Ian W. M. Smith
Charles S. Cockell
Sydney Leach *Editors*

Astrochemistry and Astrobiology

Springer

Physical Chemistry in Action

Ian W.M. Smith • Charles S. Cockell •
Sydney Leach
Editors

Astrochemistry and Astrobiology

Springer

Editors

Ian W.M. Smith
The University Chemical Laboratory
University of Cambridge
Cambridge
United Kingdom

Charles S. Cockell
School of Physics and Astronomy
University of Edinburgh
Edinburgh
United Kingdom

Sydney Leach
Laboratoire d'Etude du Rayonnement
  et de la Matière en Astrophysique (LERMA)
Observatoire de Paris-Meudon
Meudon
France

Preface

The related subjects of Astrochemistry and Astrobiology are in an era of explosive growth. Both are strongly multidisciplinary: thus, contributions to, and discussions of, these subjects involve scientists who might primarily describe themselves as astronomers, chemists, physicists, astrophysicists, molecular biologists, evolutionary biologists, etc. Proposed phenomena in both areas must be consistent with universal physico-chemical principles. A major purpose of this volume is to outline these physico-chemical principles and describe how they underpin our efforts to understand astrochemistry and to make predictions in astrobiology.

Our book comprises ten chapters, each written by an expert, or experts, in the subject matter of their chapter. Because the backgrounds of those entering the fields of astrochemistry and astrobiology can be very diverse, authors have all been asked to pitch their chapters at a level that should be understandable by this wide range of readership. Chapter 1 seeks to introduce those aspects of physical chemistry which are relevant to the discussions of various topics in astrochemistry and astrobiology to be found in the subsequent eight chapters. These later chapters can be roughly sub-divided into three (Chaps. 2, 3, and 4) that deal with topics within astrochemistry and five (Chaps. 5, 6, 7, 8, and 9) that examine aspects of astrobiology – interpreted broadly.

Major concerns in astrochemistry are (1) the identification of the molecules that exist in the cosmos and the characterisation of the physical conditions in those regions of the universe where the observed molecules are found; (2) laboratory measurements on the spectroscopy of potential molecules and on the rates and products of homogeneous and heterogeneous processes that may contribute to the formation and destruction of molecules, under the generally extreme interstellar conditions where molecules are found; (3) the creation of computer models that use laboratory data and seek both to reproduce what is found in the 'molecular universe', and to suggest what other molecules may be present and which processes appear to be especially important, so as to focus the efforts of laboratory scientists. These topics are dealt with, in turn in chapters by Maryvonne Gerin (in Chap. 2), Michael Pilling (in Chap. 3), and by Valentine Wakelam, Herma Cuppen and Eric Herbst (in Chap. 4).

In any search for life elsewhere in the universe, we only have one exemplar: life here on the Earth. Consequently, it makes sense to search for astronomical bodies which appear to offer living systems a similar environment. For planets outside the solar system, that is, exoplanets, this idea leads to the notion of a Habitable Zone – or more colloquially a 'Goldilocks Zone' – generally defined as the range of radii around a star where the temperature at a planet's surface will not be too high or too low for liquid water to exist. In addition, there may be other bodies, such as the Jovian moon, Europa, where liquid water might be stable. In Chap. 5, Lisa Kaltenegger describes the methods by which planets are detected and characterised, and how, in the future, it may be possible, using sensitive spectroscopic methods to search for biosignatures – signatures of life – in their atmospheres. The importance of water for life as we know it – and may know it – is the subject of Philip Ball's Chap. 6. He emphasises that water does not simply play a passive role in biochemistry, and considers the possibility that other solvents might support and encourage life. Of course, even in thinking about life here on Earth, we must be careful not to adopt too anthropogenic a view. Charles S. Cockell, in Chap. 7, considers the range of physical conditions – temperature, pressure, aridity, pH, etc. – which different life forms on our planet can tolerate.

In searching for – even contemplating – life on exoplanets, we may have the existence of life here on Earth to guide us, but we are severely handicapped by our ignorance about how earthly life came into being. In Chap. 8, Robert Pascal under the title 'Life, Metabolism and Energy', considers how any proposals for the emergence of life must be consistent with thermodynamic and kinetic constraints. Then, in Chap. 9, Irene Chen and her colleagues reflect on the possibility that our present biological world was preceded by one in which RNA, rather than DNA, played an important evolutionary role, and they also discuss the importance of the creation of cells and their linkage to lipids.

Sydney Leach's final chapter is different in kind from those that precede it. He writes a contemplative essay on each of the previous chapters in turn. In some places, he expands on the matters dealt with in earlier chapters, in others he inserts his own view of various topics, and in yet others he adds some extra material that might have been included earlier if space had allowed.

As the outline in the previous paragraphs indicates, the topics that are covered in the individual chapters proceed from those that might be classed as belonging to astrochemistry to those dealing with aspects of astrobiology. Nevertheless, every effort is made to bring together concepts in astrochemistry and astrobiology, which have traditionally been dealt with as separate areas of science.

Cambridge, UK   Ian W.M. Smith
Edinburgh, UK   Charles S. Cockell
Meudon, France   Sydney Leach
September 2012

Acknowledgement

We kindly attribute the name of this series to Professor Ian W.M. Smith.

Contents

Chapter 1
Aspects of Physical Chemistry

Ian W.M. Smith

Abstract   Some of those topics in physical chemistry that are especially relevant to astrochemistry and astrobiology are introduced in this chapter. I start with some discussion of the chemical elements: their relative abundances, their electronic structure, and how chemical bonds are formed in simple molecules. This leads to a discussion of how changes between energy levels lead to molecular spectra that can be used to identify molecules at a distance – even the vast distances from Earth to astronomical objects. Having considered forces within molecules, I then discuss the weaker forces between molecules, including hydrogen bonding. The next section focuses on chemical reactions from both the standpoint of thermodynamics and that of chemical kinetics. Finally, some consideration is given to surface processes, which can occur on the dust particles found in the interstellar medium, and enzyme kinetics, which is of great importance in biology.

1.1   Introduction

It is frequently stated that Physics and Chemistry are 'universal', whereas biology, dependent as it is on the environment, may differ in different parts of the cosmos. The purpose of this volume is to provide an introduction to astrochemistry and astrobiology: especially the physico-chemical principles that underpin our efforts to understand astrochemistry and predict astrobiology. In this chapter, I shall briefly review several aspects of physical chemistry which play important roles in astrochemistry and astrobiology. The coverage of the topics that I have selected is necessarily very concise. For those wishing to probe the subjects more deeply, I have given page references to (a) the 9th edition of the book *Physical Chemistry* by Atkins and de Paula [1], and (b) the book *Physical Chemistry for the Biosciences* by Chang [2].

I.W.M. Smith (✉)
The University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK
e-mail: iwms2@cam.ac.uk

1.2   The Chemical Elements and Their Atomic Structure

Hydrogen, which has the simplest structure of all atoms and the chemical formula H, is the most abundant element in the Universe [3]. Along with smaller amounts of helium (He) and very small amounts of lithium (Li), hydrogen was generated in the aftermath of the big bang in which the Universe was created. The same processes created deuterium (D or $^2_1$H),[1] the isotope of hydrogen, which has an abundance of 1.56×10^{-4} relative to H in Earth's oceans. Whereas in a hydrogen atom, the nucleus consists of just a single proton, in deuterium the nucleus consists of a proton and a neutron held together by the residual strong force or nuclear force. All the other elements[2] were created later in the history of the Universe in the process referred to as stellar nucleosynthesis. Clearly, the early stars were created only from the elements created in 'big bang' nucleosynthesis; that is, H, D, He and Li.

Stellar nucleosynthesis occurs during the 'burning' of stellar fuel – that is, the fusion of nuclei in the centre of stars. The strong repulsion between nuclei that both carry a positive charge means that such nuclear reactions only occur at the extremely high temperatures and pressures found in the centre of active stars. As one important example, I cite the formation of carbon (C) nuclei which occurs in a two-step process. First, beryllium (Be) nuclei are created by the fusion of two He nuclei,

$$^4_2\text{He}^{2+} + {}^4_2\text{He}^{2+} \rightarrow {}^8_4\text{Be}^{4+}, \tag{1.1}$$
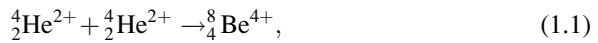
and then the reaction of the Be nucleus with a further He nucleus produces a carbon nucleus:

$$^8_4\text{Be}^{4+} + {}^4_2\text{He}^{2+} \rightarrow {}^{12}_6\text{C}^{6+}. \tag{1.2}$$
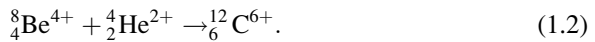
(To emphasise that these are reactions between atomic nuclei I include, as superscripts following the chemical symbol for the element, the total electric charge.)

Following their creation in the thermonuclear processes that might be termed 'stellar burning', the elements heavier than Li, principally carbon, nitrogen and oxygen, are dispersed into interstellar space by stellar winds or supernovae explosions that mark the death of certain stars. The abundances of the chemical elements have been estimated (with difficulty) by a number of authors. They do vary in different regions of the cosmos [3]. The abundances in the solar system are estimated from observations on the sun and on meteorites. Those given by Cameron [4] have been

---

[1] The notation $^2_1$H specifies the number of protons, 1, and the number of nucleons (protons + neutrons), 2. Any electrically neutral atom contains the same number of electrons and protons. To refer to an ion, a superscript after the chemical symbol is added. Thus a deuteron is signified by $^2_1$H^{1+}. The number of protons in an elemental atom corresponds to its atomic number, Z.

