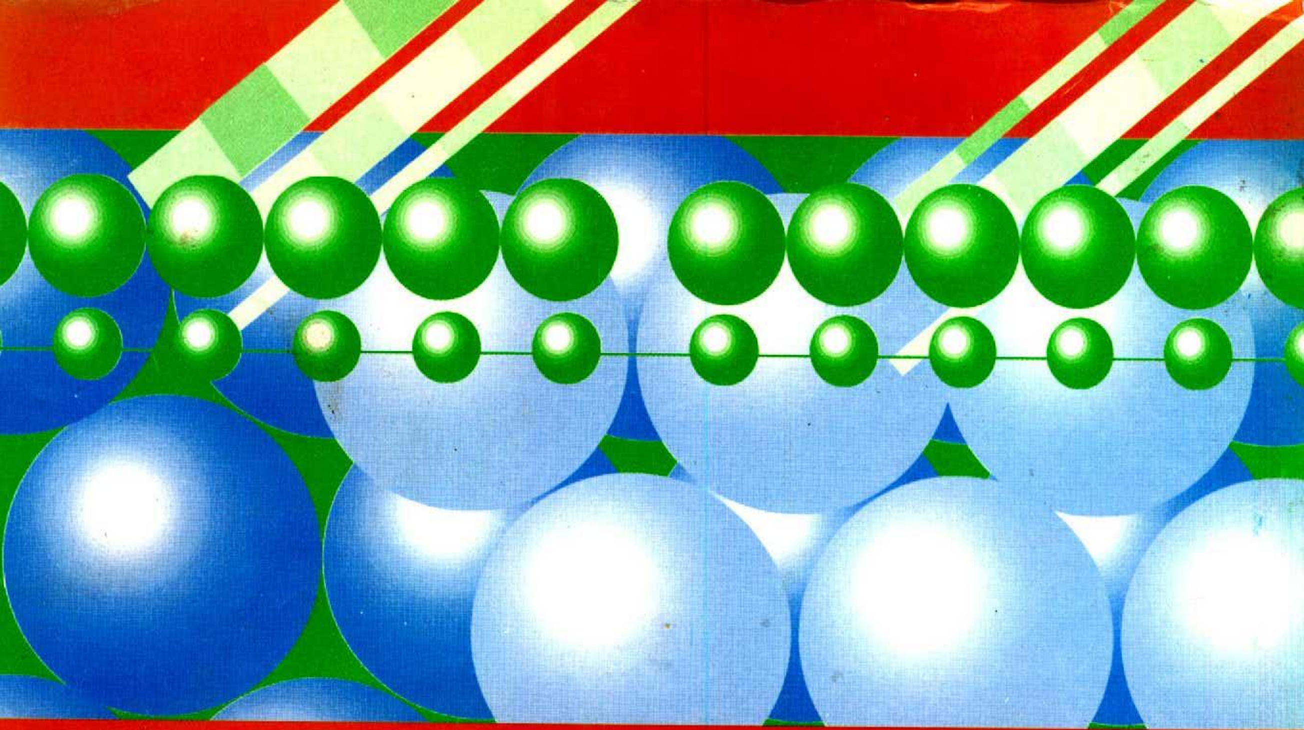

Physical Chemistry

ATKINS

sixth edition

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P.W. Atkins

Professor of Chemistry, University of Oxford, and Fellow of Lincoln College

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Preface

In preparing this edition, I have been conscious of the need to retain rigour but to make the text more accessible. I have also aimed to keep track of the ever-evolving subject of physical chemistry without producing an over-bloated text or failing to deliver an authoritative account of the subject's largely unchanging core. As usual, I have taken the opportunity that a new edition provides to rework the text at all levels of presentation. Whatever laurels may have accrued from earlier editions, I have not found them soft enough to rest on.

The pedagogical devices have been thoroughly overhauled. Each chapter retains the *Synopsis* that started the chapters in the fifth edition, but now it is more succinct. The conceptual framework of each chapter is now summarized in the *Checklist of key ideas* at the end of the chapter. The actual check boxes can be used to record mastery of, or at least familiarity with, a topic. The *Further reading* sections now follow the chapters they aim to enrich, and I give references to recent accessible articles as well as to more authoritative texts and sources of data. As well as the numerous *Worked examples*, each with their mind-focusing *Method* section and accompanying *Self-test* (note the new name), there are now a number of *Illustrations*. These succinct components provide a no-fuss demonstration of how an equation is used (units always seem to give students trouble), and a brief *Illustration* should help to show how a calculation is done without all the fuss and pomp of a full *Worked example*. Some of the *Illustrations* are also accompanied by *Self-tests*.

There are major innovations in the end-of-chapter *Exercise* and *Problem* sections. The idea behind the two categories remains: an *Exercise* is a straightforward, direct application of an item in the text. A *Problem* is more complex and may draw on the literature. In addition to the scattering of literature-based problems, there is now an additional section provided by Carmen Giunta and Charles Trapp that draws explicitly on the literature. There has always been a problem about how to apportion solutions in the *Solutions Manual* for this text: some users welcome solutions to all *Exercises* and *Problems*; others consider that only half should be answered. In an attempt to please both camps, I have almost doubled the number of *Exercises* by providing a second linked companion *Exercise* in each case. All the 'a' set are answered, as before, in the *Student's Solutions Manual*; the solutions to the 'b' set, however, are given only in the (new) *Instructor's Solutions Manual*. Answers to the *Problems* are now divided approximately equally between the *Student's Manual* and the *Instructor's Manual*.

