Astrochemistry

from Astronomy to Astrobiology

Andrew M. Shaw
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Jossey-Bass, 989 Market Street, San Francisco, CA 94103-1741, USA

Wiley-VCH Verlag GmbH, Boschstr. 12, D-69469 Weinheim, Germany

John Wiley & Sons Australia Ltd, 42 McDougall Street, Milton, Queensland 4064, Australia

John Wiley & Sons (Asia) Pte Ltd, 2 Clementi Loop #02-01, Jin Xing Distripark, Singapore 129809

John Wiley & Sons Canada Ltd, 6045 Freemont Blvd, Mississauga, ONT, L5R 4J3, Canada

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Library of Congress Cataloging-in-Publication Data:

Shaw, Andrew M.
Astrochemistry : from astronomy to astrobiology / Andrew M. Shaw.
p. cm.
Includes bibliographical references and index.
ISBN-13: 978-0-470-09136-4 (HB) 978-0-470-09137-1 (PB)
ISBN-10: 0-470-09136-3 (HB) 0-470-09137-1 (PB)
1. Cosmochemistry – Textbooks. I. Title.
QB450.S53 2006
523′.02 – dc22
2006001883

British Library Cataloguing in Publication Data

A catalogue record for this book is available from the British Library

ISBN-13: 978-0-470-09136-3 (HB) 978-0-470-09137-1 (PB)
ISBN-10: 0-470-09136-3 (HB) 0-470-09137-1 (PB)

Typeset in 10.5/12.5pt Times by Laserwords Private Limited, Chennai, India
Printed and bound in Great Britain by Antony Rowe Ltd, Chippenham, Wiltshire
This book is printed on acid-free paper responsibly manufactured from sustainable forestry
in which at least two trees are planted for each one used for paper production.

Contents

Preface

Astrochemistry draws its inspiration, language, fascination, beauty, elegance and confusion from many different disciplines: starting with astronomy, passing through physical chemistry and ending with the new ideas of astrobiology. It is this breadth of fascination that I have attempted to capture in *Astrochemistry: from Astronomy to Astrobiology.* Choosing such a broad subject comes with the serious problem of how to limit the discussion of the details to allow an appreciation of the whole. I could have written an entire book on molecular astrophysics, looking at what molecules are doing in the various environments of space. I could have looked simply at the wonders of planetary chemistry, concentrating on the solar system or even just one planet such as Jupiter. Why does it have a giant red spot? Instead, I have chosen to apply a more general boundary condition for the book taking in all of the subjects but focused on the theme of "The Origin of Life".

Astrochemistry starts with the origins of the Universe and the theory of the Big Bang, resulting in the formation of hydrogen, helium and a little lithium. Gravity pulls the matter together to form stars, galaxies and clusters of galaxies, all of which give off light in some form. The light tells the molecular story with information on the formation and evolution of stars and the role of atoms. At times these interesting subjects are buried in the disciplines of astronomy and astrophysics and I have tried to bring the pieces of the story together, concentrating on astrochemistry. The cycle of star formation ends with a supernova blowing huge quantities of material into the interstellar medium, now laden with all of the elements of the Periodic Table. Chemistry in the interstellar medium, with rather cold and tenuous conditions, is now possible and this controls the starting molecular inventory. To understand this fully, the subjects of quantum mechanics and kinetics need to be applied, through spectroscopy and chemical reaction networks, to the giant molecular clouds of the interstellar medium – the birthplace of stars and life?

Giant molecular clouds collapse to form stars and solar systems, with planets and debris left over such as comets and meteorites. Are comets and meteorites the delivery vehicles that enable life to start on many planets and move between the planets as the solar system forms, providing water and molecules to seed life? The planets have to be hospitable, however, and that seems to mean wet and warm. Carbon-based life forms and liquid water seem to be the successful life-experiment on Earth from which we can draw some more general conclusions about the requirements for life in a view towards astrobiology. A look at prebiotic chemistry and primitive life forms on Earth poses interesting questions such as what is a cell and how big does it have to be? The guiding principles for prebiotic chemistry are the laws of thermodynamics that keep the origins of life and its understanding on the straight and narrow.

Finally, and tantalizingly for this book and astrochemistry, there is Titan. The Cassini–Huygens mission is now in orbit in the Saturnian system as the book is published. The Huygens probe has already made the descent to the surface of Titan and the data have been transmitted back successfully. Scientists, astronomers, astrochemists and astribiologists are trying to understand it. I have taken a brief look at Titan as a case study to apply all that has been learnt and to review the possibilities for astrochemistry in what is surely to be a very exciting revelation of the structure and chemistry of Titan.

Throughout the book I have tried to constrain the wonders of imagination inspired by the subject by using simple calculations. Can all of the water on the Earth have been delivered by comets: if so, how many comets? How do I use molecular spectroscopy to work out what is happening in a giant molecular cloud? Calculations form part of the big hard-sell for astrochemistry and they provide a powerful control against myth. I have aimed the book at second-year undergraduates who have had some exposure to quantum mechanics, kinetics, thermodynamics and mathematics but the book could easily be adapted as an introduction to all of these areas for a minor course in chemistry to stand alone.

Units and conventions

Astronomy is probably the oldest of the subjects that influence astrochemistry and contains many ancient classifications and unit systems that have been preserved in the scientific research of today. Distances are measured in light-years or parsecs, neither of which are the standard SI unit of length: the metre. This is not surprising when a light-year is 9.5×10^{15} m and is a relatively small astronomical unit of length! The correct SI convention for a light-year would be 9.5 petametres, written as 9.5 Pm. This is formally correct but would not help you in a conversation with anybody, as most scientists cannot remember the SI prefixes above 10^{12}. I have listed the SI prefixes in Appendix A and we shall use them where appropriate. However, I will use two units of length chosen from astronomy, namely the light-year and the astronomical unit. The light-year is the distance travelled by light in 1 year or 86 400 s and 1 ly is 9.5 Pm or 9.5×10^{15} m. Usefully, the distance to the nearest star is some 4 ly. The other length unit is the astronomical unit (AU), which is the average distance from the Earth to the Sun and is 1.49×10^{11} m, with the entire solar system being approximately 150 000 AU and the distance to the nearest star some 300 000 AU.

The unit of time is the second in the fundamental list of constants but it is convenient to use years when referring to the age of the Universe, Solar System or the Earth. I have chosen to use the SI prefixes in front of the symbol yr so that 10^9 years is 1 Gyr; the age of the Universe is 15 billion years or 15 Gyr, etc., and whenever this refers to a period of time in the past then 4.5 Gyr ago will be used explicitly.

The conventions of chemistry, particularly physical chemistry, are standard and appear in all physical chemistry textbooks and will be used here. The same courtesy has been extended to organic and inorganic chemistry and biology, so that the ideas of these subjects can be linked into the common theme.

Course material

I have put together a website for the book (www.wiley.co.uk/shawastrochemistry) where I have included the figures from the book to be downloaded into lectures. I have also included some links that I have found useful, corrections when required even some possible examiation questions. I hope an adventurous professor will find these useful.