[2] These elements, heavier than lithium, are all referred to by astronomers as 'metals' – somewhat to the amusement, or bemusement, of those trained as chemists.

Fig. 1.1 Plots showing the angular distribution of the wavefunctions for the 1s and 2p orbitals of the hydrogen atom
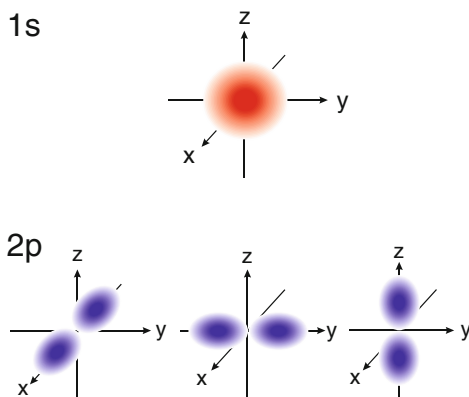
Table 1.1 Partial listing of elemental abundances relative to that of (atomic) hydrogen [4]

H	He	N	O	C	S
1.00	9.8 (−2)	1.1 (−4)	8.5 (−4)	3.6 (−4)	1.6 (−5)
Si	**Fe**	**Na**	**Mg**	**P**	**Cl**
3.6 (−5)	4.7 (−5)	2.1 (−6)	3.8 (−5)	2.8 (−7)	3.0 (−7)

updated – and cited as 'cosmic abundances' by Greenwood and Earnshaw and are displayed in Fig. 1.1 of their book [3]. A list of the abundances of some of the most common elements (and those most involved in astrochemistry and astrobiology) are given in Table 1.1; these values are those estimated by Newson [5] and given on the website: www.astrophysicsspectator.com/tables/Abundances.html.

The full list of elemental abundances show that, very approximately and with some exceptions, the elemental abundances decay exponentially with atomic number, Z, at least up to about $Z = 40$. They also roughly reflect the nuclear binding energies. There are exceptions: for example, the abundances of Li, B and Be are much lower and that of Fe is higher than would be expected by assuming an exponential decay with Z. The anomalously high relative abundance of Fe is apparently associated with the unusually high stability of the nucleus of its commonest isotope ^{56}Fe.

The chemical nature of the elements depends on their 'atomic structure'; that is the distribution of the electrons around the nucleus in the 'atomic orbitals'. A detailed treatment of this subject is beyond the scope of this chapter, but it may be useful to give a simplistic discussion of this topic based on the Periodic Table of the elements, which is reproduced as Table 1.2. In the Periodic Table, the elements are arranged in increasing order of their atomic numbers as if they are on the lines of a book. Each line is termed a 'period'. However, there is not the same number of elements on each line; rather the arrangement is such that elements of similar chemical properties are positioned in the same vertical column or 'group'. For example, the alkali metals, Li, Na, K, Rb, Cs and Fr, fall in the first column (Group 1) in the table. They are characterised by low ionisation energies – that is, relatively small amounts of energy are required to expel an electron and form the singly charged ions: Li^+, Na^+, K^+, etc. These elements readily form salts, especially

Table 1.2 Periodic Table of the Elements, showing the electron configuration of the ground state of each atom

1[a]	1[b]	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1 $1s^1$								**He** 2 $1s^2$									
2	**Li** 3 $[He]2s^1$	**Be** 4 $[He]2s^2$											**B** 5 $2s^22p^1$	**C** 6 $2s^22p^2$	**N** 7 $2s^22p^3$	**O** 8 $2s^22p^4$	**F** 9 $2s^22p^5$	**Ne** 10 $2s^22p^6$
3	**Na** 11 $[Ne]3s^1$	**Mg** 12 $[Ne]3s^2$											**Al** 13 $3s^23p^1$	**Si** 14 $3s^23p^2$	**P** 15 $3s^23p^3$	**S** 16 $3s^23p^4$	**Cl** 17 $3s^23p^5$	**Ar** 18 $3s^23p^6$
4	**K** 19 $[Ar]4s^1$	**Ca** 20 $[Ar]4s^2$	**Sc** 21 $3d^14s^2$	**Ti** 22 $3d^24s^2$	**V** 23 $3d^34s^2$	**Cr** 24 $3d^54s^1$	**Mn** 25 $3d^54s^2$	**Fe** 26 $3d^64s^2$	**Co** 27 $3d^74s^2$	**Ni** 28 $3d^84s^2$	**Cu** 29 $3d^{10}4s^1$	**Zn** 30 $3d^{10}4s^2$	**Ga** 31 $4s^24p^1$	**Ge** 32 $4s^24p^2$	**As** 33 $4s^24p^3$	**Se** 34 $4s^24p^4$	**Br** 35 $4s^24p^5$	**Kr** 36 $4s^24p^6$
5	**Rb** 37 $[Kr]5s^1$	**Sr** 38 $[Kr]5s^2$	**Y** 39 $4d^15s^2$	**Zr** 40 $4d^25s^2$	**Nb** 41 $4d^45s^1$	**Mo** 42 $4d^55s^1$	**Tc** 43 $4d^55s^2$	**Ru** 44 $4d^75s^1$	**Rh** 45 $4d^85s^1$	**Pd** 46 $4d^{10}$	**Ag** 47 $4d^{10}5s^1$	**Cd** 48 $4d^{10}5s^2$	**In** 49 $5s^25p^1$	**Sn** 50 $5s^25p^2$	**Sb** 51 $5s^25p^3$	**Te** 52 $5s^25p^4$	**I** 53 $5s^25p^5$	**Xe** 54 $5s^25p^6$
6	**Cs** 55 $[Xe]6s^1$	**Ba** 56 $[Xe]6s^2$	**La** 57 $5d^16s^2$	**Hf** 72 $5d^26s^2$	**Ta** 73 $5d^36s^2$	**W** 74 $5d^46s^2$	**Re** 75 $5d^56s^2$	**Os** 76 $5d^66s^2$	**Ir** 77 $5d^76s^2$	**Pt** 78 $5d^96s^1$	**Au** 79 $5d^{10}6s^1$	**Hg** 80 $5d^{10}6s^2$	**Tl** 81 $6s^26p^1$	**Pb** 82 $6s^26p^2$	**Bi** 83 $6s^26p^3$	**Po** 84 $6s^26p^4$	**At** 85 $6s^26p^5$	**Rn** 86 $6s^26p^6$
7	**Fr** 87 $[Rn]7s^1$	**Ra** 88 $[Rn]7s^2$	**Ac** 89 $6d^17s^2$																

[a]These digits (increasing downwards) number the 'groups'.

[b]These digits (increasing across the table) number the 'periods'.

Elements with atomic numbers from 58 (Cerium) to 71 (Lutetium) are the lanthanides or 'rare earths'. The electronic configurations of Ce is $[Xe]4f^15d^16s^2$, that of element 59 Praseodymium (Pr) is $[Xe]4f^36s^2$. Thereafter the 4f orbitals fill to element 70 Ytterbium (Yb), which has the configuration $[Xe]4f^{14}6s^2$, and Lutetium, which has the configuration $[Xe]4f^{14}5d^16s^2$.

Elements with atomic numbers of 90 (Thorium) and greater are the actinides.

with the elements towards the right-hand side of the table such as the halogens in Group 17 – but not with the noble gases in group 18, He, Ne, Ar, etc.

The construction and the development of the Periodic Table was a work of genius, based on empirical knowledge of the chemical properties of different elements. However, a full *understanding* of the chemical behaviour of atoms – and therefore their place in the periodic table only came with the emergence of quantum mechanics (1, Chaps. 7 and 8; 2, Chap. 11). A detailed discussion of this topic is certainly beyond the scope of the present book, but it is relatively straight-forward to summarise enough of the conclusions of quantum mechanics for current purposes.

A treatment of the hydrogen atom by quantum mechanics leads to the conclusion that its single electron can occupy any of a number of atomic orbitals. These orbitals are characterized by three quantum numbers given the symbols: n, l and m_l. Each orbital can accommodate two electrons which differ in their electron spin, m_s, which can only take the value $+ \frac{1}{2}$ or $- \frac{1}{2}$. In the H atom, the energy associated with the electron depends only on the value of n, the principal quantum number, which can take integral values from 1 to infinity. This energy can be expressed by the simple formula: $E_n = - R_\infty / n^2$, relative to a zero corresponding to the removal of the electron from the influence of the positive proton (i.e., ionisation). The Rydberg constant, R_∞, corresponds to the ionisation energy of the H atom (13.60 eV). The value of the second quantum number l relates to the value of the angular momentum of an electron occupying a particular orbital: l can take the value $(n - 1)$, $(n - 2)$, down to zero. Thus if $n = 3$, l can have the values 2, 1 or 0. It is because the angular momentum is 'quantised'; that is, it can only take values corresponding to $\{l(l + 1)\}^{\frac{1}{2}} \hbar$ – where $\hbar$ is Planck's constant (h) divided by 2π - that only discrete values of the energy are allowed.

