

ANDREW CLARKE



PRINCIPLES *of* THERMAL ECOLOGY

temperature, energy and life



Principles of Thermal Ecology

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Temperature, Energy and Life

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and

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Preface

This book has taken several years to write, but it has been much longer in preparation. In fact I can probably trace it right back to growing up in central London. As a young schoolchild I was a regular visitor to the local library where the staff were very tolerant of me sitting on the floor to read. I devoured anything I could find on birds and animals, and one day as I turned over the pages of a newly arrived book I came across a grainy but evocative image of a forbidding mountainous landscape. Little did I know that I would later spend almost five years of my life undertaking research at this very spot: South Georgia, an isolated island in the Southern Ocean and on the edge of Antarctica.

Fieldwork in polar regions inevitably focuses attention on temperature, and the more I thought about the links between temperature and ecology, the more interesting they became. They proved to be the focus of my entire research career, so it was perhaps inevitable that once I retired from active fieldwork, I would write a book on temperature.

Although I often referred to the classic review edited by Precht and colleagues (*Temperature and life*, Springer, 1973), for much of my research career the book I kept immediately to hand was the ground-breaking *Strategies of biochemical adaptation* by Peter Hochachka and George Somero (Saunders, 1973). With its regular revisions this has remained a definitive work for ecological physiologists. Apart from those general physiology texts that had chapters on temperature, a few highly specialised symposium volumes and *Temperature biology of animals* (Andrew Cossins and Ken Bowler, Chapman & Hall, 1987), there was nothing else available for those needing an overview of thermal ecology until Michael Angilletta's *Thermal adaptation* (OUP, 2009). This takes an innovative behavioural and

evolutionary perspective, reflecting the approach of those ecologists who work with animals in the field rather than cells or proteins in the laboratory. It therefore complements the approach I have tried to take, which is a more traditional path through physiology to ecology.

In writing this book I have been able to present some topics in the way I would like to have been introduced to them as a student. To take one example, metabolism is so much easier to understand when it is built from its foundations through a single, simple idea: energy carried by electrons is used to generate a proton gradient which powers the synthesis of ATP. With this one concept, all of the bewildering detail of the metabolic chart and the enormous evolutionary variety of microbial metabolism have a common framework. I have also been able to indulge myself by exploring the history of some topics. It has been fun to track down some of the very early literature but salutary to find that some of this did not say what I (and many others) thought it said, and that some classic references had clearly not been read for many years as they are systematically mis-cited.

Like all scientists I have benefited from support, encouragement and the continual exchange of ideas with colleagues. One of the great unspoken benefits of fieldwork in distant places is the time spent travelling, or in bad weather, when there is an opportunity to talk science away from the everyday concerns of a modern research institute. These conversations are essential to scientific development; they are where ideas are explored, errors corrected and new projects planned.

All young scientists need guidance as they set out on a career, and I was lucky to receive this from a series of outstanding mentors. In particular I

benefitted from support from two notable department heads, Dick Laws and Nigel Bonner, and also from John Lawton at the Natural Environment Research Council; in addition there was sound advice at important moments from Inigo Everson, John Croxall, John Gray and John Sargent. Throughout my career in Antarctic science I have enjoyed discussion with many colleagues, both within the institute and abroad, conversations which have done much to sharpen my thinking and eradicate errors, so thanks are due to Mike Angilletta, David Barnes, Chris Cheng, Steven Chown, Melody Clark, Pete Convey, Alistair Crame, Paul Dayton, Bill Detrich, Art DeVries, Hugh Ducklow, Brian Enquist, Inigo Everson, Ray Huey, Roger Hughes, David Jablonski, Tim Jickells, Ian Johnston, Adrian Friday, Kevin Gaston, Nick Lane, Simon Laughlin, Barry Lovegrove, Carlos Martínez del Río, Mike Meredith, John Morris, Eugene Murphy, Lloyd Peck, Hans-Otto Pörtner, Langdon Quetin, Robin Ross, Bruce Sidell, Victor Smetacek, George Somero, Chris Todd and Paul Tyler.

Science involves teamwork, and I was particularly lucky to have worked with a series of wonderful research assistants, Lesley Holmes, Liz Prothero-Thomas and Nadine Johnston. It is also a pleasure to thank two librarians at the British Antarctic Survey, first Christine Phillips and then Andrew Gray, for their outstanding professional support in tracking down every obscure historical

reference I could challenge them with. Scholarship is all about checking primary sources, and I could not have done this without them.

I am also grateful to those colleagues who agreed to read through draft chapters. All of them took care and time, and they all found things I had got wrong. Needless to say any remaining errors are down to me. My thanks to David Atkinson, Martin Baker, Chris Cheng, Melody Clark, Pete Convey, Paul Cziko, Richard Davies, Art DeVries, Jack Duman, Fritz Geiser, Michael Kearney, John King, Nick Lane, Barry Lovegrove, Andrew McKechnie, Ian Renfrew, Brent Sinclair, George Somero, Jim Staples, John Turner and Eric Wolff.

Enormous thanks are due to Ian Sherman, who tried for years to persuade me to write this book before finally succeeding, and his team at OUP, especially Lucy Nash and Bethany Kershaw, who saw it through to completion. During the writing of this book I have also received institutional support from the British Antarctic Survey, and the School of Environmental Sciences at the University of East Anglia, for which I am extremely grateful. And finally, because it is the most important, deep thanks to my patient wife, Gill, who has provided unstinting support and encouragement through my entire career.

Andrew Clarke
Norfolk, February 2017

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Plate 1. A Namib day gecko (*Rhoptropus afer*) basking on the sunny side of a dark rock to warm up. (Image courtesy Barry Lovegrove). (see page 14)

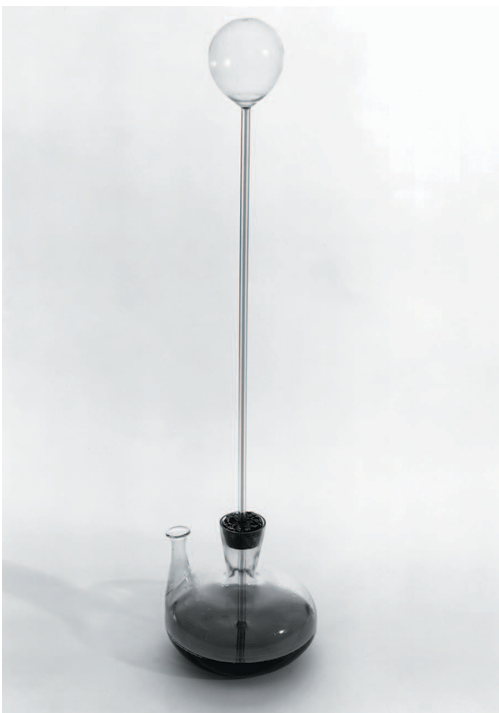


Plate 2. A reproduction of Galileo's thermoscope; the original was probably constructed in the late sixteenth century. (Image: Science Museum/Science & Society Picture Library). (see page 32)