Acknowledgements

The book started as a survey of the literature to identify a research project, which in part it did, but during the work I discovered how interesting the subject can be and decided that it would make a good lecture course. The long-suffering students at the Department of Chemistry at Exeter University have enjoyed the course on two separate occasions and in two incarnations, most latterly as CHE2057 in 2005. The students saw the book at first draft and have contributed to removing the mistakes and suggested additions, pointing out where I said too much or too little. The refinements have helped and improved the text immeasurably. I have doubtlessly introduced more mistakes and for this I must take the full credit. The integrity of the book has been improved greatly by two very conscientious reviewers, to whom I owe a debt of gratitude. I must extend thanks to all scientists around the world who helped to put together the figures for the book. Busy people spent valuable time collecting the images that have added to the wonder of the subject. The reward for writing the book will be the spark of curiosity that may flicker in the mind of the reader.

Andrew M. Shaw

1 The molecular universe

Introduction

Chemistry without numbers is poetry: astrochemistry without numbers is myth. A molecule placed around a star, in a nebula, lost in the interstellar medium, on a planet or within a cell has the potential for very complex and beautiful chemistry but unless we can understand the local conditions and how the molecule interacts with them we have no idea what chemistry is really happening. To understand astrochemistry we need to understand the physical conditions that occur within many diverse molecular environments. The exploration of the molecular universe will take us on a long journey through the wonders of astronomy to the new ideas of astrobiology

The origins of life provide the motivation and excuse to investigate astrochemistry in its broadest sense, looking at molecules and their local complex chemistry using all of the tools of physical chemistry to constrain the imagination of the astrobiologist in the field and to force a re-think of the rules of biology that are prejudiced by the experience of life on Earth. The complexity of the problem places demands on the theories of science, stretching the understanding of kinetics and thermodynamics into areas where large non-ideal systems are hard to understand, although, curiously, modelling the complex chemistry of a giant molecular cloud is not dissimilar to the models of biochemistry within a cell. The size of the chemical problem quickly grows, so that the chemistry of 120 molecules in a molecular cloud must be compared with the 4500 reactions thought to be required to make a cell work. The full understanding of the chemical reactions must be modelled as a network of coupled chemical equations, which for something as comparatively simple as a candle flame can contain 350 equations.

Our mission is to explore the molecular universe with an understanding of all of the local molecular environments and constrain possible chemical reactions using the concepts of physical chemistry. With such a wide brief we need a focus and I have chosen the origins of life on Earth and on all planets – astrobiology.

1.1 The Standard Model – Big Bang theory

About 15 billion years ago the Universe and time itself began in a Big Bang. Observations of the night sky show that stars and galaxies are moving away from

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Table 1.1 The history of the Universe according to the Standard Model

Time since $t = 0$	Temperature	Comments
10^{-43} s	10^{32} K	Gravity is now distinct from the three other forces: strong, weak nuclear and electromagnetic
10^{-35} s	10^{27} K	Inflation of the Universe – the strong force separates
10^{-12} s	10^{15} K	Weak and electromagnetic forces separate. Neutrons and protons are formed by photon–photon collisions
10^{-2} s	10^{11} K	Electrons and positrons are formed through collisions of photons
1 s	10^{10} K	The Universe becomes transparent to neutrinos
180 s	10^{9} K	Nucleosynthesis: hydrogen, deuterium, helium and some lithium
$3–7 \times 10^{5}$ s	3000 K	Light element atoms form, and the Universe is now transparent to radiation: cosmic background is emitted
10^{9} yr	20 K	Galaxies form
Present	2.726 K	Stars and galaxies

us, telling us that the Universe is expanding. Extrapolating backwards in time leads to a point of common beginning, a singularity in space-time known as the Big Bang. Temperature is critical to the phases of evolution and subsequent cooling of the Universe, producing a number of critical times, detailed in Table 1.1. They are all predictions of the Big Bang Theory or the Standard Model of Cosmic Evolution.

Einstein's theory of relativity allows for the interconversion of energy and matter through the famously simple equation $E = mc^2$. Thus collisions between high-energy photons in the primordial fireball created particle–antiparticle pairs such as protons and antiprotons. After some 180 s and at a temperature of 10^9 K atomic nuclei such as hydrogen, deuterium, helium and some lithium were formed. The first three minutes of all time were chemically the dullest with no atoms or molecules. For a further 10^6 s the light atoms continue to be formed, marking a period where matter is created by *Big Bang nucleosynthesis*.

There are a number of astronomical pieces of evidence for the Big Bang Theory as we shall see, including the recent observation of the cosmic microwave background radiation, but it is far from a complete theory. However, predictions of the theory may be tested. One such prediction is the relative abundance by mass of He, which must be at least 25 per cent of the total mass. Helium is also made in stars and must contribute to the He density of the Universe and in all observations to date the observed abundance is greater than 25 per cent. There are problems associated with matter. Why is the Universe made from matter instead of antimatter? When was this decision made to stabilise matter from high-energy photons and particle–antiparticle pairs. Further, calculations of gravitational attractions of galaxies suggest the presence of large amounts of matter that cannot be seen, so-called dark matter. What is dark matter?

Table 1.2 Relative cosmic abundances of the elements

Element	Relative abundance	Element	Relative abundance
H	1	S	1.6×10^{-5}
He	0.085	P	3.2×10^{-7}
Li	1.5×10^{-9}	Mg	3.5×10^{-5}
C	3.7×10^{-3}	Na	1.7×10^{-6}
N	1.2×10^{-3}	K	1.1×10^{-7}
O	6.7×10^{-3}	Si	3.6×10^{-6}

The majority of the Universe is made from hydrogen and helium produced during the Big Bang, although some He has been made subsequently. The relative cosmic abundance of some of the elements relevant to the formation of life is given in Table 1.2, with all elements heavier than H, He and Li made as a result of fusion processes within stars, as we shall see later. The cosmic abundance is assumed to be the same as the composition of the Sun.

1.2 Galaxies, stars and planets

All matter formed within the Big Bang is attracted to itself by the force of gravity and after about 1 billion years massive proto-galaxies form. Gravitational contraction continues in more and more localised regions to form the galaxies we know today, including our galaxy, the Milky Way. The Milky Way is in a cluster of galaxies called the 'local group' that includes the Large Magellanic Cloud, the Small Magellanic Cloud and the Andromeda Galaxy (M31). Two of these, the Milky Way and the Andromeda Galaxy, are very luminous spiral galaxies.

The Milky Way was formed within 1 billion years of the Big Bang and has a mass of 10^9 solar masses. It formed from a large cloud of hydrogen and helium that was slowly rotating. As the cloud collapsed, conservation of angular momentum required matter near the axis to rotate very fast. As a result it spreads away from the axis and forms a flat spiralled disc some 120 000 ly in diameter and about 3300 ly thick. The Sun is approximately 30 000 ly from the centre. The nuclear bulge at the core of the galaxy contains old stars, and observations suggest that it must be hugely massive. Rapid rotation around the axis of the disc requires gravity and angular momentum, hence mass, to hold it together and this produced speculation about the existence of a black hole at the centre of the Milky Way.