The orbitals with $l = 0, 1, 2, 3$, etc. are referred to as s-orbitals, p-orbitals, d-orbitals, f-orbitals, etc. Finally, m_l, which can take integral values running from $+ m_l$ to $- m_l$, refers to the spatial orientation of the orbital. An electron which occupies an orbital characterised by the same values of n and l, but different m_l, has the same energy – that is, these orbitals are degenerate – in the absence of an electric or magnetic field. There are $(2l + 1)$ orbitals for each value of l. This means that an s-orbital with a given principal quantum number can accommodate two electrons, whereas the p-orbitals with the same values of n can accommodate six electrons, d-orbitals with the same n ten electrons, and so on. As the value of the principal quantum number n increases the electron density is progressively displaced further from the nucleus. Orbitals with different values of l have different symmetries, and these can be represented by diagrams such as Fig. 1.1.

If the orbital energies given by the exact quantum mechanical solution for the H atom held for other atoms, we might expect to see the rows of the Periodic Table contain successively 2, 8, 18, 32 elements as orbitals with $n = 1, 2, 3, 4$ were filled with electrons. In reality, the relative energies of atomic orbitals (or the electrons occupying atomic orbitals) vary as the atomic number of the elements increases and, besides the attractive force between the nucleus and the electron in the H atom, there are also repulsive forces between the several electrons in the

heavier atoms. Although the problem can no longer be exactly solved by the methods of quantum mechanics, it is apparent that the energies of orbitals with the same principal quantum number increase with increasing l. Consequently, it is helpful to think of the orbitals as occupying 'shells' of similar energy: thus, the K shell consists of just the $1s$ orbital, the L shell the $2s$ and $2p$ orbitals, the M shell the $3s$ and $3p$ orbitals and the N shell the $4s$, $3d$ and $4p$ orbitals.

If we then take on board the facts that (a) each orbital can accommodate two electrons, which differ only in their spin quantum number m_s, and (b) the Aufbau principle, which states that to find the ground (or lowest energy) electron configuration the orbitals are filled in order of their ascending energy, we can arrive at the electron configurations given under the formulas of the elements given in the Periodic Table in Table 1.2. The outer – or valence – electrons largely determine the chemical behaviour of the elements and the nature of the bonding when molecules form.

Thus, if we start with a simplified consideration of diatomic molecules, we can identify two limiting kinds of behaviour. First, in the salt molecules formed from the alkali metal atoms of Group 1 and the halogen atoms of Group 17, for example NaCl, an electron is almost completely transferred from the halogen to the alkali metal and the attractive bonding forces are essentially ionic or electrostatic: the molecule is, to a good approximation, Na^+Cl^- and, and due to the separation of charge, this molecule will clearly possess an electric dipole moment. At the other extreme, two identical atoms will 'share' their valence electrons equally, hence forming a covalent bond. With two hydrogen atoms, two electrons are shared and a single covalent bond is formed; with two nitrogen atoms, six electrons, three from each atom are shared and a triple covalent bond results. The single bond in H_2 is the result of two electrons occupying a molecular orbital which can be thought of as arising from favourable overlap of the $1s$ atomic orbitals on the individual H atoms. This is classed as a σ orbital (or σ bond); the electrons occupying such orbitals do not give rise to electronic angular momentum around the interatomic axis. In N_2, there is again a σ bond; but, in addition there are two π bonds arising from the occupation of molecular orbitals arising from the overlap of p orbitals on the individual N atoms. The difference in strength of the single bond in H_2 and the triple bond in N_2 is demonstrated by the difference in their dissociation energies (D_0): 432.1 kJ mol^{-1} in the case of H_2, and 941.7 kJ mol^{-1} in N_2.

Of course, in homonuclear molecules like H_2 and N_2, the distribution of electrons must be symmetrical about a plane that bisects the internuclear axis and is perpendicular to it. Consequently, these molecules possess no electric dipole moment, which, as we shall see, has important consequences for their spectroscopy. On the other hand, heteronuclear molecules like CO, the second most abundant molecule in the universe, do possess an electric dipole moment.

The simple ideas that have been introduced in relation to diatomic molecules can be carried over to a brief discussion of bonding in polyatomic molecules: in particular, the distinction between σ bonds and $\pi-$bonds. Moreover, the structure of polyatomic molecules can be rationalised in terms of the atomic orbitals on neighbouring atoms that are used to create molecular orbitals: for example, if one

s orbital and two p orbitals are used to create three bonding molecular σ-orbitals (as in the C atoms in C_2H_4), the three bonds are aligned 120° to one another.

The element carbon is exceptional and is, of course, essential to life as we know it here on Earth. It is also present in the majority of molecules that have been definitely identified in the interstellar medium. Its electronic configuration is $2s^2 2p^2$ and, by sharing its valence electrons, it is capable of forming four σ−bonds around each C atom, as in CH_4, C_2H_6, C_3H_8 and all the other alkanes. These alkanes can be referred to as saturated molecules, because they only involve σ−bonds, between neighbouring C atoms and between C and H atoms, and there is no possibility of further H atoms adding to the molecules. This is in contrast to unsaturated molecules, such as the alkenes, C_2H_4, C_3H_6, etc., and the alkynes like C_2H_2. These are frequently formulated as $H_2C{=}CH_2$, $H_3CC{=}CH$ and $HC{\equiv}CH$, emphasising the presence of double and triple bonds. In principle, these molecules can add hydrogen, thereby becoming saturated, but many of the organic molecules identified in the interstellar medium are unsaturated, despite H_2 being, by far, the most abundant molecule in most regions where interstellar molecules are found. It is also useful to draw a distinction between these molecules, in which all the electrons are 'paired', and those species, free radicals or simply radicals, which have unpaired electrons. Important examples from the viewpoint of astrochemistry include CN, C_2H and C_4H, as well as many atoms; for example, H, C and N. Generally, radicals exhibit high reactivity, especially with unsaturated molecules and with other radicals.

The ability of carbon to form four single bonds leads to its ability to create chiral molecules. These molecules, which are very important in biology, are said to be optically active, because they rotate the plane of polarised light. In general, a molecule is chiral if it does not have a centre of inversion or a mirror plane [1, p. 426]. These properties are achieved when a carbon atom in a molecule is bound to four different atoms or groups of atoms as in, for example, CHFClBr. A chiral molecule and its mirror image form an enantiomeric pair. Though they are mirror images of one another, such pairs of molecules cannot be superimposed on one another. The amino-acid alanine, $H_2NCH(CH_3)COOH$, is an example of a chiral molecule, whereas the closely related amino-acid glycine, H_2NCH_2COOH, is non-chiral.

I have pointed out the apparently unique role that carbon plays in the 'molecules of life' on Earth. A question that naturally arises is whether any other element might play the role that carbon plays under other conditions. The most likely candidate would seem to be silicon, since Si atoms have a similar electronic configuration, $[Ne]3s^2 3p^2$, to that of C atoms, $[He]2s^2 2p^2$. One empirical argument against this possibility – at least, on Earth-like planets – invokes the fact that, on Earth, silicon is approximately a thousand times more abundant than carbon but life here makes use of carbon, not silicon, in constructing pre-biotic molecules and beyond them, life forms.

A number of factors may contribute to the different chemical and biochemical behaviour of these two elements. One is the considerable difference in their oxides: CO_2, a rather unreactive gas, and SiO_2, most commonly found as a hard crystalline

solid. CO_2 is, of course, inhaled or exhaled by terrestrial organisms, but it is hard to see how an organism could inhale or exhale SiO_2! Silane (SiH_4), the direct analogue of methane, does exist as a flammable gas. However, analogues of the larger alkanes and especially of the alkenes and alkynes are unstable; the smaller ones react vigorously with water and the large ones spontaneously decompose. In addition, silicon fails to bond to many of the other elements with which carbon forms bonds and which are necessary for metabolism. It appears that a basic reason for this difference in behaviour arises from the difference in atomic size between Si and C. Thus, the Si-Si bond length in disilane, Si_2H_6, is 0.2332 nm [6] compared with the C-C bond length of 0.1522 nm in C_2H_6 [7]. This increase in bond length means that any π bonds formed, for example, in Si_2H_4 or Si_2H_2 would be much weaker than the equivalent bonds in alkenes and alkynes. The difference between silicon and carbon, in particular the unique ability of carbon to form bonds with many other elements in molecular structures of enormous versatility, indicates that the formal regularities of the Periodic Table only tell part of the chemical story.

1.3 Energy Levels and Spectroscopy [1, Chaps. 12 and 13; 2, Chap. 14; 8]

The fact that the energy levels of atoms are 'discrete', as long as electrons are bound to the nucleus, has been introduced in Sect. 1.2. The situation is particularly simple in the case of the hydrogen atom since there is only one electron and the energy of each atomic state corresponds to that of the orbital which is occupied by the electron. Spectroscopy is the study of the interaction of electromagnetic radiation with atoms and molecules when changes or transitions occur between the quantised energy levels. Through Planck's famous relationship between the frequency (v) of radiation and the energy of the corresponding photon (E_v), $E_v = hv$, one can determine the spacing of the two energy levels between which the transition occurs. For example, the energies of the H-atom levels for which $n = 2$ and $n = 1$ are $E_n = -R_\infty/2^2$ and $E_n = -R_\infty/1^2$, respectively, so the difference in energy between them is, $(3/4)R_\infty$, and the frequency of the radiation associated with this change is $(3/4)R_\infty/h$. This transition can be observed in absorption, when external radiation of the correct frequency promotes the electron from the level with $n = 1$ to a level with $n = 2$, or emission, when the electron in the excited orbital $n = 2$ spontaneously falls into the $n = 1$ level and a photon is emitted. The photon which is absorbed or emitted corresponds to radiation at a wavelength of $\lambda = 121.6$ nm, which is often referred to as Lyman-α radiation. It is prevalent throughout the interstellar medium, but cannot be observed at the Earth's surface because it is absorbed by the terrestrial atmosphere. In certain regions of space, there is also emission from levels above $n = 2$ corresponding, for example, to the $n = 3 \rightarrow n = 2$ emission. This emission occurs

at $\lambda = 656.27$ nm and is responsible for the pink colour of several regions of the cosmos.