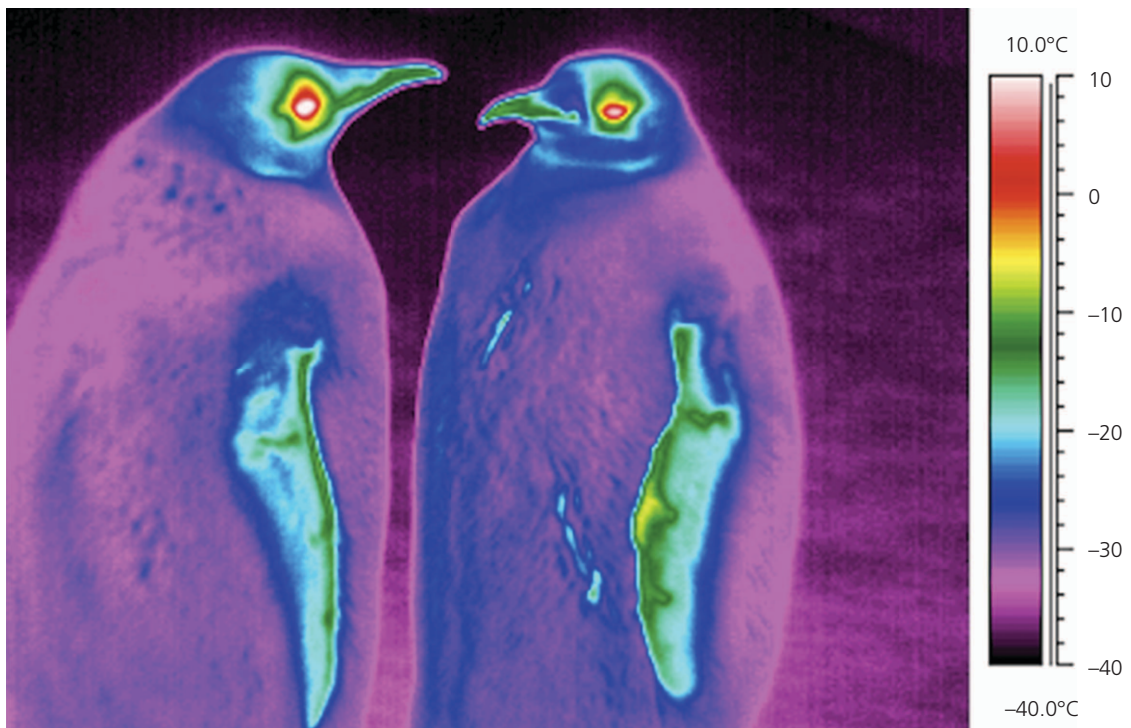


Plate 3. Two emperor penguin, *Aptenodytes forsteri*, chicks photographed with a thermal imaging camera and with the image displayed in false colour. Note how the downy juvenile coat insulates the chicks so well that their surface temperature is similar to that of the ice and snow on which they sit ($\sim -35^{\circ}\text{C}$), whereas the face and flippers are warmer ($\sim -10^{\circ}\text{C}$). The insulating layer of downy feathers and the huddling behaviour allow the chicks to maintain an internal body temperature of $\sim 38^{\circ}\text{C}$. (Image courtesy of André Ancel, IPHC/CNRS/IPEV). (see pages 45 and 64)



Plate 4. The interior of a modern Stevenson screen housing a range of thermometers (dry bulb and wet bulb mounted vertically, and maximum and minimum mounted horizontally). Also present are a torch to take readings by night and a water bottle to keep the wet bulb wet (Image Wikimedia Commons). (see page 47)



Plate 5. Emperor penguins (*Aptenodytes forsteri*) on floating sea-ice in Antarctica. This would not be possible were it not for the unusual property of ice being less dense than liquid water. (Image courtesy Pat Cooper, British Antarctic Survey). (see pages 84 and 87)



Plate 6. An image of ice shelf and ocean, showing all three phases of water present simultaneously (although only the solid and liquid states are visible). (Image courtesy Chris Gilbert, British Antarctic Survey). (see page 93)



Plate 7. The icefish *Chaenocephalus aceratus*, photographed in shallow waters at Signy Island, South Orkney Islands, Antarctica; an example of an icefish, lacking functional haemoglobin and myoglobin. (Image courtesy Doug Allan, British Antarctic Survey)



Plate 8. An example of a highly ornamented tropical gastropod (*Murex altispira*). Such ornamentation is very rare among cold-water gastropods, where the production of a carbonate skeleton is energetically more expensive. (Image Wikimedia Commons). (see page 95)