The Sun formed some 4.5 Gyr ago (Gyr is a Gigayear or 10^9 years) from its own gas cloud called the solar nebula, which consisted of mainly hydrogen but also all of the heavier elements that are observed in the spectrum of the Sun. Similarly, the elemental abundance on the Earth and all of the planets was defined by the composition of the solar nebula and so was ultimately responsible for the molecular inventory necessary for life. The solar system formed from a slowly rotating nebula that contracted around the proto-sun, forming the system of planets called the solar system. Astronomers have recently discovered solar systems around other stars and, in only the briefest of looks, this has revealed a large proportion of similar planetary systems; thus the formation of planets around stars is a common process. The distribution of mass in the solar system is primarily within the Sun but distributed rather differently among the planets. The inner planets, the so-called terrestrial planets of Mercury, Earth, Venus and Mars, are essentially rocky but Jupiter, Saturn, Uranus and Neptune are huge gas giants; this needs to be explained by the formation process. Most important, however, is the formation of a planet in a habitable zone, where liquid water can exist and have the potential for life – at least if you follow the terrestrial model.

1.3 Origins of life

The age of the Earth is established by radioisotope dating at 4.55 Gyr and for most of the first billion years it suffered major impact events capable of completely sterilising the Earth and removing any life forms. The geological fossil records reveal, however, that life existed some 3.5 Gyr ago and perhaps as early as 3.9 Gyr ago. The oldest known life forms were very simple by modern standards but already had hugely complicated structures involving membranes and genetic information. The rather surprising conclusion is that life may have developed in as little as one hundred million years and at most 0.5 billion years, to evolve from the primordial soup to a viable living organism that had adapted to its local environment.

Definitions of life

There are many problems with the definitions of life, although determining what is alive and what is not is intuitively easy. At the extremes of collections of matter are the human being and the atom, with all of the possibilities in-between. Classical definitions of life taken from biology, such as ingesting nutrients, excreting by-products, growth and reproduction, all serve as good markers of life although are almost certainly prejudiced by life on Earth. What about fire? A candle flame (Figure 1.1) clearly ingests nutrients from the air in the form of oxygen and fuel from the wax. It produces waste products; it can also grow to cover large areas and certainly looks as if it might reproduce itself by creating new fires through sparks. It is localised by both a temperature and concentration gradient and might indeed be alive. However, one flame does become a copy of itself in that it will burn whatever fuel and oxidant combination available to it. In a sense it evolves and lives for as long as it can adapt to its environment. The adaptation to the environment is seen on the right-hand side of Figure 1.1 where a candle flame is burning under conditions of zero gravity in the space shuttle. The shape of the flame in air is controlled by buoyancy: the hot air inside the candle flame air is less dense than the air around it and it rises. In zero gravity the hot air does not rise because its weight is zero and so the random thermal motion results in diffusion

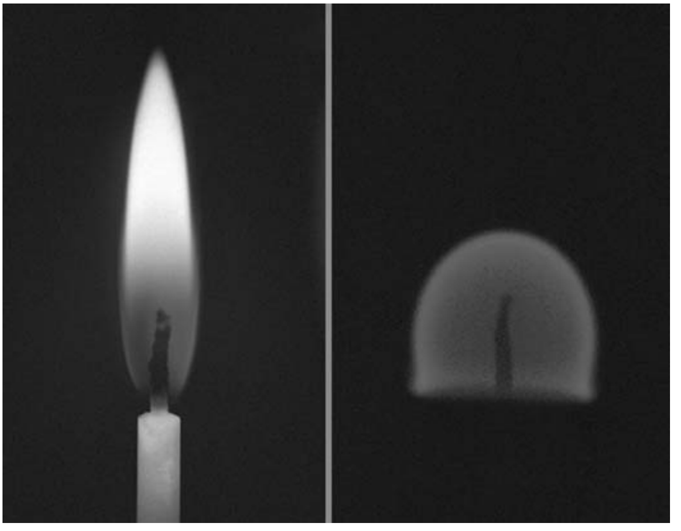

Figure 1.1 Two species of candle flame – dead or alive? The flame on the left is on Earth and the flame on the right is burning under zero gravity. (A colour reproduction of this figure can be seen in the colour section). (Reproduced from photos by courtesy of NASA)

of oxygen into the flame and combustions products away from the flame, hence the flame is now spherical. Even a complex set of chemical reactions, recognisable as a flame, has adapted to the environment. There is a consistent chemistry set within the 350 equations required to get the flame 'metabolism' chemistry to burn properly and as such it contains a recipe or a DNA. Other more impressively vague twilight life forms must include virus particles.

Viruses have no real metabolism and appear to exist in a dormant state until they find a suitable host. Then they hijack the metabolism and DNA replication apparatus of the host cell, switching the host into the production of huge numbers of copied virus particles, including some mutations for good measure. Finally, the cell bursts and the virus particles are released to infect a new host. The propagation of genetic information is important, as is the need for some form of randomisation process in the form of mutations, but it is not clear that there can be one definition for life itself. NASA has chosen the following definition:

> '*Life is a self-sustained chemical system capable of undergoing Darwinian evolution.*'

Alternatively:

> '*A system that is capable of metabolism and propagation of information.*'

Both are flaky, as even the simplest of thought will reveal.

Specialisation and adaptation

Cellular life may have arisen spontaneously, capturing whatever prebiotic debris that was present in the primordial soup. The encapsulation process provided the first specialisation within the environment, leading to compartmentalisation firstly from the external environment and then within the cell to provide areas of the protocell with dedicated adapted function. The external barrier in biology is provided by a cell membrane constructed from a bilayer of phospholipids with added sugars to make it rigid. The phospholipid molecules are amphiphilic, containing a long fatty acid chain of 10–20 carbon atoms at one end that are hydrophobic and a phosphate head group at the other end that is hydrophilic. It is the hydrophobic–hydrophilic characteristic at different ends of the molecule that make it amphiphilic. These molecules spontaneously form vesicles and membranes called liposomes in water when the concentration is above the critical micelle concentration. The network of chemical reactions trapped within a liposome could easily form a proto-metabolism but there is still the need for an information-bearing polymer.

Looking again at biology, genetic information is stored in all organisms as either DNA or RNA. These huge polymeric molecules contain the information for the replication of the building blocks of all organisms, the proteins. The four bases, G, A, T and C, pair together as A–T and G–C, the so-called Watson–Crick base pairs, which together with the deoxyribose sugar and phosphate backbone form the α-helix of the DNA molecule, shown in Figure 1.2.

The order of the bases is important along the length of the DNA and each sequence of three bases, called a triplet, represents the words in the genetic code. Each triplet codes for an amino acid so that AAA is lysine and UGU is cystine with signals for 'stop', such as UGA, and 'start' (no simple sequence but TATA is a reasonable example) to establish the beginning of a gene. More triplets are used to code for each of the 20 or so amino acids used in living organisms and the order in which they must be put together to form a protein (Figure 1.3). The information coded within the DNA is propagated from generation to generation nearly always correctly but sometimes with mistakes or mutations. Not all mistakes are bad; mistakes that provide an advantage in the local environment are good mistakes and allow evolution. The organism with the good mistake will evolve and adapt better to its surroundings, outgrowing less-well-adapted organisms.