There is a further point concerning the *Problems*. As well as suggesting deletions of tired problems and providing new replacements, Charles Trapp has collaborated with Marshall Cady to develop a series of over-arching problems, which will be found at the end of each Part. These *MicroProjects* are designed to draw on knowledge from all the chapters in each Part, and to make use of literature data. The *MicroProjects* are intended to be helpful when reviewing the material of each Part of the text, and also provide some interesting applications. Some of them require quite challenging numerical techniques, such as non-linear regression, iterative solutions of sets of coupled equations, numerical integration and differentiation, and a variety of graphing procedures. It is therefore strongly recommended that they are solved by using mathematical software, such as MathCad, Mathematica, or similar programs.

Another obvious change, apart from the design, is the complete refurbishment of the artwork. The producers of the drawing software I use (Corel) produce new versions at more than twice the rate that I produce new editions of this text, so by the time that a revision is due, I am sorely tempted to use the new opportunities that their new version provides. My taste also changes as the years go by. So, I have redrawn all the line art, and have added many new pieces. The second colour has been used more extensively and rationally. Broadly speaking, colour denotes a more abstract component of the illustration; black is closer to reality.

The contents of the chapters themselves have undergone considerable revision. The lowest level of subheadings are now numbered to make assignments easier to specify precisely. The *Introduction and orientation* ('Chapter 0') has been completely rewritten with a change in philosophy. Now I use it to introduce some of the principal background concepts, such as the Boltzmann distribution. In that way the *Molecular interpretations* can become more meaningful. Those *Interpretations*, which were introduced in the fifth edition, have been extended in this edition. They enrich the presentation of thermodynamics and go some way towards helping users who wish to emphasize quantum concepts early in the course.

There has been a number of changes in the content of the chapters. To some extent, these changes are a consequence of incorporating what was *Further information* material into the body of the text. The *Further information* sections now provide accounts of globally important background material (such as classical mechanics and partial differentiation) rather than acting as appendages for individual chapters. Thus, Chapter 1 (gases) now includes a fuller discussion of kinetic theory and collisions and Chapter 10 (electrochemistry) contains an account of the Debye–Hückel theory. I have also redistributed material over the chapters: liquid surfaces have been transferred to Chapter 6 (pure substances) and colloids to Chapter 23 (macromolecules), both from their logical but pedagogically rather awkward home among solid surfaces (Chapter 28) in the fifth edition.

The reorganization of other material (such as the relocation of adiabatic changes into Chapter 4) has avoided a certain amount of repetition, and thus has saved space too. I have managed to find more space by adopting a more succinct style of presentation where I thought it would be acceptable. I hope my readers will distinguish the length of the actual text from the wealth of pedagogical aids and end-of-chapter material that is intended to help the student in all manner of different ways.

Finally, I would like to emphasize that the central layout of the text, its division into three parts and the order of chapters, which has remained unchanged over all its editions, is there more as a trademark than as a rigidly imposed structure. I am well aware that different instructors have different views about the order in which the subject is best presented. I have always taken care to present the material in a flexible way, and know from experience that instructors have no difficulty in adapting the text to their inclinations. This edition should suit them even more than previous editions through the reorganization of material and the greater number of subheadings.

There are two supplements for this text. The *Student's Solutions Manual* has been fully revised and contains full solutions to the 'a' *Exercises* and half the *Problems*. The *Instructor's Solution Manual* is new to this edition. As indicated above, it contains full solutions to all the 'b' *Exercises*, and the other half of the *Problems*.

So much for the description of this new edition. It would not have come about without the input of so many well-wishers, both commissioned and non-commissioned. I try to acknowledge the suggestions from individuals as they arrive, and apologize for not having space to thank them more publicly here. I hope they realize that they are part of the lifeblood of the text. Many were specifically consulted in the course of the preparation of this edition, and I would like to thank all those listed on p. vii.

As to the third component of the production of a text, the first two being the author and the advisors, I would like to thank my publishers for their advice and support throughout the planning, execution, and production phases of this vast and demanding project.

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Dr Andrew A. Freer University of Glasgow
Professor Ronald Ś. Friedman Indiana University Purdue University Fort Wayne
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Mr Ping Li Cleveland State University
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Dr P.J. MacDougall Middle Tennessee State University
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Summary of contents

Contents

Conventions

SI units and IUPAC conventions are used throughout, except in a small number of cases.

The default numbering of equations is (n); however, [n] is used to denote a definition and $\{n\}$ is used to indicate that a variable x should be interpreted as $x/x^{\ominus}$ (for instance, $p/p^{\ominus}$), where $x^{\ominus}$ is a standard value. The $\{n\}$ convention simplifies the appearance of many expressions.

A subscript r attached to an equation number indicates that the equation applies only to a reversible change.

A superscript ° attached to an equation number indicates that the equation applies only to an ideal system, such as a perfect gas or an ideal solution.