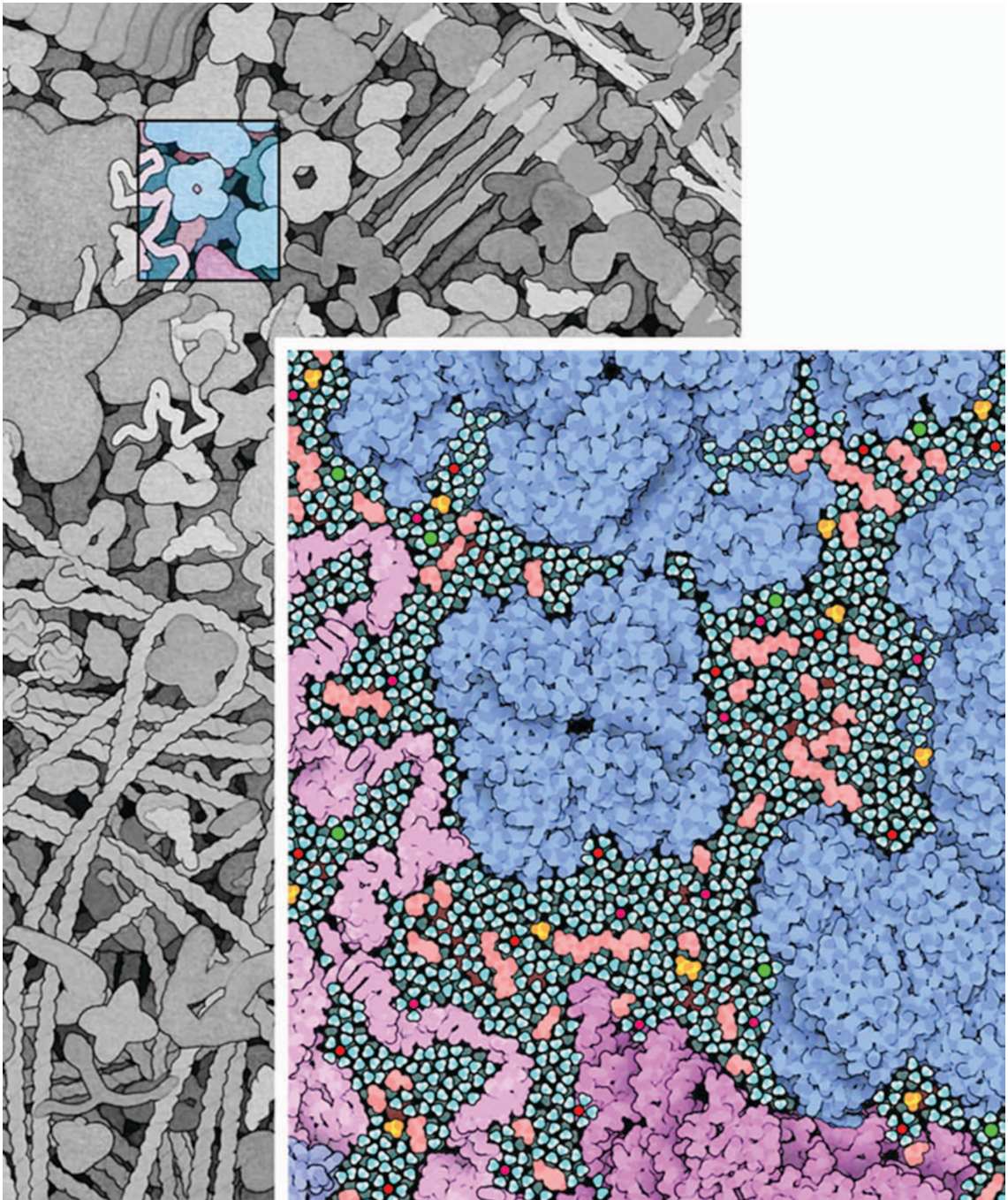


Plate 9. The crowded interior of the cell. The cytoplasm of the bacterium *Escherichia coli* at high magnification, showing the crowding of small molecules (water, ions, small metabolites) between the larger proteins and nucleic acids. The smallest molecules shown are water; note how few water molecules there may be between macromolecules. (Image courtesy David Goodsell, reproduced with permission of Springer-Verlag). (see pages 98, 102, and 114)



Plate 10. An immature *Trematomus bernachii* resting on ice in McMurdo Sound. The presence of antifreeze in this fish means that it does not freeze despite being in intimate contact with ice. (Image courtesy Paul Cziko)



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Plate 12. An example of a series of nunataks, the Behrendt Mountains in Antarctica. These isolated nunataks support microbial and microinvertebrate life, and may represent the coldest habitat with life on Earth. (Image courtesy Pete Convey, British Antarctic Survey). (see page 310)

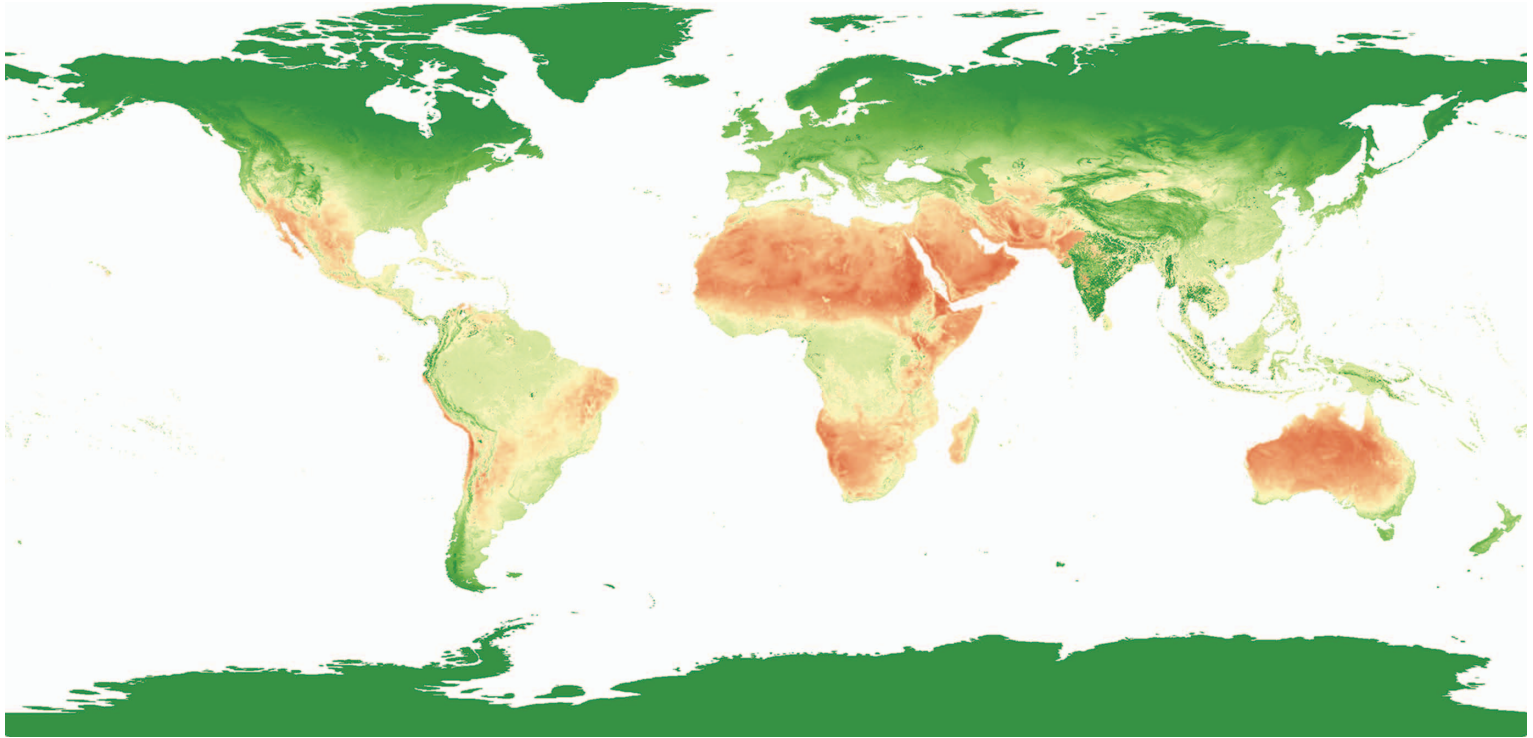


Plate 13. Map showing mean annual temperatures on land, 2002–2013. Data range from $< -10\text{ }^{\circ}\text{C}$ (green) to $> 30\text{ }^{\circ}\text{C}$ (red). Data from NASA MODIS Aqua satellite. Map courtesy Andrew Fleming, British Antarctic Survey. (see page 313)