Proteins are constructed from long chains of amino acids linked together by a peptide bond. There are 20 common amino acids that are coded within the genome and they are all of L-optical activity. Optical activity refers to the interaction of molecules with polarised light and divides molecules into three types: those that do not rotate the plane of polarisation of the light; those that rotate the plane of polarisation to the right; and those that rotate the plane of polarisation to the left. The two types of molecules that rotate light are called chiral molecules and those that do not are called achiral. The choice of one set of chiral molecules, called homochirality, over the other set is a marker for biological activity. Although amino acids may be produced in space on the ice mantles of interstellar dust grains, they are thought to be racaemic mixtures, meaning that they have equal quantities of

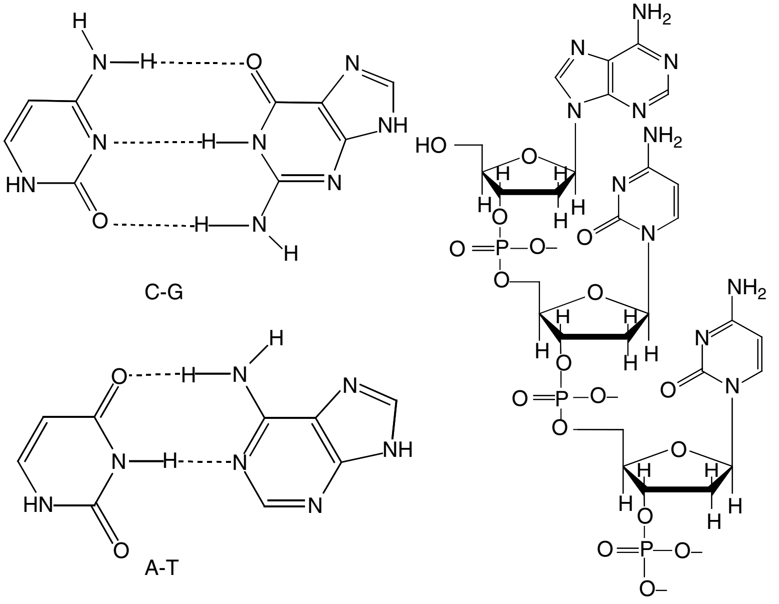

Figure 1.2 Watson–Crick DNA base pairs and the DNA backbone

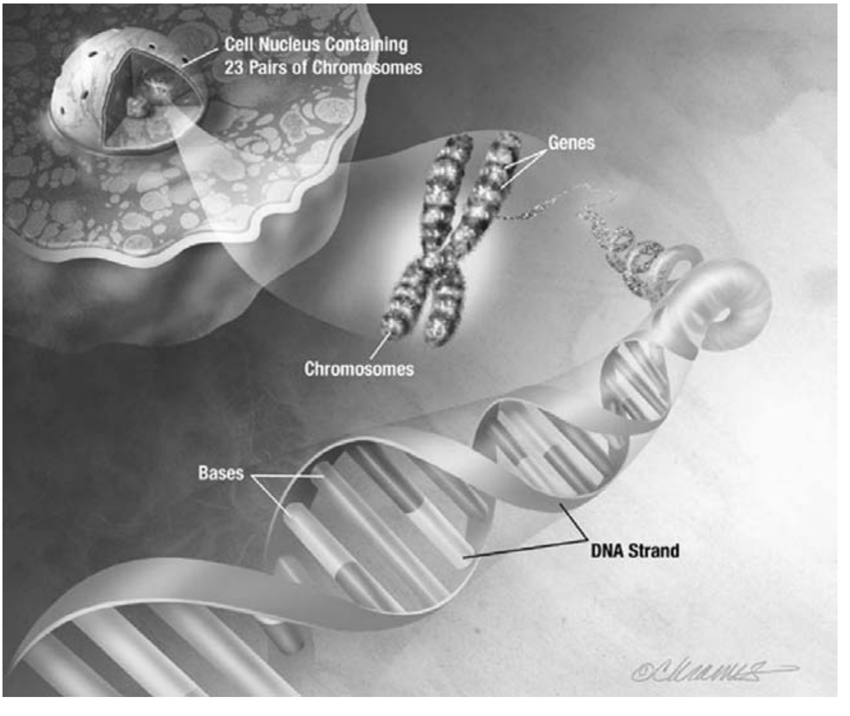

Figure 1.3 The genetic code. (Reproduced from Alzheimer's Disease Education by courtesy of the National Institute on Aging)

the L and D forms of the chiral molecules. Similar optical purity is seen in the bases of DNA and RNA and with biologically active sugars. Curiously, all sugars are D-enantiomers.

The origin of the *homochirality* is not known. There is a tiny energy difference between the optical isomers associated with a 'parity violating energy difference' of order 10^{-15}–10^{-17} J, but in general homochirality will require biological amplification favouring one enantiomer over another, i.e. 'enantiomeric amplification'. It has been suggested recently that organic synthesis in the circularly polarised light field around a star in the interstellar medium or due to chiral-specific surface reactions may also provide a mechanism for enantiomeric amplification and we shall discuss this later. Homochirality is, however, easily achieved by biological systems and may be considered as a *biomarker* – a marker for the existence of life.

It is the variety of life around the edges of the biosphere on Earth that is a testimony to its adaptation and ability to survive in harsh and extreme environments. The bacteria in the hot-water spring shown in Figure 1.4 have adapted to different temperatures and salinities.

Some bacteria require extreme temperatures, e.g. hyperthermophile organisms require hot water to live and will not survive below 90°C. The extremophile bacteria are from a general class of organisms that have adapted and thrive in extreme living conditions found in deep-sea marine environments and deep subsurface colonies. These bacteria may make up most of the collection of biological organisms on Earth that form the biota. The molecular classification of organisms based on the length of the genome suggests that the last common ancestor was a hyperthermophile

Figure 1.4 Hyperthermophile bacteria at Prismatic Lake in Yellowstone National Park. (A colour reproduction of this figure can be seen in the colour section). (Reproduced from a photo of Prismatic Lake by courtesy of National Park Service, Yellow Stone National Park)

bacterium. Far from being descended from the apes, we are actually descended from bugs. Measurements of the survival of bacteria in space suggest that, in the form of spores or dried cells, the survival in space is possible at least for the 6 years that the experiments have been taking place. The transfer of life from planet to planet is then a real possibility. The recent extensive analysis of meteorite ALH84001 suggests that there may be structures within the rock that look like fossil organisms. The meteorite was ejected from the surface of Mars probably by a collision and then made a rapid transit to Earth perhaps as quickly as 60 000 years. This meteorite express-delivery service suggests that not only are we descended from bugs but perhaps even from Martian bugs.