The spectra of atoms are different for the different elements and their observation can therefore identify the presence of particular elements. An important example is the Fraunhöfer lines. These are observed as dark (that is, absorption) lines on the spectrum of the sun and the elements responsible for several of these lines were identified by noting their coincidence with the wavelengths emitted when the same elements were heated; for example, in a Bunsen flame. In the sun, these lines appear in absorption because the background source is hotter than the medium through which the radiation is passing, whereas they are observed in emission from a flame since the background is cooler than the sample.

Quantisation, or the existence of discrete energy levels, is not confined to the energies associated with the motion of electrons. Once we move to molecules, it is necessary additionally to consider the energy levels that are associated with other motions: in particular, with the overall rotation of the molecule and with the molecular vibrations in which the nuclei move their positions relative to one another. The interpretation of molecular spectra is facilitated by the fact that the gaps between energy levels associated with different kinds of motion are quite different, with the result that the spectra associated with them occur at different wavelengths or frequencies in the electromagnetic spectrum.

A further result is that it is generally possible to think of each *bound* electronic state of a molecule to possess its own manifold of vibrational energy levels and, for each of these vibrational states, there will be a manifold of more closely spaced rotational levels. The electronic potential energy (V) of each state of a molecule depends on the instantaneous nuclear geometry. For diatomic molecules (e.g., AB), V depends on the internuclear separation (r_{AB}), and this variation can be represented by a potential energy curve as shown in Fig. 1.2. This figure is also used to represent schematically some of the vibrational and rotational levels associated with this electronic state. For diatomic molecules, there is just one molecular vibration and two rotations about perpendicular axes through the centre-of-mass. With molecules comprised of more than two atoms (N), it is impossible to represent how V depends on all the coordinates required to define the instantaneous geometry. If the molecule is non-linear, it possesses three moments of inertia and three overall molecular rotations, together with $(3N - 6)$ vibrations; linear molecules have two equivalent rotations (like a diatomic molecule) and $(3N - 5)$ vibrations.

Promoting *small* molecules from their lowest or ground electronic state to excited electronic states generally requires radiation in the ultraviolet region of the electromagnetic spectrum. However, observations of the spectra of astronomical sources reveal a large number of absorption features (see Fig. 1.3) referred to as the diffuse interstellar bands [9, 10]. Almost a 100 years after their discovery, the carriers of these bands remain uncertain, though they are generally attributed to neutral or ionised polyatomic molecules.

Because the Earth's atmosphere absorbs wavelengths below about 300 nm, [11] observations at lower wavelengths (for example, of H_2 and CO) generally require
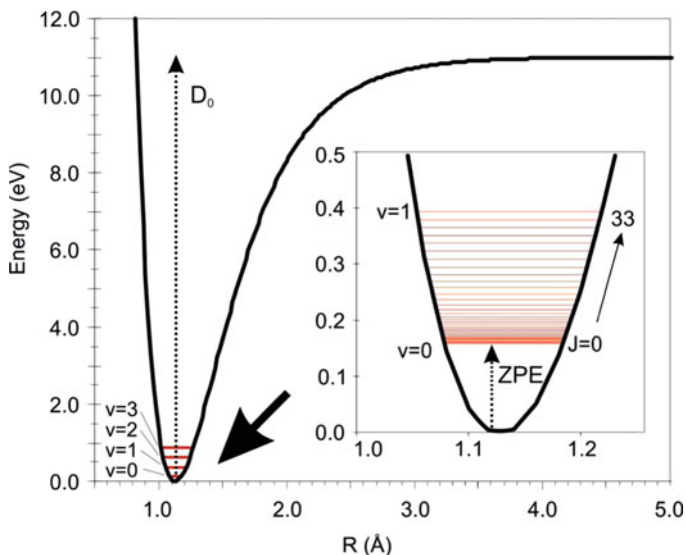
Fig. 1.2 The potential energy curve for the electronic ground state of CO. The *inset* shows (on a very different scale) the spacing of low-lying vibrational and rotational energy levels. v and J are the vibrational and rotational quantum numbers. ZPE shows the 'zero-point energy' between the minimum of the potential energy curve and the lowest quantum state and D_0 is the dissociation energy
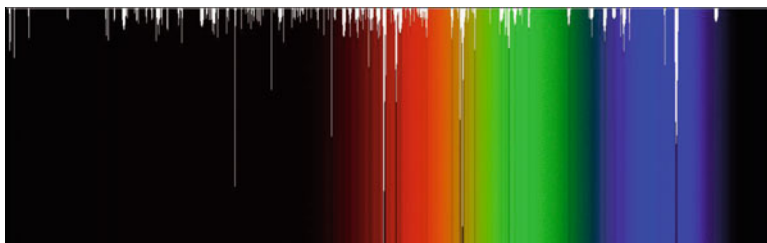

Fig. 1.3 Picture showing the diffuse interstellar bands (Courtesy of NASA/JPL-Caltech)

that the spectrometers are deployed on space platforms. Exceptions to this general rule are the diatomic species CH, CH^+ and CN which absorb at wavelengths above 300 nm and were the first molecules to be identified in the interstellar medium [12] from observations of their absorption lines. Observations of the electronic absorption spectra of H_2 and CO between 91.5 and 111.2 nm are particularly important as they enable the relative abundances of these molecules, the commonest in the interstellar medium, to be established [13]. It is especially important in relation to H_2, since it has no rotational and only very weak vibrational spectra – for reasons that will soon become apparent. Consequently, CO, which is relatively easy to observe, is often employed as a marker for H_2 based on the relatively few but very important observations of the [CO]:[H_2] ratio.

The majority of the 160 or so gas-phase molecules[3] that have been positively identified in the interstellar medium, ranging from diatomics to molecules containing 13 atoms [14], have been observed via their rotational emission spectra; that is, by observation of the characteristic frequencies that are emitted as a molecule undergoes a transition from one rotational energy level to a second level lower in the manifold. The wavelengths associated with such transitions are sufficiently long that (a) they are not significantly scattered by the dust particles that are present in the dense interstellar clouds, where many of the interstellar molecules are found, and (b) the radiation is transmitted through the Earth's atmosphere, which is transparent at most of the wavelengths characteristic of these emissions.

For diatomic and other linear molecules, the energies of rotational levels are given (to a good degree of approximation) in terms of a rotational quantum number (N) and the moment of inertia (I_{AB}) by the expression:

$$E_N = N(N + 1)\hbar^2/2I_{AB}. \tag{1.3}$$

The spacing, or energy difference, between the successive levels ($N + 1$) and N is therefore $2(N + 1)\,\hbar^2/2I_{AB}$. This can be converted to a frequency by dividing by h and to the reciprocal of a wavelength by further dividing by c, the speed of light. The wavelength of the $N = 1$ to $N = 0$ transition in CO is 2.6 mm.

Observation of rotational transitions not only identifies the molecules present in the interstellar medium but can also be used to infer both the abundance of that molecule and the physical conditions – the gas density and the temperature – in the regions from which the observed radiation is emitted. Assigning the observed frequencies to particular molecules involves a comparison with rotational spectra from laboratory experiments: mostly obtained using the technique of Fourier transform microwave spectroscopy [15]. Its application to potential interstellar molecules is far from straightforward, since the species of interest are frequently unstable and must be produced 'on the fly' [16]. Before definitely assigning the molecules responsible for frequencies observed from the interstellar medium, more than one coincidence with laboratory frequencies should be observed for each molecule, and allowance must be made for 'Doppler shifts' arising from motions of the source of radiation, which are particularly large for observations from galaxies other than our own.

Having identified a molecule, the next objective is to estimate its (relative) abundance – generally expressed relative to that of H_2. The first stage in this procedure is to measure the absolute strength of the transitions that are observed. Quantum mechanics demonstrates (a) that molecules without an electric dipole moment (like H_2) do not undergo *pure* rotational transitions, and (b) in molecules that have a dipole moment the transitions are limited by selection rules: for example, in linear molecules, N can only change by one; that is, $\Delta N = \pm 1$.

---

[3] This total does not include the isotopomers of several species that have also been observed.

Quantum mechanics also yields an expression for the Einstein spontaneous emission coefficient (the reciprocal of the mean radiative lifetime) [8]:

$$A_{(N+1)\to N} = \frac{64\pi^4 v^3}{3(4\pi\varepsilon_0)hc^3} \, \mu_{D(N+1),N}^2 \tag{1.4}$$

where v is the frequency of the transition and $\mu_{D(N+1),N}$ is the transition dipole moment, which in the case of rotational transitions corresponds to the permanent electric dipole moment of the molecule. To take one example, the A coefficient for the $N = 1$ to $N = 0$ transition in CO is 2.16×10^{-7} s^{-1}, corresponding to a mean radiative lifetime of *ca.* 54 days. However, it should be noted that, because of the v^3 factor in (1.4), $A_{(N+1)\to N}$ increases rapidly with N.