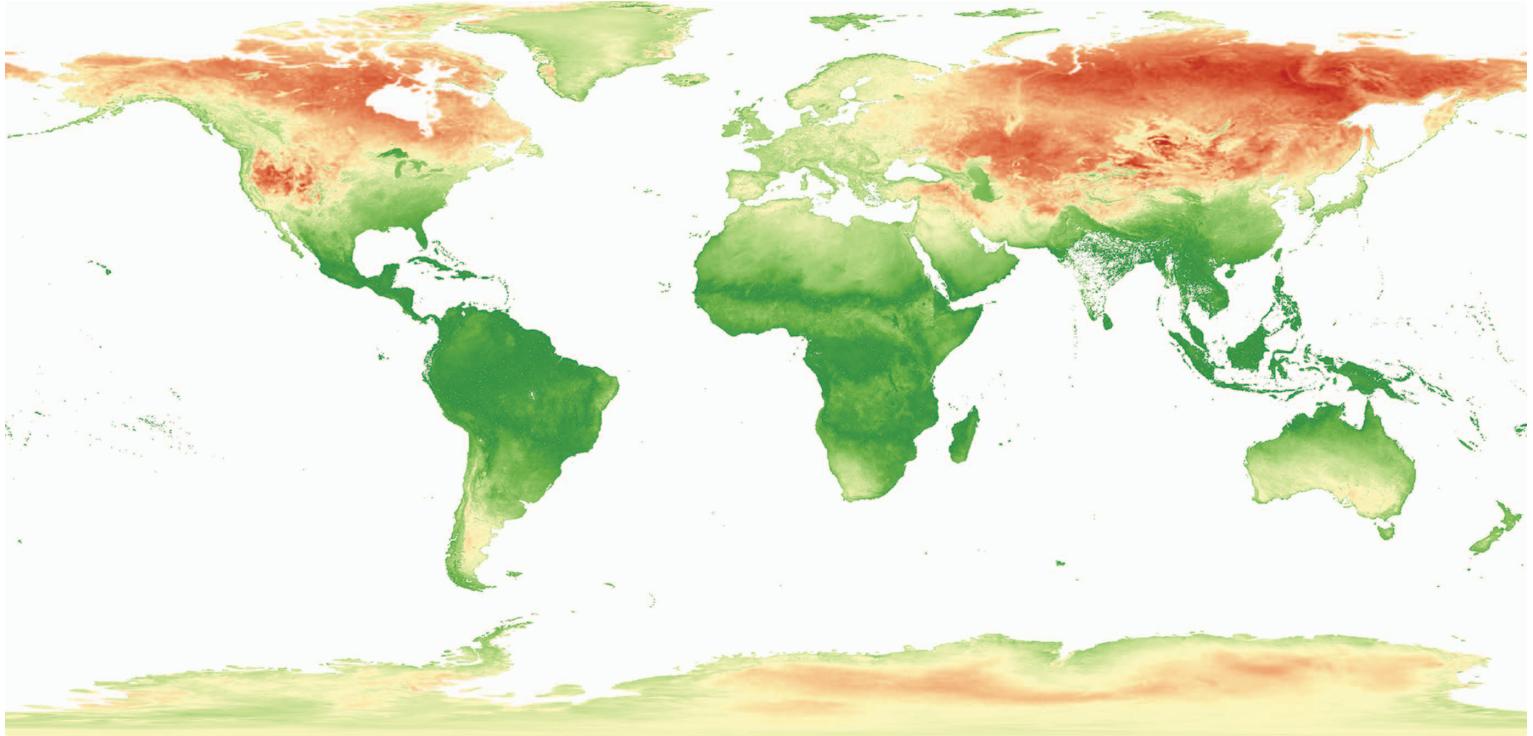


Plate 14. Map showing seasonality of temperature (mean difference between January and June temperatures). Data range from < 10 K (green) to > 40 K (red). Data from NASA MODIS Aqua satellite. Map courtesy Andrew Fleming, British Antarctic Survey. (see page 313)

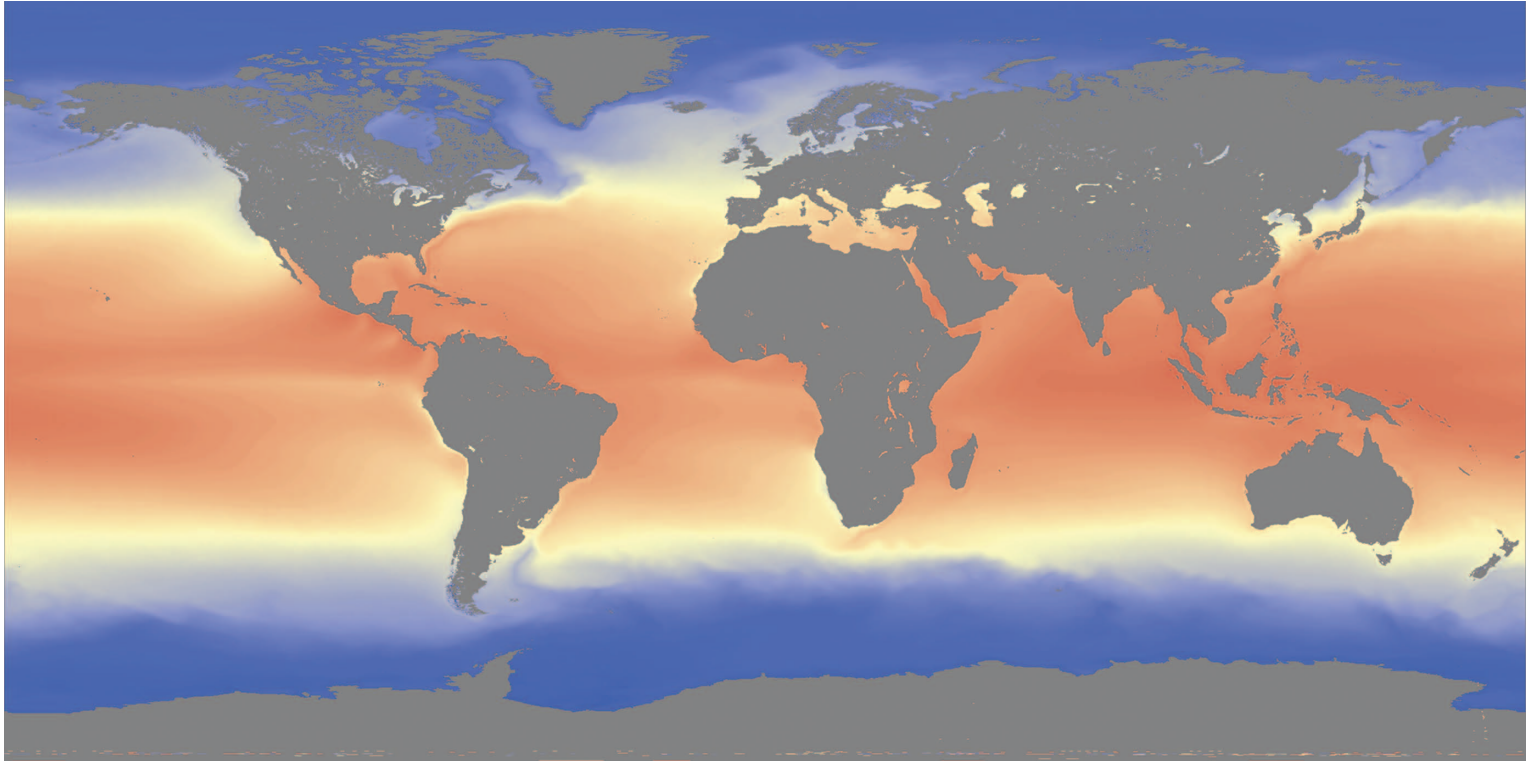


Plate 15. Map showing mean sea surface temperature, 2002–2013. Data range from $< 0\text{ }^{\circ}\text{C}$ (blue) to $> 28\text{ }^{\circ}\text{C}$ (red). Data from NASA MODIS Aqua satellite. Map courtesy Andrew Fleming, British Antarctic Survey. (see page 315)