1.4 Other intelligent life

The prospect of intelligent life anywhere in the Universe has been puzzling astronomers and recently astrobiologists, and there have been some attempts to estimate probabilities. This led Drake to construct a now famous equation that collects the ideas together: the Drake equation. It is a mathematical representation of factors relating the probability of finding life and, in particular, an intelligent civilisation elsewhere in the Universe. This is an extreme example of 'hypothesis multiplication' and should be treated with caution. The equation is written:

$$N_c = R_s f_p n f_l f_I f_c L \tag{1.1}$$

where N_c is the number of intelligent civilisations in the Universe with whom we might communicate, R_s is the rate of formation of stars in the galaxy, f_p is the fraction of stars that have planetary systems, n is the average number of habitable planets within a star's planetary system, f_l is the fraction of habitable planets upon which life arises, f_I is the fraction of habitable planets upon which there is intelligent life, f_c is the fraction of civilisations interested in communicating and L is the average lifetime of a civilisation.

The problem comes with assessing the values of the factors to place within the equation and this leads to some very optimistic or pessimistic estimates.

- R_s: There are approximately 10^{11} stars in our galaxy and given that the age of the galaxy is some 10 Gyr the rate of star formation is then approximately 10 stars per year.

- f_p: This could be as large as 0.5 but may be complicated by binary stars and other local factors: pessimistically it is 0.01 and optimistically 0.3–0.5.

- n: Our solar system may have had as many as three habitable planets (Earth, Mars and maybe Venus, at least for a while), however giant planet formation may have removed inner terrestrial-type planets by collision during the formation process: optimistically it is 3, pessimistically 0.01.

- f_l: Is life the product of a collection of simple chemical processes, in which case it should be everywhere, or is it more of a fluke: optimistically it is 1, pessimistically 10^{-6}.
- f_I: Intelligence on Earth took 4.5 Gyr to evolve and many stars do not live this long (dependent on their mass) so they choose some extremes: optimistically it is 0.5 and pessimistically 10^{-6}.
- f_c: If they are like human beings then everybody wants to talk so, lets say, 1.0.
- L: This has been a few tens of years in the case of our civilisation and we may yet destroy ourselves within 10 000 years: optimistically it is 1 billion years and pessimistically 100 years.

Performing the optimistic sum gives $N_c = 5 \times 10^9$ and the pessimistic sum gives $N_c = 10^{-13}$.

The Drake equation is a just a mathematical way of saying 'who knows' but it does allow the factors that might control the origins of life to be identified; that said, it is probably the worst calculation in the book.

1.5 Theories of the origin of life

There is no one correct theory for the origin of life on Earth or any habitable planet, although many have been presented. The current set of ideas is summarised in Figure 1.5. Aside from the theory of creation, which seems particularly hard to test, the testable theories of the origins of life divide into two: *extraterrestrial* or panspermia, the theory that life was seeded everywhere somewhat randomly; and *terrestrial*, that life originated *de novo* on Earth or other habitable planets around other stars. The theories of terrestrial origin are more favoured but the recent discovery of habitable planets and life within any solar system suddenly makes panspermia more likely.

Terrestrial theories divide into an organic or inorganic origin for life. If life started with organic molecules, how were these molecules formed from prebiotic conditions, perhaps in what Darwin called a 'little warm pool' or a primordial soup theory? The endogenous production of organic material provides a continuous link from a prebiotic planet to a complete organism. However, conditions may have been habitable for organic material from outside the planet, exogenous origin, to land on Earth, perhaps delivered by meteorites or comets. The energy source for life could also be organic such as in photosynthesis or inorganic chemistry around hydrothermal vents. Indeed, perhaps inorganic material surfaces catalysed the formation of the first set of self-replicating molecules or a primitive organism called a 'surface metabolite'?

Extraterrestrial theories suggest that life is formed wherever the chemistry will allow the formation of life, either randomly or perhaps directed by some guiding

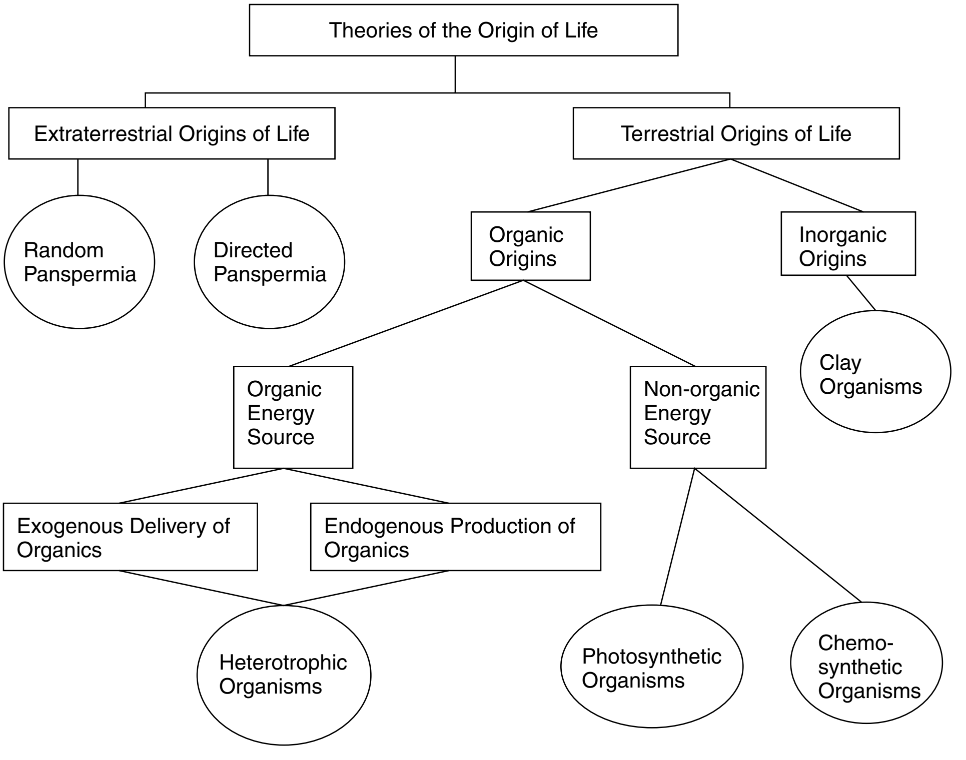

Figure 1.5 Theories of the origins of life. (Reproduced from Davis and McKay 1966 by courtesy of Kluwer Academic Publishers)

force. The discovery of extrasolar planets with a habitable zone that allows liquid water to exist suggests that conditions with the right energy balance and molecular inventory could produce life spontaneously. The idea of a prebiotic planet capable of supporting life must be ubiquitous. The temptation, however, is to assume that what we see today has a direct lineage with the prebiotic Earth or any planet and this cannot be the case. Mass extinction events abound in the fossil record on Earth, not least of which is the famous meteorite impact that killed the dinosaurs, as seen in Figure 1.6. Impacts in the early stages of the formation of the Earth were very common, as is witnessed by the cratering scars on the surface of the Moon. A similar stream of meteorite impacts must also have collided with the Earth and a large meteorite, several kilometres in diameter, certainly impacted on the surface of the Earth near the Yucatan peninsula in Mexico some 65 million years ago. The Chicxulub crater shows an impact large enough to cause global heating of the Earth's atmosphere and vaporisation of some if not all of the oceans, wiping out the dinosaurs and many more apparently evolutionally fragile species on the planet at the time.