To explain how the observations on different lines from the same molecule can be used to infer the gas density and temperature at the source, it is necessary to spend a moment explaining how molecules are distributed over their rotational levels in a situation where these populations are in equilibrium and, equivalently, a single temperature (T) describes the distribution. The distribution is then described by the Boltzmann distribution law [1, p. 567], which states that the population (N_i) in a particular level (i) depends on the energy of the level (E_i) and its degeneracy (g_i) – that is, the number of quantum states that possess the energy E_i - according to the expression:

$$N_i \; \alpha \, g_i \exp(-E_i/k_B T) \tag{1.5}$$

where α represents 'is proportional to'. Based on this formula, the fraction (f_i) of an ensemble of molecules that occupy a particular level i is given by:

$$f_i = g_i \exp(-E_i/k_B T)/\Sigma_i g_i \exp(-E_i/k_B T) \tag{1.6}$$

where the denominator defines the partition function, q, associated with the manifold of levels that are being considered.

For the rotational levels of a linear molecule, $g_i = (2N + 1)$ and $E_i = N(N + 1)\hbar^2/2I_{AB}$ so that:

$$f_N = (2N + 1)\exp(-N(N + 1)\hbar^2/2I_{AB} k_B T)/q_{rot} \tag{1.7}$$

If the rotational levels are closely spaced compared with $k_B T$, the summation sign in the denominator of the expression on the right-hand side of (1.6) can be replaced by an integration and q_{rot}, the rotational partition function, is given by

$$q_{rot} = (2I_{AB} k_B T)/\hbar^2 \tag{1.8}$$

Equation (1.7) describes the distribution of an interstellar molecule over its rotational levels under two different equilibrium circumstances. First, at very low densities, as in the background interstellar medium, the distribution will be in

equilibrium with the background radiation field, which corresponds to a temperature of 2.725 K. Second, at high densities, the distribution will be maintained by collisions and the temperature inferred from the rotational distribution corresponds to the translational temperature of the surrounding gas.

In practice, the distribution of a molecule over its rotational levels may not be described by a single temperature. This is because the A coefficient depends strongly on the rotational level, because of the v^3 factor in (1.4), whereas the rate at which collisions re-distribute molecules amongst rotational levels is almost independent of N. As a result, by careful analysis of the rotational distribution inferred from the relative intensities of several lines, and possibly some modelling, both the gas density and the translational temperature can be estimated [17] (for further discussion, see Chap. 2).

As Fig. 1.2 shows, the spacing between successive vibrational levels in a molecule is generally greater than that between (low-lying) rotational levels but much less that that between neighbouring electronic states. The frequencies associated with transitions between neighbouring vibrational levels fall in the infrared part of the electromagnetic spectrum. The application of infrared spectroscopy to the study of interstellar molecules is hampered by absorption in the Earth's atmosphere. The value of infrared spectroscopy has been greatly enhanced in recent years by the deployment of spectrometers mounted on satellites, such as the *Infrared Space Observatory* (ISO), the *Spitzer Space Telescope* and the *Herschel Space Observatory*.

Both infrared absorption and infrared emission spectra have added to our knowledge of the molecules present in the cosmos. In the former case, a suitable star can be used as a background source. Such studies are useful in identifying small gas-phase molecules such as CO_2 and C_2H_2 which have no permanent electric dipole moment, and therefore no pure rotational transitions. The equivalent requirement in respect of vibrational transitions is that the vibrational motion must bring about a change in the electric dipole moment. This is true, for example, for both the asymmetric stretching mode of CO_2 and its bending vibration. However, homonuclear diatomic molecules, like H_2, N_2 and O_2, have no permanent electric dipole moment, nor does their vibrational motion generate one. Therefore they do not undergo rotational transitions, and their 'quadrupole-allowed' vibrational transitions are much weaker than those which cause changes in the electric dipole of a molecule.

So far I have only considered the spectroscopy of gas-phase species that are free to rotate. This is not true of molecules adsorbed onto dust grains. However, such species do exhibit infrared spectra resulting from vibrational transitions, although the infrared absorptions are broader and not always easy to assign [17]. Those that have been assigned with certainty include H_2O, CO and CO_2. The spectra of larger molecules become too weak and non-specific for proper identification.

Infrared emission from many regions of the interstellar medium is dominated by what are often called the unidentified infrared bands (UIBs). As shown in Fig. 1.3, these broad features are observed at several wavelengths between 3 and 15 μm [18]. They are attributed to vibrational transitions associated with the C−H and C−C stretching vibrations (at *ca.* 3.3 and 6–8 μm, respectively) and CH in-plane and CH out-of-plane bending modes (at *ca.* 8.5 and 10–15 μm, respectively) in large
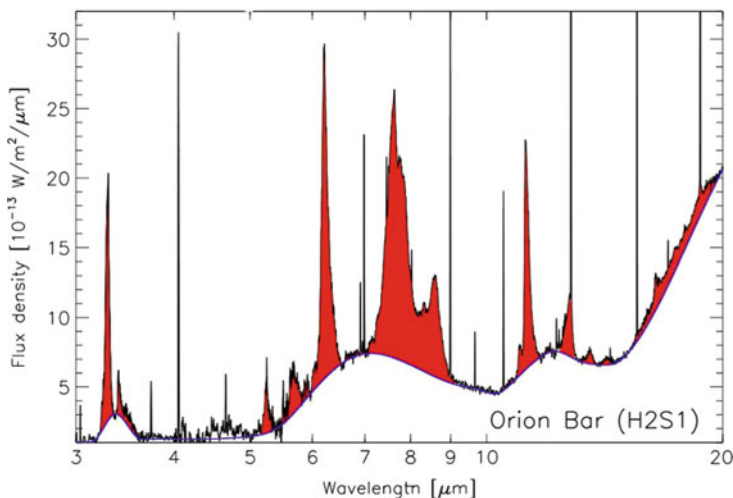
Fig. 1.4 The IR emission spectrum observed from the Orion bar (Adapted from Peeters [18])

aromatic molecules (i.e., polycyclic aromatic hydrocarbons: PAHs). These molecules are probably promoted to electronically excited states by the absorption of ultraviolet light from nearby stars and then undergo a process known as internal conversion by which the electronically excited molecules are converted by a radiationless transition to high vibrational levels of the electronic ground state. These molecules relax by undergoing successive vibrational transitions. The emission spectra are too broad and unstructured to identify which particular PAHs are responsible for the observed emission bands (Fig. 1.4).

1.4 Intermolecular Forces and Hydrogen Bonding [1, Chap. 17; 2, Chap. 13; 19, 20]

In Sect. 1.2, I made some brief remarks about chemical bonding – especially bonding in diatomic molecules. These comments were illustrated in Fig. 1.1 by a representative potential energy curve showing how the electronic energy varies with internuclear separation in the bound state of a diatomic molecule. In addition, I gave values of the dissociation energies for H_2 (432.0 kJ mol^{-1}) and for N_2 (941.7 kJ mol^{-1}), as examples of molecules held together by a single and triple bonds. In general, the strength of chemical bonds is reflected in their dissociation energies (D_0 – as shown in Fig. 1.2), which vary between *ca.* 100 and *ca.* 1,000 kJ mol^{-1}; for example, $D_0 = 148.9$ kJ mol^{-1} for I_2 and 1071.9 kJ mol^{-1} for CO.

As well as these strong forces *within* molecules, there are weaker attractive (and, at shorter internuclear separations, strong repulsive) forces *between* molecules; that

is, intermolecular forces, frequently referred to as van der Waals forces. Again, the interaction between two non-bonding atoms can be represented by a potential energy curve but now the depth of the minimum (usually denoted by ε) is typically two orders-of-magnitude smaller than D_0 for a chemical bond; for example, in the interaction between two argon atoms, the minimum on the potential energy curve lies only 1.2 kJ mol^{-1} below the energy at large separation, and this minimum is found at an internuclear separation of 0.376 nm, much longer than a chemical bond. Despite their relative weakness, intermolecular forces are important in a number of ways. For example, they are the forces that cause gases to depart from ideal gas behaviour and they are responsible for condensation. The fact that the boiling points of the noble gases increase in the order helium to xenon is a reflection of the parallel increase in ε from 88 J mol^{-1} for He $-$ He to 2.34 kJ mol^{-1} for Xe $-$ Xe [21].

Gas phase reactions that are important at the very low temperatures (*ca.* 10 K) found in the cold cores of dense interstellar clouds must have no barrier along the path of minimum potential energy leading from reactants to products or, in other words, no activation energy. The rates of such reactions are controlled by the ability of the long-range intermolecular forces to bring the reactants into a close collision: a process generally referred to as 'capture'. For systems where the long-range potential only depends on the separation of the two reactants, it is relatively easy to estimate the rate coefficients for close collisions. One first needs to define an *effective* potential energy which takes into account that angular momentum must be preserved in the collision and the energy associated with orbital motion increases as the separation (R_{AB}) between the two colliding species (A and B) decreases:

$$V_{eff}(R_{AB}) = \left[E_{trans} b^2 / R_{AB}{}^2 \right] - C / R_{AB}{}^{-n} \tag{1.9}$$

In this equation, the intermolecular attraction is assumed to be proportional to $R_{AB}{}^{-n}$ and the first term on the right of the equation represents the energy associated with the orbital motion for collisions, where E_{trans} is the energy associated with relative motion of the colliding pair and b is the impact parameter, which is the closest distance the centres of the two particles would approach in the absence of intermolecular forces. One can obtain [21] an expression for the cross-section for close collisions by: (1) finding the value of R_{AB} ($R_{AB,max}$) at which $V_{eff}(R_{AB})$ has its maximum value (by differentiating the right-hand-side of (1.9) and setting the result to zero); (2) finding the corresponding value of $V_{eff}(R_{AB})$, that is, $V_{eff}(R_{AB, max})$, and (3) using these results to find the maximum value of b at which collisions with relative energy E_{trans} can 'surmount' the 'centrifugal barrier', $V_{eff}(R_{AB, max})$. Finally, one can obtain a rate coefficient for close collisions by multiplying the expression for the cross-section by the Maxwell-Boltzmann expression for the distribution of relative velocities and integrating the result.