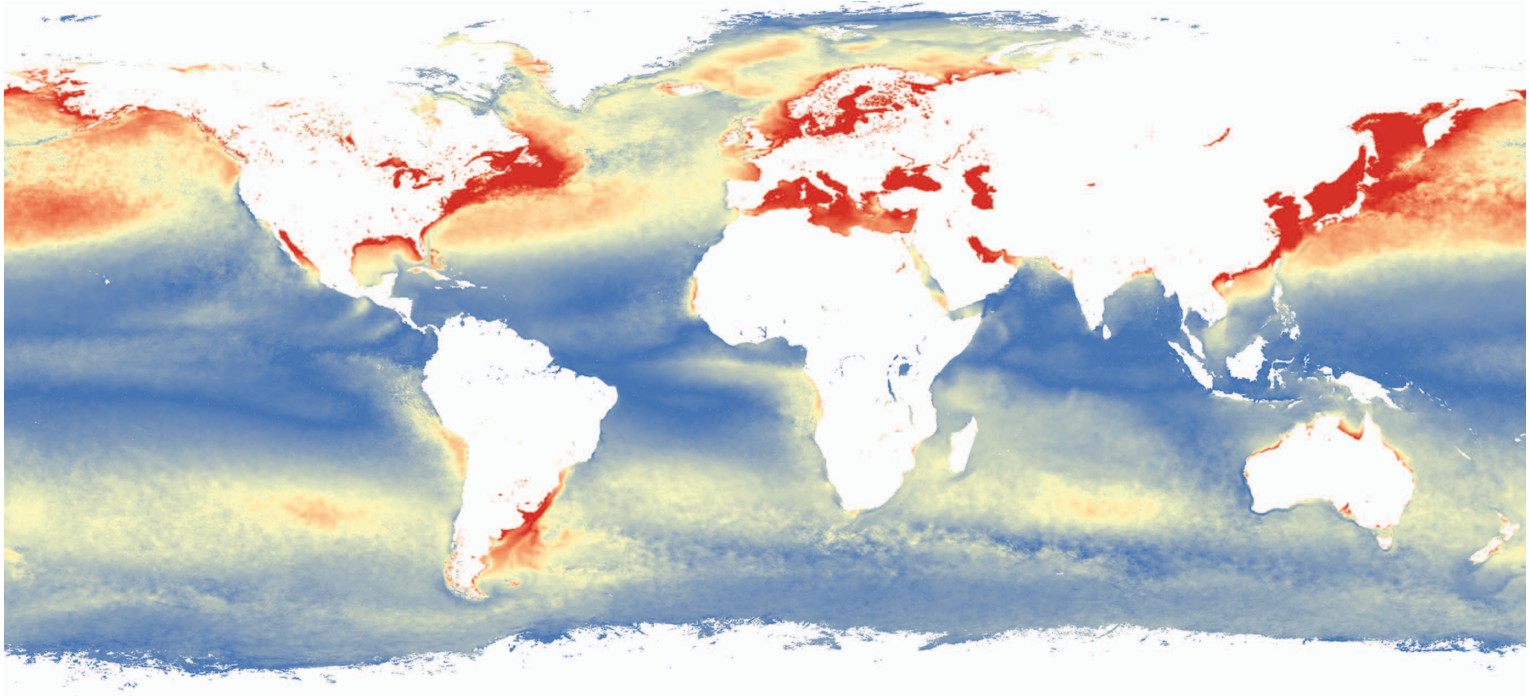


Plate 16. Map showing seasonality of sea surface temperature (mean difference between January and June temperatures). Data range from < 5 K (blue) to > 20 K (red). Data from NASA MODIS Aqua satellite. Map courtesy Andrew Fleming, British Antarctic Survey. (see page 315)