Evidence for early collisions is also present in the fossil record, suggesting that the diversity of species present on Earth has been reduced considerably on several occasions, perhaps removing some 90 per cent of species. Some organisms

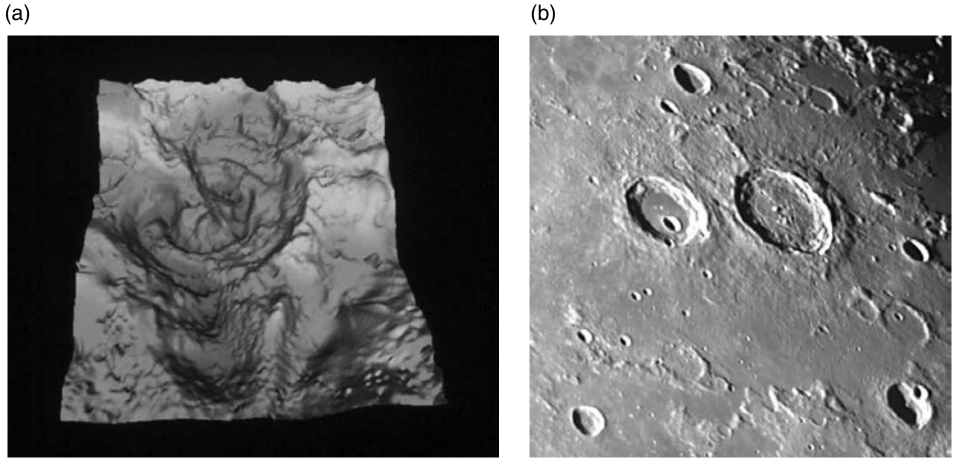

Figure 1.6 Impact frustration: (a) the Chicxulub crater, seen as a three-dimensional gravity map, thought to be responsible for the extinction of the dinosaurs; (b) the cratered surface of the Moon. (Reproduced from photos by courtesy of NASA)

may have survived by collecting biologically active molecules from the debris of other species. Replication and amplification result in the formation of the complex processes of translation and transcription of the genome, synthesis of proteins and the design of cellular metabolism. How modern life evolved may be a very different question to how life occurs spontaneously as a product of prebiotic chemistry and may look very different to the astrobiologist in the field. Astrobiology cannot be limited to the ideas of biology on Earth.

Concepts and calculations

Concepts	
Standard Model	The theory of the origins of the Universe
DNA base pairs	The general structure of the information-bearing molecule used in biology on Earth
Homochirality	The general idea of biomarkers for the existence of life, in this case a preference for one optical isomer over another
Extraterrestrial origins of life	Life was delivered to the Earth (or any planet) by meteorites of cometary material, leading to the idea of panspermia
Terrestrial origins of life	The molecules of life were built on Earth, perhaps in the primordial soup or little warm pool
Impact frustration	A process typified by the extinction of the dinosaurs where the Earth's surface may have been sterilised of all life forms by the impact of a large meteorite or comet
Calculations	
Drake equation	Use of this equation, including estimates of the optimistic and pessimistic calculations, for the existence of other life forms

2
Starlight, galaxies and clusters

Introduction

Look into the sky, day or night, and you will see starlight, light that when separated into its constituent wavelengths contains information about the stars. Whether it is our local star, the Sun, or many millions of not so local stars, there may be other worlds sharing the galactic starlight. Possibly the simplest form of light familiar even to early man was the light associated with heat. The red embers of a camp fire or the yellow colour of a candle flame are all due to the simplest model of starlight called black body radiation.

2.1 Simple stellar models – black body radiation

The simplest models of stars treat a mass of hydrogen and helium as a radiating black body that goes through a formation process, a mid-life and then a death in a sequence of events controlled by its initial mass. A black body is an object that absorbs and emits all wavelengths of radiation with equal efficiency. This produces a continuum electromagnetic emission spectrum over all wavelengths against which absorption features associated with the elements and molecules present in the stars can be seen. Properties that define a black body are:

1. A black body with $T > 0$ K emits radiation at all wavelengths;
2. A hotter black body emits more light at all wavelengths than a colder body;
3. A hotter black body emits more of its radiation at shorter wavelengths;
4. Black bodies emit and reflect radiation at all wavelengths with equal efficiency.

Black bodies have formed an important part in the development of the theory of quantum mechanics and were studied by the early quantum physicists, producing a number of laws relating the temperature of the black body to the photon flux, the

Astrochemistry: from astronomy to astrobiology. Andrew M. Shaw

luminosity and the most intense wavelength, culminating in a complete description of the wavelength–intensity relation known as Planck's Law from which we see for the first time Planck's constant.

Stefan–Boltzmann Law

The first of the laws is the Stefan–Boltzmann Law relating the amount of energy emitted from a black body, F, to its temperature T:

$$F = \sigma T^4 \tag{2.1}$$

where F is the total flux or power per unit area, T is the temperature of the black body in Kelvin and σ is Stefan's constant $\sigma = 5.67 \times 10^{-8}\ \mathrm{W\,m^{-2}K^{-4}}$.

Example 2.1
The part of the Sun that we can see is called the photosphere and has a surface temperature of 5780 K. The solar flux from every square metre of the surface is then given by Equation 2.1:

$$F_{\mathrm{Sun}} = 5.67 \times 10^{-8}(5780)^4 \qquad (\mathrm{W\ m^{-2}\ K^{-4}})(\mathrm{K^4})$$

$$F_{\mathrm{Sun}} = 6.3 \times 10^7\ \mathrm{W\ m^{-2}}$$

Luminosity

The luminosity of a star, L, is the total rate at which energy is radiated by the black body over all wavelengths. Assuming that the star is a sphere, the total surface area is given by $A = 4\pi R^2$, where R is the radius of the star, then the luminosity of the star is given by:

$$L = 4\pi R^2 \sigma T^4 \tag{2.2}$$

This quantity is the total amount of radiation at all wavelengths radiating through the surface of the sphere and is simply the Stefan-Boltzmann Law multiplied by the surface area of the photosphere.

Example 2.2
The luminosity of the Sun may be calculated from Equation 2.2 knowing the radius of the Sun to be $R_{\mathrm{Sun}} = 6.96 \times 10^8$ m:

$$L_{\mathrm{Sun}} = 4\pi R^2 \times 5.67 \times 10^{-8}(5780)^4 \quad (\mathrm{m^2})(\mathrm{W\ m^{-2}\ K^{-4}})(\mathrm{K^4})$$

$$L_{\mathrm{Sun}} = 3.8 \times 10^{26}\ \mathrm{W}$$

Wien's Law

Turning now to the wavelength distribution of the starlight. The emission from a black body must, by definition, produce radiation at all wavelengths, i.e. a wavelength distribution. It turns out for a black body that the wavelength at which the maximum radiation flux occurs is characteristic of the temperature and is given by Wien's Law:

$$\lambda_{\max} = \frac{w}{T} \tag{2.3}$$

where Wien's constant $w = 2.9 \times 10^{-3}$ m K and gives a value for $\lambda_{\max}$ in metres.