Cross-references of the form eqn n are to equations within the current chapter; those of the form eqn $N.n$ are to equations in Chapter N.

The symbol $p^{\ominus}$ denotes 1 bar (10^5 Pa) exactly and $b^{\ominus}$ denotes $1\ \mathrm{mol\,kg^{-1}}$ exactly.

When referring to temperature, T denotes a thermodynamic temperature (for example, on the Kelvin scale) and θ a temperature on the Celsius scale.

For numerical calculations, unless otherwise specified, assume that zeros in data like 10, 100, 1000, etc. are significant (that is, interpret such data as 10., 100., 1000., etc.).

0

Introduction: orientation and background

This chapter introduces some basic ideas which it will be useful to know about even before they are introduced formally. All the new material will be dealt with in greater detail later in the text.

Physical chemistry is the branch of chemistry that establishes and develops the principles of the subject. Its concepts are used to explain and interpret observations on the physical and chemical properties of matter. Physical chemistry is also essential for developing and interpreting the modern techniques used to determine the structure and properties of matter, such as new synthetic materials and biological macromolecules.

The structure of science

The observations that physical chemistry organizes and explains are summarized by scientific laws. A **law** is a summary of experience. Thus, we shall encounter the laws of thermodynamics, which are summaries of the relations between bulk properties, and particularly observations on the transformations of energy. We shall also encounter the laws of quantum mechanics, which summarize observations on the behaviour of individual particles, such as molecules, atoms, and subatomic particles. The first step in accounting for a law is to propose a **hypothesis**, which is essentially a guess at an explanation in terms of more fundamental concepts. Dalton's atomic hypothesis, which was proposed to account for the laws of chemical composition, is an example. When a hypothesis has become established, perhaps as a result of the success of further experiments it has inspired or by a more elaborate formulation (often in terms of mathematics) that puts it into the context of broader aspects of science, it is promoted to the status of a **theory**. We shall encounter a number of theories in this text: among them will be the theories of chemical equilibrium, atomic structure, and the rates of reactions.

A characteristic of physical chemistry (like other branches of science) is that, to develop theories, it adopts models of the system it is seeking to describe. A **model** is a simplified version of the system that focuses on the essentials of the problem. Once a successful model has been constructed and tested against known observations and any experiments the model inspires, it can be made more sophisticated and incorporate some of the complications that the original model ignored. Thus, models provide the initial framework for discussions, and reality is captured rather like a building is completed, decorated, and furnished. We shall encounter a number of such models. One example is the **kinetic model** of gases, in which a gas is regarded as a collection of particles in ceaseless, random motion. Another example is the **nuclear model** of an atom, and in particular a hydrogen atom, which is used as a basis for the discussion of the structures of all atoms. A third very important type of example is that of a **perfect gas**, which is an idealized model of the gaseous state of matter. This model, which is also the starting point of the discussion of **real gases**, or actual gases, is the basis of many thermodynamic expressions.

It is often convenient to preserve the form of equations developed on the basis of a simple model in any elaboration of the model. The advantage of such a procedure is that the appearance of many equations is then preserved and they remain familiar. An example of such a modification is the replacement of a concentration term in certain thermodynamic expressions (such as an equilibrium constant) by an effective concentration called an **activity**. Physical chemistry helps to make this a practically useful procedure by establishing a relation between the effective concentration and the true concentration.

Matter

A **substance** is a distinct, pure form of matter. The **amount of substance**, n (more colloquially 'number of moles' or 'chemical amount'), in a sample is reported in terms of a unit called a **mole** (mol). The formal definition of 1 mol is that it is the amount of substance that contains as many objects (atoms, molecules, ions, or other specified entities) as there are atoms in exactly 12 g of carbon-12. This number is found experimentally to be approximately 6.02×10^{23}.[1] If a sample contains N entities, the amount of substance it contains is $n = N/N_A$, where N_A is the **Avogadro constant**: $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$. Note that N_A is a quantity with units, not a pure number. Conversely, if the amount of substance is n (for example, 2.0 mol O_2), then the number of entities present is nN_A (in this example, 1.2×10^{24} O_2 molecules).

A distinction is made in chemistry between extensive properties and intensive properties. An **extensive property** is a property that depends on the amount of substance in the sample. An **intensive property** is a property that is independent of the amount of substance in the sample. Two examples of extensive properties are mass and volume. Examples of intensive properties are temperature, mass density (mass divided by volume), and pressure. A **molar property**, X_m, is the value of an extensive property, X, of the sample divided by the amount of substance present in the sample. A molar property is intensive because the value of an extensive property X is proportional to the amount of substance, n, so $X_m = X/n$ is independent of the amount of substance in the sample. An example is the molar volume, V_m, the volume of a sample divided by the amount of substance in the sample (the volume per mole). The one exception to the notation X_m is the **molar mass**, which is denoted simply M. The molar mass of an element is the mass per mole of its atoms. The molar mass of a molecular compound is the mass per mole of molecules, and the molar mass of an ionic compound is the mass per mole of formula units.[2] The names 'atomic weight' and 'molecular weight' are still widely used in place of molar mass, but we shall not use them in this text.