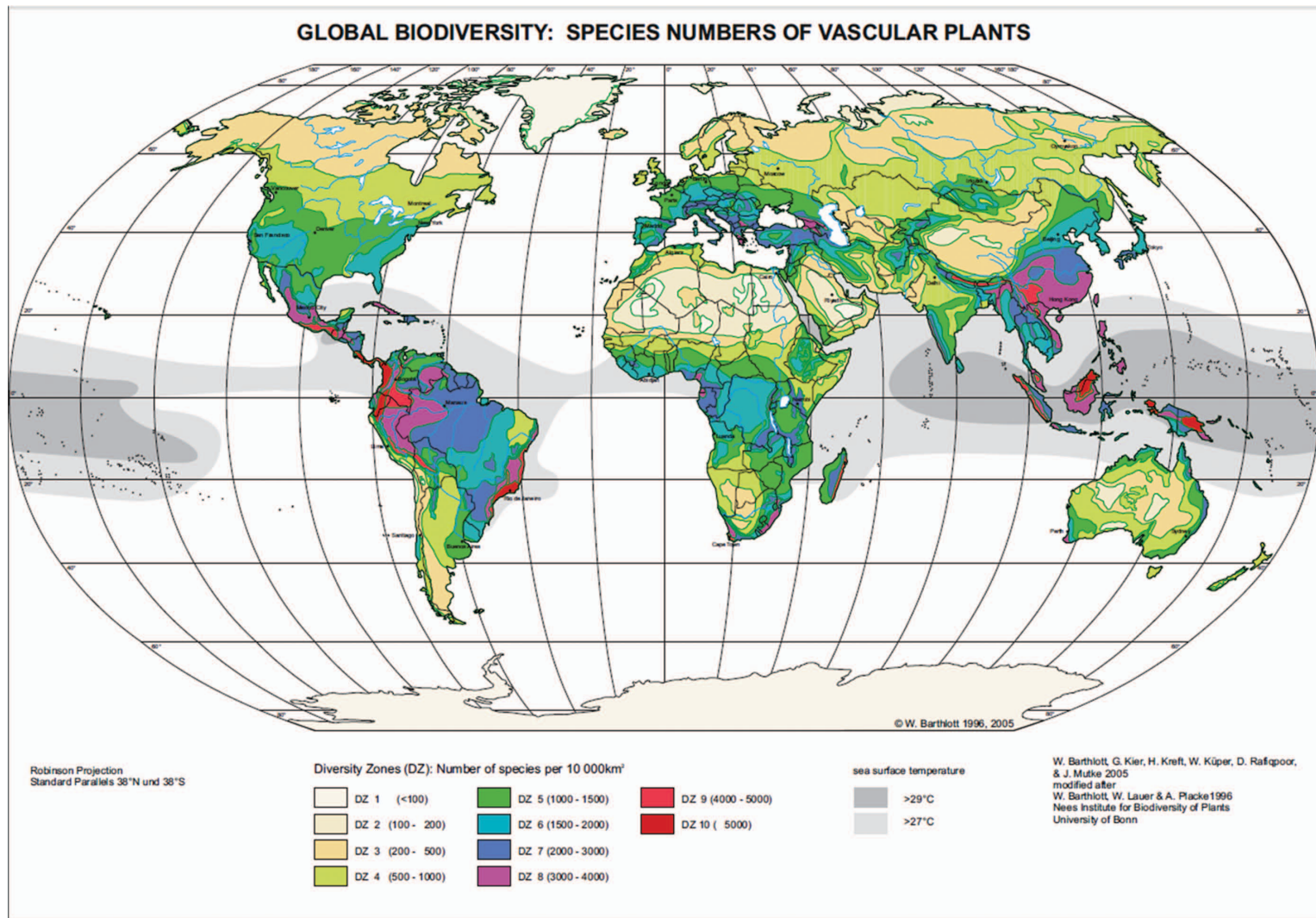


Plate 17. Map of flowering plant species diversity, plotted as number of species per 10 000 km². Map courtesy Wilhelm Barthlott, University of Bonn. (see pages 333 and 342)

Introduction

With the ratification of long tradition, the biologist goes forth, thermometer in hand, and measures the effects of temperature on every parameter of life. Lack of sophistication poses no barrier; heat storage and exchange may be ignored or Arrhenius abused; but temperature is, after time, our favourite abscissa. One doesn't have to be a card-carrying thermodynamicist to wield a thermometer.

Steven Vogel¹

Temperature affects everything. It influences all aspects of the physical environment and governs any process that involves a flow of energy, setting boundaries on what an organism can or cannot do. Temperature is at once the most pervasive aspect of the environment in relation to the physiology and ecology of organisms, and also probably the most frequently measured. But, as Steven Vogel expressed so memorably (above), ecologists are not always rigorous in their approach to temperature. Even today it is possible to find newly published studies which confuse temperature with energy, or muddle temperature and heat.

This book is not intended to be a thorough review of the entire field of thermal ecology. It could not be, for the field is now so enormous that any such review would be massive and unreadable². Instead my aim is to provide a simple path through the subject, hoping that the key principles emerge clearly.

When dealing with a subject as vast as the relationship between organisms and temperature, it is helpful to break the subject down into manageable blocks. The material in this book falls into three basic broad topic areas:

1. The flow of energy in and out of the organism.
2. The influence of temperature on what an organism can do.
3. How these affect the way an organism interacts with its environment, including other organisms around it.

This is a fairly traditional approach but it allows us to establish a rigorous framework for understanding how organisms perform before we move to the ecological consequences.

The first four chapters deal with physics. Why physics in an ecology book? The short answer is because it is important, and while the basics of thermal physics can be found in any standard textbook they are not always presented in a way that is helpful to an ecologist. The book therefore opens with a simple treatment of energy, work and heat (these are not the same things) and then relates these to temperature (which is different again); these topics are covered in Chapters 2 and 3. This involves the tackling some simple thermodynamics, but despite this subject's daunting reputation the basic concepts are straightforward and they lay important foundations for a treatment of how organisms exchange energy with the environment (Chapter 4).

The next two chapters (5 and 6) could be seen as forming what musicians would call a bridge passage, in that they link the thermal physics section with the thermal physiology that follows. The first of these chapters is concerned with water. Organisms are mostly water and water is a most unusual substance. So unusual in fact that its quirks and peculiarities are integral to why life on Earth exists at all. Moreover, the way water behaves as its temperature changes affects all of physiology and ecology. Without water there is no life and

without an understanding of water's eccentricities our knowledge of physiology is incomplete. The chapter that follows then deals with what happens when water freezes, a more widespread ecological challenge than is often appreciated.

The central section deals with the relationship between organism performance and temperature. The first chapter of this section (7) tackles the fundamentals of how reaction rate is affected by temperature, including the important issue of how best to capture this relationship mathematically. This leads naturally to a discussion of metabolism at the whole organism level (Chapter 8). The next two chapters deal with the regulation of body temperature, first in ectotherms (Chapter 9) and then in mammals and birds (Chapter 10). Endothermy allows mammals and birds to maintain a high and stable body temperature, but it is expensive, and so when food is short it can be relaxed either by short-term torpor or longer-term hibernation (Chapter 11). We follow this by examining a highly influential attempt to build a coherent integrated theory of how temperature affects whole-organism metabolism, the Metabolic Theory of Ecology (Chapter 12). Finally in this section we explore how temperature and energy influence the adult size of an organism, and how fast it grows to achieve this (Chapter 13).

In the final section we explore thermal ecology itself. Having examined how just one feature of the environment, temperature, affects organism performance, we now add the important extra dimension of interactions with other organisms. The first chapter (14) sets the scene by examining the broad-scale relationship between temperature and life on Earth. In it we explore what might be the thermal limits to life on Earth, asking whether there is anywhere on the planet with liquid water at temperatures that preclude life. This is also something of a bridge chapter, and it is followed (Chapter 15) by an examination of the potential links between temperature, climate and diversity, asking the question of how (if at all) purely physical factors influence the number and variety of species living in a particular place. This chapter also touches upon the important aspect of deep time.

We then tackle the important subject of how organisms are responding to climate change (Chapter 16). This is such an important topic that it requires a detailed treatment. We start by seeing how the Earth's

climate is regulated and why it is now changing. This necessitates some atmospheric physics and a little oceanography, because a thorough grasp of the way climate is regulated is essential for understanding its effects on organisms. It also needs a strong historical perspective because it is only once we can distinguish long-term climate change caused by man from the natural variability that characterises the Earth's climate system that we can understand what is happening to the flora and fauna. This chapter may spring a surprise or two, for not all of the much-discussed examples of recent climate change are necessarily caused by man and his activities (but many others are). The book then concludes with a very brief survey of what I believe to be the principles of thermal ecology.

In many of the physiological and ecological chapters I have taken time to introduce the basics of the topic before moving on to explore the influence of temperature. For example in discussing the way temperature influences metabolism in Chapter 8 I first lay out some of the principal features of metabolism. While this might seem to be duplicating material to be found in any standard physiology or ecology text, it is important. 'Metabolism' can mean different things to physiologists and ecologists, so I feel it is essential to establish precisely what I mean by the term. I have taken a similar approach in discussing the influence of temperature on growth and its relationship with diversity³.

Examples are important and I have used these extensively, mixing classic studies with more recent work and where possible selecting examples from all continents and across diverse taxa. I have also, quite deliberately, concentrated on referring back in history to the key studies that defined particular disciplines. These are two reasons for this (well, the third is that I find the history fascinating). The first is that, as the French philosopher Auguste Comte famously commented, to understand a science it is necessary to know its history. In some cases, such as thermodynamics, history provides a clear and logical way to introduce a potentially difficult topic; in others, such as temperature, it is simply a fascinating intellectual story.