We can distinguish two simple but important cases where the long-range attraction between two molecules (or atoms) varies as $R_{AB}{}^{-n}$: (1) for an ion interacting with a polarisable molecule, $n = 4$, and (2) for two neutral molecules, dispersion forces give rise to an attraction with $n = 6$. These attractive forces increase the rate coefficient for close collisions above the value estimated for 'hard-spheres' by

factors of *ca*. 5 for ion-molecule collisions (independent of temperature), and *ca*. 2 for neutral-neutral collisions at 298 K [21].

In the case where $n = 4$, the simple treatment outlined above, and generally referred to as the Langevin model, yields an expression for the rate coefficient that is independent of temperature and which can be calculated knowing the polarisability of the molecule (and the reduced mass associated with the collision). Because the charge-induced dipole attraction is strong, the model can be applied to many ion-molecule reactions with reasonable success. For the interaction between an ion and a polar molecule, the long-range energy depends also on a second term which depends on orientation: that is, the angle between the axis of the dipole and the line joining the centres of the two species. The effect of the charge-dipole interaction is to increase the rate of 'capture', especially at low temperatures [12]. The adaptation of these models to reactive collisions between ions and neutral molecules will be dealt with in more detail in Chap. 3.

When the two collision partners are electrically neutral, the long-range mutual attraction is much weaker. In addition to dispersion forces, responsible for the $-R_{AB}^{-6}$ term in the expression for the long-range potential, it is generally necessary to include a number of other contributions arising from the asymmetric distribution of electrical charge in the two species, to the long-range potential [19]. These include: dipole-dipole, dipole-quadrupole, dipole-induced dipole interactions. The strength of these attractions depends not only on the separation between the molecules but also on their orientation with respect to one another. A version of transition state theory [21, 22] suitable for estimating the rate coefficients for neutral-neutral 'barrierless' reactions has been described [23]. This method calculates contributions to the reactivity for collisions with specified collision energy and total angular momentum and averaging over the various possible orientations is included to allow for the angular dependence of the long-range intermolecular potential. It has been applied, with fair success, to reactions between pairs of free radicals, for which it is difficult to determine rate coefficients experimentally, especially at low temperatures.

Amongst the strongest intermolecular attractive forces are those between ions and polar molecules. They play an important role in the solution of salts in water [2, Sect. 5.7]; for example:

$$NaCl(s) + water \rightarrow Na^+(aq) + Cl^-(aq). \tag{1.10}$$
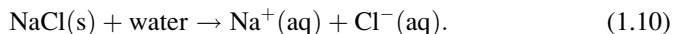
The enthalpy change associated with this process can be estimated by constructing a thermochemical cycle and well-known values of the enthalpies associated with processes such as: (1) the formation of dissolved NaCl from Na(s) and $\frac{1}{2}Cl_2(g)$, (2) the sublimation of Na(s), (3) the ionisation of Na(g), (4) the dissociation of $\frac{1}{2}Cl_2(g)$, (5) the capture of an electron by Cl(g). The conclusion is that the enthalpy of hydration; that is, the enthalpy associated with

$$Na^+(g) + Cl^-(g) \rightarrow Na^+(aq) + Cl^-(aq) \tag{1.11}$$
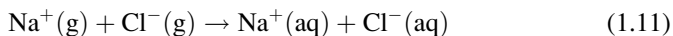
is $-783.4 \, \text{kJ} \, \text{mol}^{-1}$. This is a measure of the strong ion-dipole interactions between one mole of the two ions with the water molecules that form hydration spheres around them. The large, negative, value of the enthalpy of hydration plays the predominant part in determining the high solubility of salts in water. Strictly, of course, it is also necessary to consider the entropy of hydration, since it is the Gibbs energy change that occurs on dissolving a salt which determines the equilibrium constant for (1.10) (see (1.20), below) and hence the solubility of the salt. In general, the entropy of hydration of gaseous ions is negative, reflecting the ordering of the water molecules around the dissolved ions when hydration occurs.

At the other extreme from the dissolution of salts in water, we can consider the creation of ideal solutions or mixtures. In these cases, the enthalpy of mixing is zero (or, in reality, close to zero) and it is the increase in entropy which thermodynamically drives the mixing process. The paradigm for ideal solutions is a mixture of two closely related compounds, say benzene and toluene. The intermolecular forces between benzene-benzene, toluene-toluene, and benzene-toluene pairs are very similar, so that there is no net change in the strength of the interactions as these two liquids are mixed and hence the enthalpy of mixing is very small. One result of this is that the partial vapour pressures of the two components are proportional to their mole fraction in the mixture (Raoult's Law) and it can be shown that the change in Gibbs energy results entirely from the positive change in entropy that occurs on mixing.

An important and interesting class of solutes are those classed as *amphiphilic*, meaning they contain both *hydrophobic* groups (often referred to as their tails) and *hydrophilic* groups (their heads). The hydrophobic tail is often a large alkyl group, whereas the hydrophilic head might be ionised or strongly polar. The balance between the water-hating and water-loving properties of parts of these molecules will depend, *inter alia*, on the length of the hydrocarbon tail, and the strength of the interaction between the head and the solvent water molecules. Amongst these molecules are soaps and surfactants which accumulate at an interface between, for example, oil and water phases. Where there is only the water solvent available, at a sufficient concentration (the critical micelle concentration) and temperature (the Krafft temperature), soap molecules can aggregate to form micelles, which are clusters of molecules containing *ca*. 100–1,000 molecules, in which the hydrophobic tails are in the centre of the micelles and the hydrophilic heads are on the periphery. With still longer hydrophilic tails, surfactant molecules, such as the carboxylic acid, $CH_3(CH_2)_{16}COOH$ (stearic acid), congregate at the surface of water with their hydrophilic heads within the water and the tails sticking out of the water. Such films lower the surface tension of the solute and demonstrate behaviour, in two dimensions, that is analogous to that of real gases in three dimensions.

In addition to forming micelles, amphiphiles can also form double layers or membranes, in which the hydrophobic tails in each component of the layer point towards one another and intermingle whilst the hydrophilic heads point outwards into the water or aqueous solution on either side of the membrane. In lipid bilayers, which are important in biology (see Chap. 9), the constituent molecule can be a

phospholipid, such as phosphatidic acid, which has a negatively charged phosphate head and two long hydrocarbon tails.

Earlier in this section, I contrasted the interaction energies for a chemical bond with the much smaller energies associated with the intermolecular forces arising from dispersion forces and the non-symmetric charge distributions in a pair of interacting molecules. Of intermediate strength is the hydrogen bond. A hydrogen bond arises between a proton donor, say $X-H$, and a proton acceptor, Y, where X and Y are electronegative atoms such as F or O. Generally, as in the water dimer, there is a strong directional attraction of the $X - H$ bond to an electron-rich region on Y. The strength of such bonds varies widely but 30 kJ mol^{-1} is a sensible upper limit to normal hydrogen bonds. Hydrogen bonds can form between molecules when $X - H$ and Y are in different molecules and an intermolecular hydrogen bond forms, or within a single molecule; that is, intramolecular hydrogen bonds can form. Because the strengths of hydrogen bonds are comparable with thermal energies at room temperature (where $RT \approx 2.5$ kJ mol^{-1}), the bonds can make and break relatively easily under ambient conditions. As a result they are of prime importance in biology, not least in binding single strands of DNA into the double helix.

One simple piece of evidence for hydrogen bonding comes from a comparison of the boiling points of a range of hydride compounds. The boiling points of the hydrides of the group 14 (see Table 1.1) elements (i.e., CH_4, SiH_4, GeH_4 and SnH_4), in which hydrogen bonding is not possible, rise monotonically as one should expect – reflecting the increase in molar mass and polarisability. However, for the hydrides of groups 15, 16 and 17, the boiling points for the lightest compounds are anomalously high – a result that is attributed to the existence of intermolecular hydrogen bonding.

Much has been learnt about hydrogen bonding from the application of rotational and vibrational spectroscopy [24, 25] to small, hydrogen-bonded, clusters formed in the super-cold environment of molecular jets. In the case of water, accurate structural information has been obtained on the clusters $(H_2O)_n$ from the dimer ($n = 2$) to the hexamer ($n = 6$) and theoretical calculations have been performed [20] that agree well with the experimental observations [26]. However, it is not easy to transfer what has been learnt from these studies to the structure of liquid water where hydrogen bonding is doubtless responsible for its unusual, indeed unique, properties. Water is so important, as a solvent and as a participant in biology, that it is the subject of Chap. 6. Here, I note that the temperature range in which it is liquid, (273.15–373.15 K under a pressure of 1 bar), and therefore available as solvent to accommodate and promote chemical and biological processes, is rather narrow. This has led, in astrobiology, to the concept of a habitable zone or Goldilocks zone: that being the range of distances from a star where an Earth-like planet can maintain liquid water on its surface, that being a prerequisite for life – or, at least, life as we know it.