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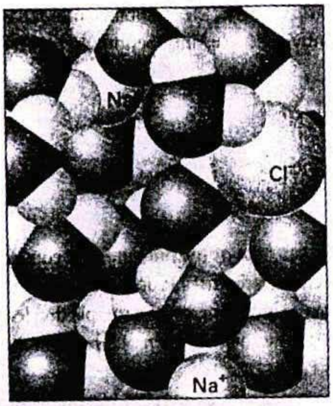
[1] More precise values of the fundamental quantities and conversion factors introduced in this chapter are given inside the front cover.

[2] A formula unit is an assembly of ions corresponding to the chemical formula of the compound; so the formula unit NaCl consists of one Na^+ ion and one Cl^- ion.



0.1 A schematic indication of the relative sizes of ions and molecules and the average separation of ions in a 1 M NaCl aqueous solution. There are typically about three H_2O molecules between ions. Cations tend to be found near anions, and vice versa. Cations are hydrated by weak bonding with the O atoms of neighbouring H_2O molecules; anions are hydrated by weak bonding through the H atoms.

The **molar concentration** ('molarity') of a solute in a solution refers to the amount of substance of the solute divided by the volume of the solution. Molar concentration is usually expressed in moles per litre ($mol\,L^{-1}$ or $mol\,dm^{-3}$; 1 L is identical to $1\,dm^3$). A solution in which the molar concentration of the solute is $1\,mol\,L^{-1}$ is prepared by dissolving 1 mol of the solute in sufficient solvent to prepare 1 L of solution. Such a solution is widely called a '1 molar' solution and denoted 1 M. The term **molality** refers to the amount of substance of solute divided by the mass of solvent used to prepare the solution. Its units are typically moles of solute per kilogram of solvent ($mol\,kg^{-1}$).

The development of an appreciation of events on an atomic scale is a valuable talent in physical chemistry. In a 1 M NaCl(aq) solution, the average separation between oppositely charged ions is about 1 nm, which is enough to accommodate about three H_2O molecules (Fig. 0.1). A dilute solution typically means a solution of molar concentration of no greater than about $0.01\,mol\,L^{-1}$. In such solutions, the ions are separated by about 10 H_2O molecules.

Energy

The central concept of all explanations in physical chemistry, as in so many other branches of physical science, is that of **energy**. A formal definition of this quantity will be given in Part 1; here we shall make use of the somewhat bald definition: *energy is the capacity to do work*. We shall often make use of the apparently universal law of nature that *energy is conserved*; that is, energy can be neither created nor destroyed. Therefore, although energy can be transferred from one location to another (as when water in a beaker is heated by electricity generated in a power station), the total energy available is constant.

0.1 Contributions to the energy

There are two contributions to the total energy of a system from the matter it contains. The **kinetic energy**, E_K, of a body is the energy it possesses as a result of its motion. For a body of mass m travelling at a speed v, the kinetic energy is $\frac{1}{2}mv^2$, so a heavy body travelling rapidly has a high kinetic energy. A stationary body has zero kinetic energy. The **potential energy**, V, of a body is the energy it possesses as a result of its position. The zero of potential energy is arbitrary. For example, the gravitational potential energy of a body is often set to zero at the surface of the Earth; the electrical potential energy of two charged particles is set to zero when their separation is infinite.

No universal expression for the potential energy can be given because it depends on the type of interaction the body experiences. However, there are two common types of interaction that give rise to simple expressions for the potential energy. One is the potential energy of a body of mass m in the gravitational field close to the surface of the Earth (a gravitational field acts on the mass of a body). If the body is at a height h above the surface of the Earth, then its potential energy is mgh, where g is a constant called the **acceleration of free fall**, $g = 9.81\,m\,s^{-2}$, and $V = 0$ at $h = 0$ (the arbitrary zero mentioned previously). Of greater importance in chemistry is the potential energy of a charged body in the vicinity of another charged body (an electric field acts on the charge carried by a body). If a particle (a point-like body) of charge q_1 is at a distance r in a vacuum from another particle of charge q_2, then their potential energy is given by the expression

$$V = \frac{q_1 q_2}{4\pi\varepsilon_0 r} \tag{1}$$

The constant ε_0 is the **vacuum permittivity**, a fundamental constant with the value $8.85 \times 10^{-12}\,C^2\,J^{-1}\,m^{-1}$. Note that, as remarked previously, $V = 0$ at infinite separation. This very important relation is called the **Coulomb potential energy** and the interaction it describes is called the **Coulomb interaction** of two charges. The Coulomb interaction is important in chemistry because we deal frequently with the interactions between the charges of electrons, nuclei, and ions.