The second reason is that modern science advances so rapidly that for students starting out on a research career there is often little time to look backwards at where and how their chosen topic of

study arose. The requisite nod to the development of the topic typically consists of citation to a popular recent review article (often unread). While this is understandable, it is also unfortunate: the field of thermal ecology has several examples of old concepts being rediscovered, or inadvertently renamed, and presented as novel. It is a salutary lesson to explore history, especially as it can remind us that the pioneers of our science were smart.

1.1 A note on units

I have standardised on the use of SI units. These will be familiar to anyone with a scientific or engineering background. The SI (Système international d'unités) was developed in France and adopted at about the same time as the Greenwich meridian was taken to define zero longitude. Ironically, given the subject of this book, SI units are least strictly observed in the field of temperature. The SI unit of temperature is the Kelvin (K, not °K, as we shall see in Chapter 3), but ecologists rarely use this because it is inconvenient over the range of temperatures in which they are most interested. Instead we use Celsius, while in North America Fahrenheit is still widely used domestically. In this book I have opted for clarity and given temperatures in Celsius, but with the SI unit added where needed.

However for technical reasons that are discussed in Chapter 3, wherever temperatures are manipulated mathematically, I have used exclusively SI units. This leads to a slightly unfamiliar presentation where a particular temperature may be given in Celsius, as this is familiar, but temperature differences and rates are given in SI units (for example the difference between the melting and boiling point of water is 100 K, and rates of temperature change are given as K per unit time). This approach is not always intuitive, and can cause problems with some referees and journal editors, but it is rigorous and I remain unrepentant.

1.2 General principles and the importance of natural history

Ecologists are a varied bunch. Some are motivated by finding general principles, others are interested in why various species do things differently. I am fascinated by both. I want to know how and to

what extent organisms are constrained by the laws of physics, and I have spent most of my professional life thinking about how temperature affects organisms. As an undergraduate I spent a summer field season in Svalbard and like many before me, and since, I became fascinated by the polar regions. For my doctoral thesis I worked for over two years in the Antarctic, at South Georgia. My animal (we always think of the species we work on as 'our' animal) was a small benthic shrimp, *Chorismus antarcticus*, and I became intrigued as to why this species showed such marked seasonality in its growth when the annual variation in seawater temperature was only a few degrees. I had been taught by ecologists who knew the North-East Atlantic where everything was (apparently) driven by seasonal temperature change, and yet this omnivorous animal remained highly seasonal in an environment that was only mildly seasonal in terms of temperature. I was perplexed. And why, despite the low temperature of the water, did it grow so fast in summer? Was its growth limited by food, or temperature or both? These questions have continued to fascinate, for as is so often the case in ecology, simple questions turn out to have complex answers.

As well as pursuing a career as a professional ecologist, I have been a birder for as long as I can remember. The process of learning to identify birds raised quite different questions. I grew up in England where we have three leaf-warblers (*Phylloscopus*), similar in appearance but with different songs. Careful work by the early naturalists had established the subtle differences in habitat that meant you tended not to find all three species together, but when I eventually made it to the Himalaya and far eastern Asia I was confronted with a bewildering array of species of leaf-warblers which defied immediate explanation⁴.

These are the two contrasting features of ecology: the simple underlying rules and the bewildering detail. These two ways of looking at ecology are not, or should not be, mutually exclusive. Their interplay can be exemplified by a plot of basal metabolic rate as a function of size (Figure 1.1). I have chosen to plot data for fish, as these data came from a study of fish energetics I did with Nadine Johnston in the 1990s, but I could equally have used data for mammals, birds, reptiles, insects or any one of several groups of marine invertebrates.

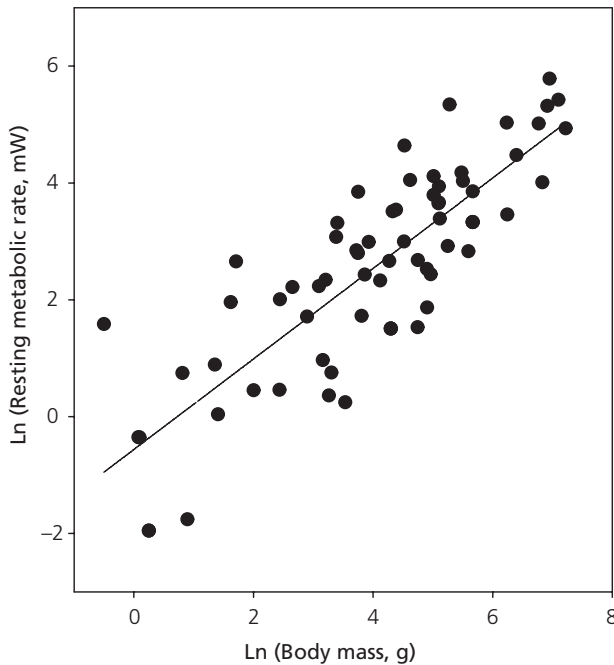


Figure 1.1 Standard metabolic rate in teleost fish as a function of body mass. Each data point represents the standard metabolic rate of a fish of the median body mass for the fish used in the original study. There is one data point per species, and the data have not been corrected for temperature. Metabolic rate data have been converted to SI units before plotting, and the line is fitted by least-squares linear regression.

This plot has three key features. The first is so obvious that it might easily be overlooked: the plot is clearly linear. To achieve this, however, both variables have been transformed (in this case to natural logs). The second feature is that the relationship has a clearly defined slope, and the third is that there is marked variance about the line.

The slope of a fitted least-squares regression line is less than unity (it is actually 0.78 for this data set). Since we might have expected the slope to be unity, so that a doubling of size would lead to a doubling of oxygen demand, a slope of 0.78 suggests the influence of one or more constraints of some type. Much effort has gone into elucidating what the constraint(s) might be, and why the slope is what it is (this is discussed in Chapters 8 and 12). The variance about the line reflects ecological variety and is a measure of the extent to which evolution has been able to work around these constraints. In simple terms, the slope reflects the constraint(s) of physics and the variance reflects evolution and ecology. To see ecology in the round we have to understand both: we need to recognise the constraints under which organisms operate, and the extent to which these can be circumvented.

In recent years there has been a dramatic revival of interest in broad patterns in ecology. A key

factor in this has been the availability of electronic data storage and powerful computers for analysis, but the raw material for these broad-scale analyses stems from the dedicated work of thousands of fieldworkers and natural historians, professional and amateur, who have documented the details of the lives of myriads of organisms from all over the world. Sometimes satirised by the ignorant as ‘stamp collecting’ or ‘pebble counting’, this enormous body of work provides the basis without which ecological generalisations would not be possible.

The analysis of large ecological data sets to detect patterns over large spatial scales (typically continental or global) has become known as macroecology. More recently the analysis of patterns in the physiological performance of organisms over similarly large scales has been termed macrophysiology⁵. Both will feature throughout this book.

Macroecology and macrophysiology involve the statistical analysis of large data sets. These analyses range from the simple, concentrating on defining the dominant patterns, to the highly complex, examining the subtle ecological signals contained in the variance. Which approach is best depends on the question of interest. There is, however, an

important point which is often missed in the strident arguments to be found in this literature: the nature of the individual.