1.5 Chemical Reactions: Thermodynamics and Kinetics [1, Chaps. 2, 3, 21, and 22; 2, Chaps. 3, 4, 6, and 9; 22]

Chemical models of the interstellar medium (see Chap. 4) contain *ca.* 4,500 gas-phase reactions. The vast majority of these are bimolecular reactions; that is, they occur as the result of binary collisions between, for example, an ion and a neutral species, two neutral species, and ions or molecules with electrons. The rate of such elementary processes, expressed in terms of the change in concentration with time (t) of the reactant or product species, is proportional to the product of the concentrations of the two reactants. If the reactants are represented by **A** and **B** and the products by **C** and **D**, the reaction is:

$$\mathbf{A} + \mathbf{B} = \mathbf{C} + \mathbf{D} \tag{1.12}$$

and, for the rate of the reaction, we can write:

$$-d\,[\mathbf{A}]/dt = -d[\mathbf{B}]/dt = +d[\mathbf{C}]/dt = +d[\mathbf{D}]/dt = k_f(T)[\mathbf{A}][\mathbf{B}] \tag{1.13}$$

Here, the square brackets denote concentrations in units of molecule cm^{-3}, or simply cm^{-3}, so that $k_f(T)$, the rate constant or rate coefficient for the 'forward' reaction between **A** and **B**,[4] has units of cm^3 molecule^{-1} s^{-1}, or cm^3 s^{-1}, and (T) is included to emphasise that rate coefficients generally depend on temperature.

Chemical reactions proceed towards *equilibrium*, when there is no further net chemical change. At this point, 'reactants' and 'products' will still be present and, at a microscopic level, reactants will continue to form products and products to form reactants, but the rates of these processes have become equal. For the reaction represented by (1.12), this equality can be represented by the equation:

$$k_f(T)[\mathbf{A}]_e[\mathbf{B}]_e = k_r(T)[\mathbf{C}]_e[\mathbf{D}]_e \tag{1.14}$$

Here, $k_f(T)[\mathbf{A}]_e[\mathbf{B}]_e$ and $k_r(T)[\mathbf{C}]_e[\mathbf{D}]_e$ are the equal rates of the forward and reverse reaction. The symbols $[\mathbf{A}]_e$, $[\mathbf{B}]_e$, $[\mathbf{C}]_e$ and $[\mathbf{D}]_e$ are the concentrations of the species at equilibrium. The equilibrium constant can be expressed, in terms of the concentrations at equilibrium, as:

$$K_c(T) = \frac{[\mathbf{C}]_e[\mathbf{D}]_\mathbf{e}}{[\mathbf{A}]_e[\mathbf{B}]_e} \tag{1.15}$$

Combining (1.14) and (1.15) shows that $K_c(T)$ is the ratio of the rate coefficients for the forward and reverse reactions:

---

[4] By convention, the 'forward' reaction is that proceeding from left to right in the chemical equation, and the 'reverse' reaction is that proceeding from right to left.

$$K_c(T) = k_f(T)/k_r(T) \tag{1.16}$$

The application of thermodynamics to chemical reactions enables equilibrium constants to be calculated from a knowledge of the macroscopic thermal, or microscopic molecular, properties of the reactants (**A** and **B**) and the products (**C** and **D**). Using statistical thermodynamics [20], the equilibrium constant for a reaction involving gas-phase species, can be expressed, in terms of the per unit volume partition functions, (q_i/V), for the reactants and products, by

$$K_c(T) = \frac{(q_C/V)(q_D/V)}{(q_A/V)(q_B/V)} \exp(-\Delta E_0/k_B T) \tag{1.17}$$

ΔE_0 is the difference between the energies of the zero-point energy levels[5] in the products and in the reactants. If the sum of the zero-point energies for **C** and **D** is lower than the sum of the zero-point energies for **A** and **B**, ΔE_0 is negative (the reaction is exoergic) and $K_c(T)$ is greater than one: frequently very much greater than one since $-\Delta E_0$ is often $\gg k_B T$. This is true for many reactions that occur in the very low temperature ($T \approx 10$ K) cold cores of dense interstellar clouds. As a result, in modelling the chemistry in these environments, it is generally only necessary to include reactions proceeding in an exoergic direction. Interesting exceptions to this rule are those reactions where isotope exchange is involved [21]; for example:

$$H_3^+ + HD = H_2D^+ + H_2 \tag{1.18}$$

In such cases, the values of $-\Delta E_0$ and K_c are determined by the difference between the sums of the zero-point energies for the products and reactants. For reaction (1.18), $(-\Delta E_0/k_B)$ is equal to *ca.* 187 K. Although this is small relative to the same quantity for most chemical reactions, it is nevertheless much larger than the temperature in the cold regions of dense interstellar clouds where many molecules are found. Consequently, the observed fractions of many deuterated molecules are far larger than would be expected simply on the basis of the cosmic abundance of deuterium relative to hydrogen.

In classical thermodynamics, as distinct from statistical thermodynamics, the equilibrium constant for a reaction involving only gas-phase species is expressed in terms of the 'reduced' partial pressures of the reactants and products at equilibrium; that is, the partial pressures divided by the standard pressure (p^o), which is 1 bar. In these terms, the equilibrium constant can be expressed as;

---

[5] Associated with each vibration in a molecule, there is 'zero-point energy' corresponding approximately to $\frac{1}{2}hv$ where v is the frequency of the vibration. Consequently, as shown in Fig. 1.2, the lowest vibrational energy level with the quantum number $v = 0$, has an energy $\frac{1}{2}hv$ above the minimum of the potential energy curve.

$$K(T) = \frac{(p_{e,C}/p^o)(p_{e,D}/p^o)}{(p_{e,A}/p^o)(p_{e,B}/p^o)} \tag{1.19}$$

It should be noted that $K(T)$ will always be dimensionless, even when there are unequal numbers of products and reactants in the balanced chemical equation. For the elementary reaction, of the type represented by (1.12), $K_c(T)$ will not only be dimensionless but will also have the same numerical value as $K(T)$.

Classical thermodynamics relates the equilibrium constant, $K(T)$, to the standard Gibbs energy for the reaction, $\Delta_r G^o$, by the equation:

$$RT \ln K(T) = -\Delta_r G^o \tag{1.20}$$

When $\Delta_r G^o$ is negative the reaction is said to be exoergic and $K(T)$ is greater than 1, frequently much greater than 1, and when $\Delta_r G^o$ is positive the reaction is said to be endoergic and $K(T)$ is less than 1. Using the Gibbs-Helmholtz equation that relates Gibbs energy to enthalpy and entropy, we can write:

$$ln\, K(T) = -\Delta_r H^o / RT + \Delta_r S^o / R \tag{1.21}$$

In these equations, the sign Δ_r denotes the difference between the sum of the specified thermodynamic quantity for the products and that for the reactants, the superscript ^{o} denoting that the species are in their thermodynamic standard state, for gases 1 bar. These quantities can be derived from 'thermal measurements': that is, measurements of heats evolved for particular reactions, molar specific heats and latent heats. Such quantities can be determined (and then tabulated) for relatively stable species. When $-\Delta_r H^o \gg RT$, the value of the first term on the right-hand-side of (1.21) is likely to dominate the second term, and $K(T)$ for such strongly exothermic reactions can be huge, meaning that $k_f(T) \gg k_r(T)$.

Although thermodynamics has its uses in respect of astrochemistry, it is clear that the abundances of interstellar molecules are not determined by thermodynamics but rather by kinetics [27]. The relatively large observed abundances of free radicals and unsaturated hydrocarbon molecules clearly support this statement. It is useful to start a discussion of kinetics by recalling (1.16), writing it in logarithmic form, and then differentiating that equation with respect to $(1/RT)$:

$$ln\, K_c(T) = ln\, k_f(T) - ln\, k_r(T) \tag{1.22}$$

$$d\, ln\, K_c(T)/d(1/RT) = d\, ln\, k_f(T)/d(1/RT) - dln\, k_r(T)/d(1/RT) \tag{1.23}$$

The Van't Hoff equation expresses how $K_c(T)$ depends on temperature; that is:

$$d \ln K_c(T)/d(1/RT) = \Delta_r U^o / RT^2 \tag{1.24}$$

Van't Hoff then argued that the individual rate coefficients, $k_f(T)$ and $k_r(T)$, are influenced by temperature by two different energies, E_f and E_r, whose difference is $\Delta_r U^{\mathrm{o}}$, so that (1.20) becomes [28]:

$$\Delta_r U^{\mathrm{o}}/RT^2 = E_f/RT^2 - E_f/RT^2 \tag{1.25}$$

Van't Hoff recognized that generally $\Delta_r U^{\mathrm{o}}$ depends on temperature and therefore the energies E_f and E_r may also be temperature-independent: if they are not, then E_f and E_r correspond to the activation energies (E_{act}) for the forward and reverse reactions and the rate coefficients vary with temperature according to what is usually designated as the Arrhenius equation:

$$k(T) = A \exp(-E_{\mathrm{act}}/RT) \tag{1.26}$$

Extending van't Hoff's argument, one can combine (1.20) and (1.22) to derive an equation which relates the rate coefficients to changes in *Gibbs energy*:

$$\ln k_f(T) - \ln k_r(T) = -\Delta_r G_c{}^{\mathrm{o}}/RT = -\Delta_f G_{act,c}{}^{\mathrm{o}}/RT + \Delta_r G_{act,c}{}^{\mathrm{o}}/RT \tag{1.27}$$

indicating that the rate coefficients for the forward and reverse reactions depend on the Gibbs energies of activation – therefore involving entropic, as well as enthalpic, factors. This argument leads to the definition of the transition state for a reaction being the point along the pathway leading from reactants to products where the free energy has its maximum value. The relationship between $-\Delta_r G_c{}^{\mathrm{o}}$, $\Delta_f G_{act,c}{}^{\mathrm{o}}$, and $\Delta_r G_{act,c}{}^{\mathrm{o}}$ is illustrated in Fig. 1.5.