Example 2.3
Taking the surface temperature of the Sun to be 5780 K and substituting into Equation 2.3 gives:

$$\lambda_{\max} = \frac{2.9 \times 10^{-3}}{5780} \frac{\text{m K}}{\text{K}}$$
$$\lambda_{\max} = 5.01 \times 10^{-7} \text{ m} = 501 \text{ nm}$$

This is an interesting result, as with an absorption maximum in the blue-green part of the spectrum that is close to but not coincident with an absorption maximum in the spectrum for chlorophyll (see Figure 2.2).

Inverse Square Law

The amount of radiation reaching Earth from the Sun is fundamental to the energy balance of the planet and, for that matter, all planets around any star. Measuring the amount of energy arriving at the top of the atmosphere with a satellite-borne detector gives a flux of $f = 1370$ W m^{-2}. But the radiation from the Sun is distributed equally in all directions and so this figure represents the amount of energy landing on every square metre of a sphere of radius d equal to the distance between the Earth and the Sun. This distance is called one astronomical unit, or 1 AU, and is 1.5×10^{11} m with an error of $\pm 1.5 \times 10^{3}$ m!

The amount of radiation passing through each square metre depends on how far away you are from the star. Placing the star at the centre of a sphere radiating energy in all directions, at a distance of d from the star, the area of the sphere is given by $4\pi d^2$. As the sphere gets bigger the area of the sphere increases with d^2, so the amount of radiation on each square metre falls by $1/4\pi d^2$ – the Inverse Square Law.

Example 2.4
The calculation for flux arriving at the Earth requires the Sun's luminosity and the distance from the Sun. The total solar flux ($F_{\text{Sun}} \times$ total area of the Sun) gives solar luminosity $L_{\text{Sun}} = 3.8 \times 10^{26}$ W and the flux at the Earth, f, is given by:

$$f_{\text{Earth}} = \frac{3.8 \times 10^{26}}{4\pi\ (1.5 \times 10^{11})^2} \quad \frac{\text{W}}{(\text{m})^2} \tag{2.4}$$

$$f_{\text{Earth}} = 1362\ \text{W}\,\text{m}^{-2}$$

Note the potential confusion between luminosity of the Sun L and the flux at the Earth. The latter is quite naturally written as the amount of radiation arriving on every square metre of the Earth's surface and analogously the flux per square metre from the black body is also F. This calculation requires the total amount of radiation emitted by the Sun to be known, which is the luminosity of the Sun and not its flux.

Planck's Law for black body radiation

The Stefan–Boltzmann Law and Wien's Law for black body radiation have been unified into Planck's Law for black body radiation, from which Planck's constant was first introduced. Planck's analysis of the spectral distribution of black body radiation led him to an understanding of the quantisation of energy and radiation and the role of the photon in the theory of radiation. The precise law relates the intensity of the radiation at all wavelengths with the temperature and has the form:

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5 \left[\exp\left(hc/\lambda kT\right) - 1\right]} \tag{2.5}$$

where λ is the wavelength in metres, c is the speed of light and Planck's constant $h = 1.636 \times 10^{-31}$ J s. Plotting the curves for a number of temperatures yields a characteristic shape for the intensity of black body radiation, as shown in Figure 2.1.

The most intense curve in Figure 2.1 is for the Sun with a surface temperature of 5780 K, showing a maximum at 501 nm as calculated from Wien's Law. Interestingly, 48 per cent of the radiation emitted from the Sun is in the visible region of the spectrum from 400 to 800 nm. However, the energy flux (as opposed to the photon flux) from the Sun depends on the energy of each photon. The energy of the photon is related to the wavelength by the equation:

$$E = \frac{hc}{\lambda} \tag{2.6}$$

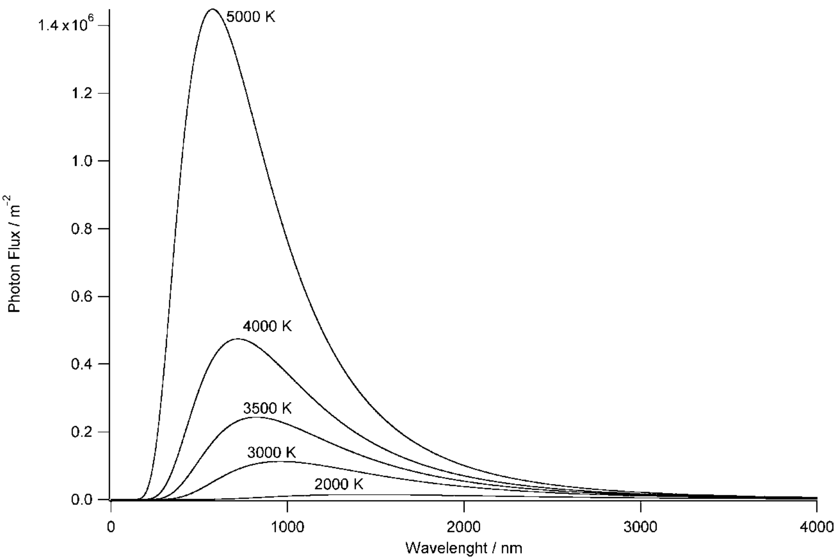

Figure 2.1 Planck curves for black bodies of different temperatures

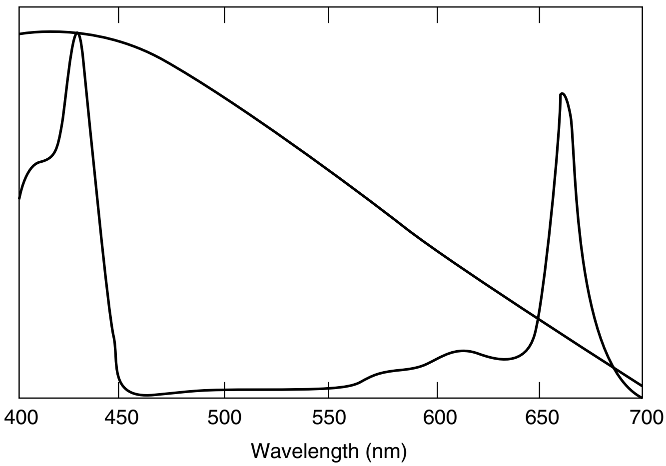

Figure 2.2 Absorption spectrum of chlorophyll overlaid with the energy flux from the Sun

where E is the energy, h is Planck's constant, c is the speed of light and λ is the wavelength of the radiation. The total energy flux from the Sun is the product of the photon flux and the photon energy, which has been overlaid on the absorption spectrum for chlorophyll in Figure 2.2.

The absorption maximum of chlorophyll at short wavelength is coincident with the maximum of the energy flux from the Sun, which might suggest that life around stars with similar temperature will also have evolved energy-trapping molecules such as chlorophyll. The longer wavelength absorption maximum is due to the porphyrin ring structure of chlorophyll that has been optimised for the short wavelength maximum. This raises the interesting question that if a porphyrin ring is chosen as the light-harvesting structure, the 'leaves' on any planet around a Sun-like star will also appear green. The energy flux from the star will determine the colour of life on any orbiting planet. In short, life will look the same around stars of similar temperatures.