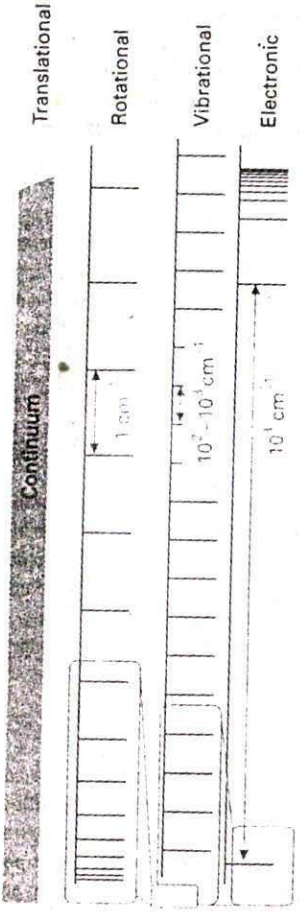
0.2 Energy units

The SI[3] unit of energy is the joule (J), which is defined as[4]

$$1\ \mathrm{J} = 1\ \mathrm{kg\,m^2\,s^{-2}} \qquad [2]$$

A joule is quite a small unit of energy: for instance, each beat of the human heart consumes about 1 J. The unit is named after the nineteenth-century scientist J.P. Joule, who helped to establish the role of energy in science. The molar energy is the energy of a sample divided by the amount of substance; it is normally expressed in joules per mole ($\mathrm{J\,mol^{-1}}$) or a multiple of this unit, most commonly kilojoules per mole ($\mathrm{kJ\,mol^{-1}}$).

Although the joule is the SI unit of energy, it is sometimes convenient to employ other units. One of the most useful alternative energy units in chemistry is the **electronvolt** (eV): 1 eV is defined as the kinetic energy acquired when an electron is accelerated through a potential difference of 1 V. The relation between electronvolts and joules is $1\ \mathrm{eV} \approx 1.6 \times 10^{-19}\ \mathrm{J}$. Many processes in chemistry involve energies of a few electronvolts. For example, to remove an electron from a sodium atom requires about 5 eV. Calories (cal) and kilocalories (kcal) are still encountered in the chemical literature: by definition, 1 cal = 4.184 J. An energy of 1 cal is enough to raise the temperature of 1 g of water by 1 °C.



0.2 A representation of the quantization of the energy of different types of motion. Free translational motion in an infinite region is not quantized, and the permitted energy levels form a continuum. Rotation is quantized, and the separation increases as the state of excitation increases. The separation between levels depends on the moment of inertia of the molecule. Vibrational motion is quantized, but note the change in scale between the ladders. The separation of levels depends on the masses of atoms in the molecule and the rigidities of the bonds linking them. Electronic energy levels are quantized, and the separations are typically very large (of the order of 1 eV).

0.3 Equipartition

A molecule has a certain number of degrees of freedom, such as its ability to translate (the motion of its centre of mass through space), rotate around its centre of mass, or vibrate (as its bond lengths and angles change). Many physical and chemical properties depend on the energy associated with each of these modes of motion. For instance, a chemical bond might break if a lot of energy becomes concentrated in it.

The **equipartition theorem** is a useful guide to the average energy associated with each degree of freedom when the sample is at a temperature T.[5] There are two parts to the theorem, one qualitative and the other quantitative. The qualitative part of the theorem tells us that all degrees of freedom have the same average energy. That means that the average kinetic energy of motion parallel to the x-axis is the same as the average kinetic energy of motion parallel to the y-axis and to the z-axis, and each rotational degree of freedom also has the same energy. That is, in a normal sample, the total energy is equally 'partitioned' over all the available modes of motion. One mode of motion is not especially rich in energy at the expense of another.

To introduce the quantitative part of the theorem we have to be more precise about what we mean by 'degree of freedom'. From now on, we shall refer to a *quadratic term* in the energy, a term for the kinetic or potential energy that appears as the square of a coordinate or a velocity (or momentum). For example, because the kinetic energy of a body of mass m free to move in three dimensions is $\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$, there are three quadratic terms. The equipartition theorem then goes on to say that the average energy associated with each quadratic term is equal to $\frac{1}{2}kT$, where T is the temperature and k is a fundamental constant called the **Boltzmann constant**. This constant has the value $1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}$. The

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[3] We use SI units throughout this text; SI stands for *Système international*, a systematic, coherent set of units based on the metric system. Conversions to alternative units will be given where appropriate.

[4] Equation numbers in square brackets indicate a definition.

[5] Here and throughout this text, the symbol T will denote temperature on a scale that begins at 0 for the lowest attainable temperature, which is found empirically to lie at −273.15 °C. Later we shall see that this scale corresponds to the Kelvin scale.

Boltzmann constant is related to the gas constant by $R = N_A k$. In passing, it should be noted that one reason why R occurs in so many formulas, including those apparently wholly unrelated to gases, is that it is really the fundamental constant k appearing in disguise. The quantity kT, which has the value 4×10^{-21} J (more briefly 4 zJ, where z, zepto, is the uncommon but useful SI prefix for 10^{-21}) at 25 °C, or 26 meV, is an indication of the average energy carried by a mode of motion at a temperature T.

An important point is that the equipartition theorem is derived from classical physics, and when quantization is important (see below) the theorem is inapplicable. Broadly speaking, we can be confident about using it for average translational motion in gases, guardedly confident about applying it to the rotation of most molecules, and not apply it to their vibrational motion.