It was apparently a student of Van't Hoff, D. M. Kooij, who first allowed for the temperature-dependence of $\Delta_r U^{\mathrm{o}}$, E_f and E_r by proposing a modified form of (1.26):

$$k(T) = A'T^m \exp(-E'_{\mathrm{act}}/RT) \tag{1.28}$$

This equation and slight variants of it are frequently referred to as the modified Arrhenius equation and sometimes as the Kooij equation, and are often used to express the temperature dependence of the rate coefficients in kinetic databases compiled for use in modelling atmospheric, combustion and astrochemical environments. For example, in KIDA (a Kinetic Database for Astrochemistry [29]), rate coefficients and their temperature dependences are expressed by the equation:

$$k(T) = \alpha(T/300)^{\beta} \exp(-\gamma/T) \tag{1.29}$$

For many reactions between free radicals and neutral *saturated* molecules, $k(T)$ increases with temperature and β and γ in (1.29) both have positive values. The reactions between CN and H_2 and C_2H and H_2, that is

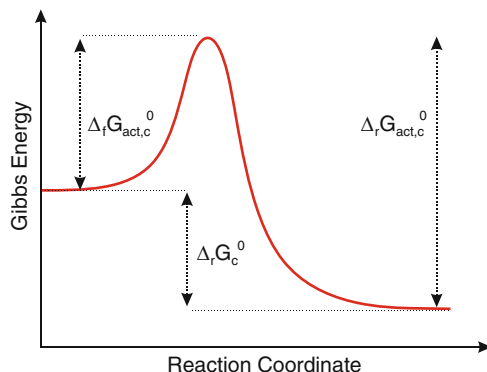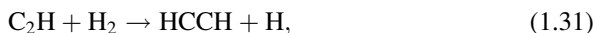$$CN + H_2 \rightarrow HCN + H \tag{1.30}$$

Fig. 1.5 Variation of Gibbs energy along the path for reaction, showing the relationship between the standard Gibbs energy for a reaction and the Gibbs energies of activation for the forward and reverse reactions

$$C_2H + H_2 \rightarrow HCCH + H, \tag{1.31}$$

provide examples [30]. For reaction (1.30), $\beta = 2.60$ and $\gamma = 960$ K, and for (1.31) $\beta = 2.32$ and $\gamma = 444$ K. The rate coefficients for these reactions are very small at low temperatures and they cannot play a role in the colder environments in the interstellar medium.

On the other hand, the rate coefficients for a number of reactions between strongly electronegative radicals (like CN) and unsaturated molecules increase as the temperature is lowered below 300 K [31]. For these reactions and those between two free radicals, it seems that there is no energy barrier preventing facile formation of a reactive intermediate which then decomposes to the final products. The values of the rate coefficients for such 'barrier-less' reactions are sometimes determined by 'capture'; that is, the bringing together of the reactants under the influence of long-range forces [see above, Sect. 1.4]. As discussed in Chap. 3, this is the mechanism for most reactions between ions and neutral molecules.

Up to this point, I have emphasised the application of thermodynamics to systems in the gas-phase. In solution, particularly in aqueous solutions where so much of biology occurs, the description of thermodynamic behaviour has to undergo some changes [1, Chap. 5; 2, Chaps. 5, 6 and 7]. In particular, it is impossible to apply statistical thermodynamics, an alternative definition of 'standard state' must be employed, and because the values of $\Delta_f H^o$ and S^o (and hence $\Delta_f G^o$) cannot be determined using the thermal properties of the species, they are *relative*, rather

than *absolute*. In practice, the standard state is usually defined as that at unit activity, where activities can be thought of as concentrations corrected for non-ideal behaviour; that is departures from Henry's Law and Raoult's Law. The values of $\Delta_f H^o$, S^o and $\Delta_f G^o$ are evaluated relative to the same quantities for aqueous H^+ ions at unit activity; to put it another way, these three quantities are set equal to zero for aqueous H^+ ions, and the values for any other aqueous ion are found from measurements on reactions in which that ion and $H^+(aq)$ play a role.

These measurements are frequently made using electrochemical methods. The relationship between the Gibbs energy for the reaction ($\Delta_r G$) in an electrochemical cell and the potential (E) of the cell measured when no current is being withdrawn is

$$-v F E = \Delta_r G \qquad (1.32)$$

The quantity F is the Faraday constant and has the value 96,485 C mol^{-1}. The cell reaction can be written as the difference between the reactions at the right-hand and left-hand electrodes. Thus for the well-known Daniell cell, Cu^{2+} ions are reduced at the right-hand electrode (the cathode):

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad (1.33)$$
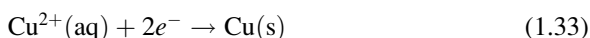
and, at the left-hand electrode (the anode), Zn^{2+} ions are oxidised:

$$Zn^{2+}(aq) + 2e^- \leftarrow Zn(s) \qquad (1.34)$$
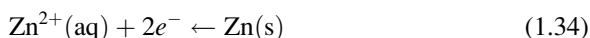
so that the overall cell reaction is:

$$Cu^{2+}(aq) + Zn \rightarrow Cu(s) + Zn^{2+}(aq). \qquad (1.35)$$
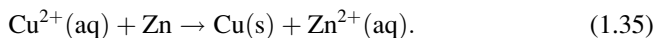
The integer v in (1.29) refers to the number of electrons included in the equations representing the reduction and oxidation processes; that is, 2 in (1.33) and (1.34). E is, of course, independent of the choice of v but $\Delta_r G$, an *extensive* quantity, does depend on it.

If E is evaluated with all the constituents in their standard states, then (1.32) yields $\Delta_r G^o$, the standard Gibbs energy for the cell reaction, so that combining (1.20) and (1.32):

$$RT \ln K = v F E^o \qquad (1.36)$$

When the left-hand electrode in an electrochemical cell is a hydrogen electrode, where the reaction is

$$H^+(aq) + e^- \rightarrow \tfrac{1}{2}H_2(g) \qquad (1.37)$$

The value of E measured under, or interpolated to, standard conditions, that is E^o, corresponds to the standard electrode potential for the right-hand electrode. (1.36) can be used to find the standard Gibbs energy change for the reaction occurring at this electrode, and measurements of how E varies with temperature yield values of $\Delta_r H^o$ and $\Delta_r S^o$. The value of E^o for any other cell can be calculated from the difference of the standard electrode potentials for the two electrodes.

The substances taking part in the 'half-reaction' at an electrode are frequently referred to as a redox couple and can generally be written as:

$$\text{Ox} + ve^- \rightarrow \text{Red} \tag{1.38}$$

In compilations of standard electrode potentials, it is usual to write the half-reactions in this way; that is with electrons on the left-hand side. For the processes represented by (1.33) and (1.34), the standard electrode potentials at 298 K are 0.34 V and -0.78 V, so that E^o for the cell is 1.10 V and $\Delta_r G^o$ for the overall reaction written in (1.35) is -101.1 kJ mol^{-1}.

The conventional standard state for aqueous hydrogen ion (unit activity, pH $= 0$) corresponds to very strongly acidic conditions and is inappropriate to normal biological conditions. Therefore, in biochemistry it is common to adopt pH $= 7$, that is a hydrogen ion activity of 10^{-7}, as the standard state. This difference between the definitions of the standard state is only important when a reaction involves $H^+(aq)$ ions, as in:

$$A + vH^+(aq) \rightarrow P \tag{1.39}$$

Of course, such reactions are important in biochemical systems. The difference in the standard free energy of reaction using the biological standard state of $a = 10^{-7}$ and the usual chemical one of $a = 1$ is $v\,RT \ln 10^{-7}$, which amounts to -39.93 kJ mol^{-1} for $v = 1$ and $T = 298$ K. This type of reaction is more spontaneous (has a higher negative value of the standard Gibbs energy) at pH 0 than at pH 7. An example of such a reaction is the interconversion of the reduced and oxidised forms of nicotinamide adenine dinucleotide (NADH and NAD$^+$), which is a co-enzyme (see Sect. 1.6) found in all living cells [2, Chap. 6],

$$\text{NADH} + H^+ \rightarrow \text{NAD}^+ + H_2 \tag{1.40}$$
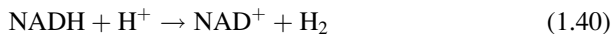
For the oxidation of NADH to NAD$^+$, the change in standard Gibbs energy using pH $= 0$ as the standard state is -21.8 kJ mol^{-1} but is $+ 18.1$ kJ mol^{-1} for pH 7.

In biochemistry, a main function of NAD$^+$ is its involvement in electron transfer reactions. Thus, the conversion of NADH to NAD$^+$ releases two electrons that can then be used to reduce O_2 to water:

$$\text{NAD}^+ + H^+ + 2e^- \rightarrow \text{NADH} \tag{1.41}$$