The black body radiation model for the continuum radiation from stars works well but it is not quite right. Careful consideration of the radiation profile shows deviations from the curves shown in Figure 2.1 due to the structure of the star itself. These deviations form the basis of a more detailed analysis including the effects of circulation within the star and will be left to others to explain; we shall use black body radiation as our model for stars.

2.2 2.725 K – cosmic microwave background radiation

One of the most impressive demonstrations of black body radiation is also a very powerful test of the Big Bang model of the origin of the Universe. The discussion of the Big Bang in Chapter 1 revealed an explosion of a ball of energy, converting the photon energy into matter and antimatter particle pairs and back again into photons. The expansion of the Universe would result in the cooling of this radiation. At around 4000 K hydrogen atoms formed and photon-matter scattering helped the cooling process, all of which suggest that there should be some of this remnant radiation left, albeit very cold. This fossil radiation should be from a pure black body and should show the Planck curve for its characteristic temperature. Various groups set about calculations of the temperature of the radiation, initially coming up with answers from 5 to 25 K; therein lies a detection problem. The black body temperature of the Earth is of order 275 K and there is hence a lot of background thermal radiation.

The development of new low-temperature detection technology and the launch of the Cosmic Background Explorer (COBE) satellite by NASA in 1989 helped to resolve this problem. The results from these observations were amazing – an almost perfect black body curve (Figure 2.3) with a black body temperature of 2.725 ± 0.002 K and a maximum wavelength of the radiation at $\lambda_{max} = 1.05$ mm.

Now we have to be careful when making these measurements due to the relative motion of the observer with respect to a radiation source – the Doppler Effect. More of this in Chapter 3 but in general when you are moving towards the source of radiation the wavelength of the radiation looks shorter than it really is and is said to be blue-shifted, and receding from a light source makes the wavelength look longer or red-shifted. So you have to make allowances in the determination of λ_{max} for the complete relative motion of the Earth relative to the radiation. The simplest correction is for the motion of the Earth around the Sun and then, more complicatedly, the Sun towards the centre of the Milky Way and the Milky Way towards the centre of the cluster of galaxies called the Local Group and, if that was not enough, how the Local Group is falling towards the Virgo cluster of

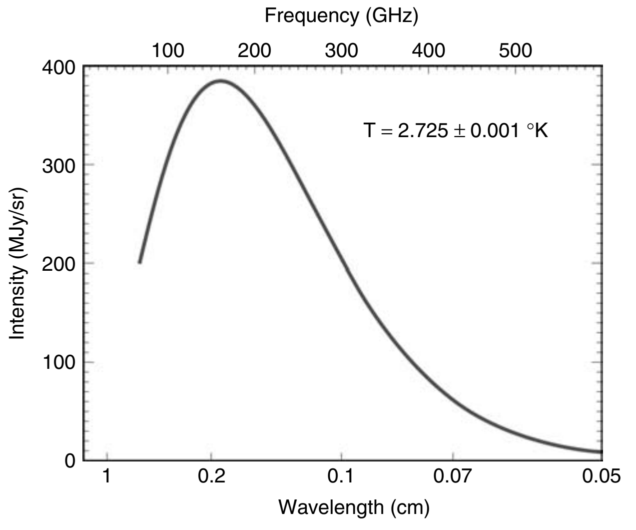

Figure 2.3 An almost-perfect black body spectrum for the cosmic background radiation. Figure courtesy of NASA/COBE Science Team

galaxies. It is curious how one scientific measurement produces estimates of lots of other quantities, especially when the first measurement has the accuracy of the 2.725 ± 0.002 K Planck curve. We now have an estimate for how fast the Local Group is falling towards the Virgo cluster: 570 km s^{-1}. We will explore more of the structure of the Milky Way and the galactic hierarchy later.

Returning to the origin of the Universe and the 2.725 K background, a further important observation is that the presence of the radiation is isotropic – it is seen equally intense in all directions, as the theory for a Big Bang predicts. This is strongly supporting evidence for the age of the Universe to be set at 15 Gyr. There are several interesting conclusions from the Planck curve: the beginning of the Universe was a quiet place and if there had been massive star formation it would have perturbed the black body curve; the Universe was hot at the start and has been cooling ever since; the radiation is *isotropic* – it is seen in all directions; and variations in the temperature are very small, of the order 1.6×10^{-5} K.

2.3 Stellar classification

Now that we have a simple model for the continuum spectrum of the stars based around the Planck curve, the temperature and the luminosity, we can make some observations and classifications of the stars. There are some constellations that dominate the night sky in both the northern and southern hemispheres and even a casual look should inspire wonder. Star hopping in the night sky should lead to the simplest observation: not all stars have the same colour. A high-quality photograph of the constellation of Orion (see page 2 of the colour plate section) shows stars with very different temperatures and colours: these should be visible to the naked eye. The black body radiation laws tell us that this is due to the surface photosphere temperature and must contain information on the structure, age, composition and evolution of the star from which a complete classification has been derived.

Assuming that the radiation from a star follows a black body distribution, the ratio of the intensity of one colour against another is characteristic of the temperature of the star. This is achieved practically by placing a filter over the telescope and allowing only radiation from a part of the spectrum to be detected, and then blocking out another part of the spectrum and comparing the relative intensities. Astronomers choose the region from 400 to 500 nm, calling this the Blue or B region, and the band of radiation from 500 to 600 nm, calling this, for historical reasons, the Visible or V region. Hence it is possible to derive the B/V ratio as a measure of the temperature of the star. Of course the assumption underlying this temperature determination is that the star has a black body spectrum that follows the Planck curve. At this point a historical concept enters the discussion – magnitude.

Stellar magnitude

Astronomy is an ancient subject that has grown up with some curious conventions and standards, not least of which is the brightness of stars. This fundamental property is the first thing to be observed with the naked eye – clearly one star appears brighter than another. Based on the apparent relative brightness of stars to the naked eye, the astronomer Hipparchus constructed a catalogue of the stars, ranking their brightness into six categories called magnitudes. The brightest stars are of first magnitude and the faintest are of sixth magnitude. The magnitude of a star is still listed with the entries of stars in modern stellar catalogues following the tradition set by Hipparchus some 2000 years ago.

The naked eye classification is scientifically not very satisfying. Astronomers have now standardised the concept of magnitude and it remains part of the working vocabulary, however cumbersome it may seem, especially to a non-astronomer. The standardisation comes from quantitative observations showing that first magnitude stars are about 2.5 times brighter than second magnitude stars to the naked eye and that the ratio between the first and sixth magnitude stars is nearly 100. In 1850 this became the standard, so that a difference of one magnitude between two stars is $100^{1/5} = 2.512$ and some standard stars were chosen to calibrate the entire scale. The natural scientific measure of a star's relative brightness, however, is obviously the relative fluxes of radiation and the stellar magnitude difference is related to relative flux by:

$$m_1 - m_2 = 2.5 \log \left(\frac{f_2}{f_1} \right) \tag{2.7}$$

where f_1 and f_2 are the measured fluxes and m_1 and m_2 are the stellar magnitudes. Hence the two stars in Gemini, the twins called Castor and Pollux, have magnitudes