0.4 The quantization of energy

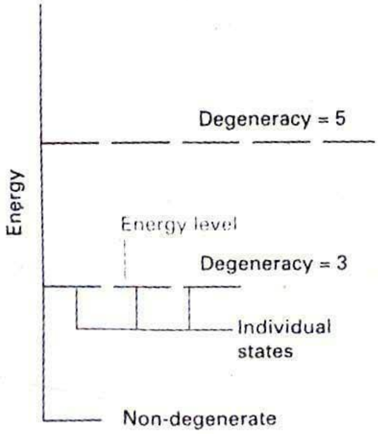
The great revolution in physics that occurred in the opening decades of the twentieth century and which introduced **quantum mechanics** is of crucial importance to chemistry. Chemistry is concerned with the behaviour of subatomic particles, particularly electrons, and it is essential to use quantum mechanics when dealing with such small particles. The feature of quantum mechanics that distinguishes it from the **classical mechanics** of Newton and his immediate successors is that matter has a wave-like character. That is, instead of particles and waves being distinct entities, particles have some of the properties of waves and waves have some of the properties of particles. For instance, if a particle has a linear momentum p (the product of mass and velocity, $p = mv$), then according to quantum mechanics it also has (in some sense) a wavelength, λ, given by the **de Broglie relation:**

$$\lambda = \frac{h}{p} \tag{3}$$

where h is the **Planck constant**, a fundamental constant with the value 6.6×10^{-34} J s.

Another feature of quantum mechanics is that energy is **quantized**, or confined to certain discrete values. These permitted energies are called **energy levels** and their values depend on the species. The quantization of energy is most important—in the sense that the allowed energies are widest apart—for particles of small mass confined to small regions of space. Consequently, quantization is very important for electrons in atoms and molecules, but usually unimportant for macroscopic bodies.

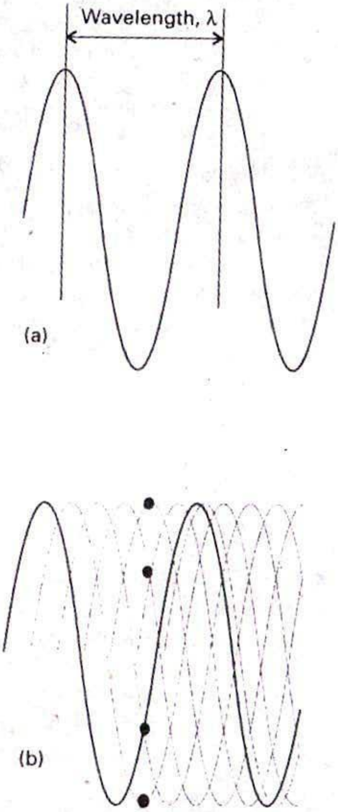
(a) The energies of material objects



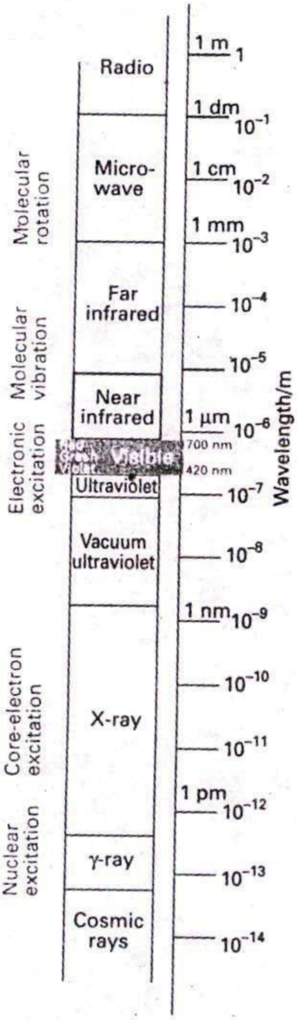
0.3 Several distinct states may correspond to the same energy. That is, each energy level may be degenerate. Three energy levels are shown here, possessing one, three, and five distinct states.

For particles in containers of macroscopic dimensions the separation of translational energy levels is so small that for all practical purposes their translational motion is unquantized (Fig. 0.2). The separation between energy levels is small for molecular rotational motion, larger for molecular vibrational motion, and greatest for the energies of electrons in atoms and molecules. The separations of energy levels for a small molecule are about 10^{-23} J (0.01 zJ) for rotational motion (which corresponds to 0.01 kJ mol^{-1}), 10^{-20} J (10 zJ) for vibrational motion (10 kJ mol^{-1}), and 10^{-18} J (1 aJ, where a is another uncommon but useful SI prefix, standing for atto, and denoting 10^{-18}) for electronic excitation (10^3 kJ mol^{-1}). The relative values are consistent with the validity of the equipartition theorem for translational and rotational motion, but not for the other modes.

A final point in this connection is that we need to be aware that more than one state can correspond to a given energy level. For example, a molecule can rotate in one plane at a certain energy, but it may also be able to rotate in a different plane with the same energy; each different orientation of rotational motion corresponds to a distinct rotational state of the molecule. The number of individual states that belong to one energy level is called the **degeneracy** of that level (Fig. 0.3). If there is only one state of motion corresponding to a



0.4 (a) The wavelength, λ, of a wave is the peak-to-peak distance. (b) The wave is shown travelling to the right at a speed c; at a given location, the instantaneous amplitude of the wave changes through a complete cycle (the four dots show half a cycle) as it passes a given point, and the frequency, ν, is the number of cycles per second that occur at a given point. Wavelength and frequency are related by $\lambda\nu = c$.



0.5 The regions of the electromagnetic spectrum and the types of excitation that give rise to each region.

particular energy, then we say that the level is non-degenerate. Be very careful to distinguish the energy levels (the ladder of possible energies) from the states that correspond to each 'rung' of the ladder.

(b) The energy of the electromagnetic field

An electromagnetic field is an oscillating electric and magnetic disturbance that spreads as a wave through empty space, the vacuum. The wave travels at a constant speed called the speed of light, c, which is about $3 \times 10^8\ \mathrm{m\,s^{-1}}$. As its name suggests, an electromagnetic field has two components, an electric field that acts on charged particles (whether stationary or moving) and a magnetic field that acts only on moving charged particles. The electromagnetic field is characterized by a **wavelength**, λ, the distance between the neighbouring peaks of the wave, and its **frequency**, ν, the number of times per second at which its displacement at a fixed point returns to its original value (Fig. 0.4; the frequency is measured in hertz, where $1\ \mathrm{Hz} = 1\ \mathrm{s^{-1}}$). The wavelength and frequency of a wave are related by

$$\lambda\nu = c \tag{4}$$

Therefore, the shorter the wavelength, the higher the frequency. The characteristics of a wave are also reported by giving the **wavenumber**, $\tilde{\nu}$, of the radiation, where

$$\tilde{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \tag{5}$$

The wavenumber can be interpreted as the number of complete wavelengths in a given length. Wavenumbers are normally reported in reciprocal centimetres ($\mathrm{cm^{-1}}$), so a wavenumber of $5\ \mathrm{cm^{-1}}$ indicates that there are 5 complete wavelengths in 1 cm. It is useful to note that the relations $E = h\nu$ and $\nu = c\tilde{\nu}$ can be combined to convert energies to wavenumbers; it turns out, for instance, that $1\ \mathrm{eV} \approx 8066\ \mathrm{cm^{-1}}$. The classification of the electromagnetic field according to its frequency and wavelength is summarized in Fig. 0.5.

Quantum mechanics adds to this wave-like description of electromagnetic radiation by introducing the concept of particle-like packets of electromagnetic energy called **photons**. The **intensity** of the radiation is determined by the number of photons in the ray: an intense ray consists of a large number of photons; a feeble ray consists of only a few photons. A human eye can respond to a single photon; a lamp rated at 100 W (where $1\ \mathrm{W} = 1\ \mathrm{J\,s^{-1}}$; W denotes the watt) generates about 10^{19} photons each second, but even so takes several hours to generate 1 mol of photons. The energy of each photon is determined by its frequency, ν, by

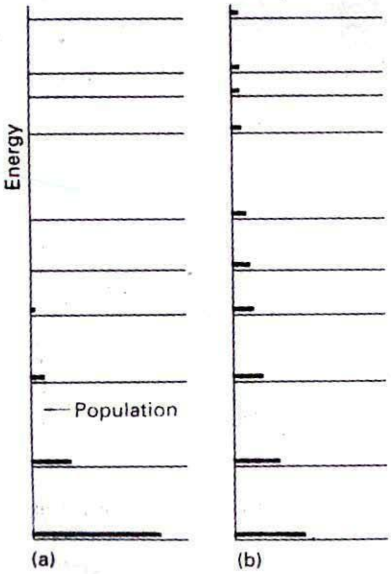
$$E = h\nu \tag{6}$$

This relation implies that photons of microwave radiation have lower energy than photons of visible light (which consists of shorter wavelength, higher frequency radiation). It also implies that the energies of photons of visible light increase as the light is changed from red (longer wavelength) to violet (shorter wavelength).

0.5 The populations of states

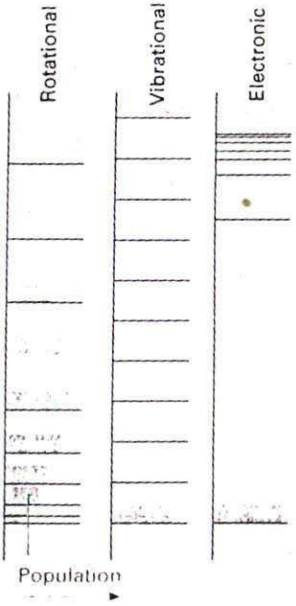
The continuous thermal agitation that the molecules experience in a sample at $T > 0$ ensures that they are distributed over the available energy levels. One particular molecule may be in one low energy state at one instant, and then be excited into a high energy state a moment later. Although we cannot keep track of the energy state of a single molecule, we can speak of the average numbers of molecules in each state; these average numbers are constant in time provided the temperature remains the same. The average number of molecules in a state is called the **population** of the state.

Only the lowest energy state is occupied at $T = 0$. Raising the temperature excites some molecules into higher energy states, and more and more states become accessible as the temperature is raised further (Fig. 0.6). Nevertheless, whatever the temperature, there is always a higher population in a state of low energy than one of high energy. The only exception occurs when the temperature is infinite: then all states of the system are equally populated.

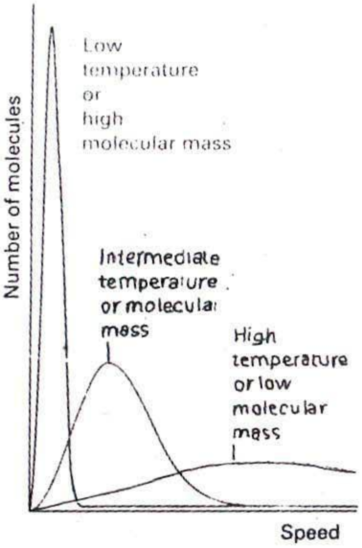


0.6 The Boltzmann distribution predicts that the population of a state decreases exponentially with the energy of the state. (a) At low temperatures, only the lowest states are significantly populated; (b) at high temperatures, there is significant population in high-energy states as well as in low-energy states. At infinite temperature (not shown), all states are equally populated.

The formula for calculating the populations of states of various energies is called the **Boltzmann distribution** and was derived by the Austrian scientist Ludwig Boltzmann



0.7 The Boltzmann distribution for three types of motion at a single temperature. There is a change in scale between the three stacks of levels (recall Fig. 0.2). Only the ground electronic state is populated at room temperature in most systems, and the bulk of the molecules are also in their ground vibrational state. Many rotational states are populated at room temperature as the energy levels are so close. The peculiar shape of the distribution over rotational states arises from the fact that each energy level actually corresponds to a number of degenerate states in which the molecule is rotating at the same speed but in different orientations. Each of these states is populated according to the Boltzmann distribution, and the shape of the distribution reflects the total population of each level.



0.8 The essential content of the Maxwell distribution of molecular speeds is summarized by this diagram. Note how the maximum in the distribution moves to higher speeds as the temperature is increased or, at constant temperature, we consider species of decreasing mass. The distribution also becomes wider as its peak moves to higher speeds.

towards the end of the nineteenth century. This formula gives the ratio of the numbers of particles, N_i/N_j, in states with energies E_i and E_j as

$$\frac{N_i}{N_j} = \mathrm{e}^{-(E_i - E_j)/kT} \qquad (7)$$

An important point concerning the interpretation of the Boltzmann distribution is that it refers to the populations of *states*, not levels. Because the Boltzmann distribution refers to states, all the members of a degenerate set of states belonging to the same energy level will have the same population. We shall see a consequence of this feature shortly.

A typical energy separation between the ground state and the first electronically excited state of an atom or molecule is about 3 eV, which corresponds to 300 kJ mol^{-1}. In a sample at 25 °C (298 K) the ratio of the populations of the two states is about e^{-121}, or about 10^{-53}. Therefore, essentially every atom or molecule in a sample is in its electronic ground state. The population of the upper state rises to about 1 per cent of the population of the ground state only when the temperature reaches 10^4 °C. The separation of vibrational energy levels is very much less than that of electronic energy levels (about 0.1 eV, corresponding to $10\ \mathrm{kJ\,mol^{-1}}$), but nevertheless at room temperature only the lowest energy level is significantly populated. Only about 1 in $e^4 \approx 60$ molecules is not in its ground state. Rotational energy levels are much more closely spaced than vibrational energy levels (typically, about 100 to 1000 times closer), and even at room temperature we can expect many rotational states to be occupied. Therefore, when considering the contribution of rotational motion to the properties of a sample, we need to take into account the fact that molecules occupy a wide range of different states, with some rotating rapidly and others slowly.

The important features of the Boltzmann distribution to bear in mind are that the distribution of populations is an exponential function of energy and temperature, and that more states are significantly populated if they are close together in comparison with kT (like rotational and translational states), than if they are far apart (like vibrational and electronic states). Moreover, more states are occupied at high temperatures than at low temperatures. The illustration (Fig. 0.7) summarizes the form of the Boltzmann distribution for some typical sets of energy levels.

The Boltzmann distribution takes a special form when we consider the free translational motion of noninteracting gas molecules. Different energies now correspond to different speeds (because the kinetic energy is equal to $\frac{1}{2}mv^2$), so the Boltzmann formula can be used to predict the proportions of molecules having a specific speed at a particular temperature. The expression giving the proportion of molecules that have a particular speed is called the **Maxwell distribution**, and has the features summarized in Fig. 0.8. The bulge in the distribution represents the fact that the kinetic energy of a molecule depends on its speed, and there are many ways of obtaining a given value of the speed v with different values of the components v_x, v_y, and v_z relative to the three axes, particularly when the speed is high. In other words, translational energy levels are highly degenerate, and the degeneracy increases with energy. Therefore, although the populations of individual states decrease with increasing energy (and hence speed), there are many more states of a given energy at high energies and the product of this rising degeneracy and the falling exponential function has a bulge at an intermediate energy.

Notice how the tail towards high speeds is longer at high temperatures than at low, which indicates that at high temperatures more molecules in a sample have speeds much higher than average. The speed corresponding to the maximum in the graph is the most probable speed, the speed most likely to be found for a molecule selected at random. The illustration also shows how the distribution varies with mass for some components of air at 25 °C. The lighter molecules move, on average, much faster than the heavier ones.

Further reading

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