The mathematics that describe the behaviour of atoms and provide our understanding of the effect of temperature on chemical reactions (discussed in Chapter 7) assume that all the atoms in the population are identical: one atom of oxygen or one molecule of glucose behaves exactly as another. On this assumption are built simple equations that describe the bulk behaviour of a large number of atoms or molecules to a very high degree of accuracy and precision.

Organisms are not like this: every species is different from all others, for each has a unique evolutionary history. This history is reflected in the chemical makeup of the species: indeed we use differences in nucleic acid chemistry to reconstruct that history. Furthermore, not all individuals within a species are identical, either in their history or their physiological performance. The statistical techniques used by ecologists were developed specifically to cope with this variability between individuals⁶.

There is a really important issue here: the extra variability introduced by the process of evolution makes it difficult to predict the thermal behaviour of an organism from first principles. We cannot, for example, start from physics and build a mechanistic model of how insect metabolism will (or should) vary with habitat temperature; its physiology is just too complicated. Furthermore even if we could do this, the variability between individuals of a species means that the answer would be different for each and every individual. All we can do is observe how metabolism varies with temperature in the species of interest and describe the relationship statistically. The results of such an analysis may point to the existence of a constraint (as in Figure 1.1), and may even give hints as to what that constraint might be. We need to remember, however, that a description is all that it is. If we want to use the relationship to predict what might happen in different circumstances, say for an organism larger than any in the data set, or for a different temperature, we have to be careful. If we do not know the mechanism underpinning the pattern we describe, and typically we do not, we cannot know how reliable our prediction is.

This emphasises how important it is to have an interplay between ecologists interested in fundamental principles who aim for simple patterns and ecologists interested in the natural history underpinning the variability in the observed patterns. Neither is complete in itself, and both are essential to our understanding of Nature. We could not have a better example of this than in the famous final paragraph of Darwin's *Origin of species*, which captures both the profundity of Darwin's grasp of a simple fundamental process and his wonder at the outcome.

Notes

1. This quotation comes from the opening chapter of Steven Vogel's delightful book *Life in moving fluids* (Vogel 1981). Reproduced with permission of Princeton University Press.
2. The thorough review by Precht et al. (1953) runs to 779 pages, and the field has grown enormously since then.
3. Definitions are important for clarity of communication, in science as elsewhere. Otherwise we live in the looking-glass world, where as Humpty Dumpty said to Alice 'When I use a word . . . it means just what I choose it to mean — neither more nor less'. This comes from Lewis Carroll's *Through the looking-glass, and what Alice found there* (1871).
4. It was the English parson and naturalist Gilbert White (1720–1793) who first recognised the differences between *Phylloscopus collybita* (Chiffchaff), *Phylloscopus trochilus* (Willow Warbler) and *Phylloscopus sibilatrix* (Wood Warbler), and described these in his famous collection of letters to Thomas Pennant and other leading naturalists, *The natural history and antiquities of Selbourne* (1789). The Himalaya is now recognised as the centre of diversification for leaf-warblers (Family Phylloscopidae). The classic description is Ticehurst (1938), and a modern review is Price (2010).
5. The term 'macroecology' was coined by James Brown and Brian Maurer in a paper in *Science* in 1989. Both subsequently developed the idea in books (Brown, 1995; Maurer 1999). Macrophysiology was introduced by Chown et al. (2004) and Gaston et al. (2009).
6. The foundations of ecological statistics were laid by the English mathematician and biologist Sir Ronald Fisher (1890–1962). Of particular importance was his development of analysis of variance (ANOVA) and maximum likelihood techniques (see Fisher et al. 1943). He was one of the founders, along with J.B.S. Haldane and Sewall Wright, of population genetics.

Energy and heat

It frequently happens, that in the ordinary affairs and occupations of life, opportunities present themselves of contemplating some of the most curious operations of nature; and very interesting philosophical experiments might often be made, almost without trouble or expence (*sic*) by means of machinery contrived for the mere mechanical purposes of the arts and manufactures.

Count Rumford (Benjamin Thompson)¹

No ecologist wanting to understand how organisms interact with their environment can afford to ignore the fundamental aspects of energy and how it flows. Whether our concern is a bacterium in a hot spring, a lichen on a frozen mountain-top or a coral on a tropical reef, we need to know what heat is, why energy flows and how heat and temperature are related.

In this chapter we will examine the nature of energy and heat, laying the foundation for the discussion of temperature that follows. In doing so, we will introduce some key concepts from thermodynamics. This is a topic which frightens many a biologist, but it need not. The basic ideas are straightforward (well, maybe except for entropy) and a grasp of these is important for any ecologist interested in temperature, metabolism or energy flow. It will help avoid some of the mistakes which can still be found in the ecological literature, where it is not uncommon to see heat and temperature confused, entropy misunderstood and some fundamental concepts ignored.

Part of the reason for this may be that heat and temperature are such familiar features of everyday life that we feel intuitively we understand them. Like many animals we possess sensors which give us an indication of the temperature of both ourselves and our environment, sensors that are essential to our wellbeing. They tell us when we are too warm or too cool, and they warn us that fires are

hot and ice is cold. And yet these very same sensory systems also make us aware that things may not be quite so straightforward. For example steel feels cold whereas wood feels warm, even when we know instinctively (or can show with a thermometer) they are actually at the same temperature. And once we had thermometers to hand, we could see that objects supplied with the same amount of heat change temperature at different rates. It is even possible for considerable quantities of heat to be supplied to an object while its temperature remains unmoved, as in the melting of ice.

Clearly temperature and heat are different things. While a grasp of this difference goes back, as so often in science, to the ancient Greeks, the modern science of thermodynamics only developed at the time of the Industrial Revolution in the late eighteenth and early nineteenth centuries. Although the two events are often linked causally, the improvement in the performance of steam engines actually proceeded quite independently of the intellectual formulation of concepts of heat and energy. Indeed the Industrial Revolution was well underway, with locomotives pulling trains and steam engines powering industry, decades before the concept of energy was developed².

Energy is central to the thermal ecology of organisms, and so we start by examining this most basic topic of all.

2.1 Energy

Energy is one of the fundamental concepts in all of science, and the flow of energy has been central to our view of how organisms and ecosystems function since the very start of ecology. We might therefore expect physicists to have a very clear idea of what energy is. Surprisingly, this is not so.

2.1.1 What is energy?

Ask any scientist what energy is and you are likely to get the reply that energy is *the capacity to do work*. This is the definition we were probably all taught at school³. The problem with this definition, however, is that it tells us what energy *does*, not what energy *is*. Moreover, it leaves us with the problem of then explaining the nature of work. One reason that energy is so difficult to define or describe, and thus remained elusive for so long, is that unlike physical quantities such as mass, volume or pressure, it is not directly measurable. We cannot place an object into an instrument and obtain a measure of its energy content; all we can do is infer its energy from other characteristics, such as its temperature or the ability to do work⁴.

This difficulty was explained in typically idiosyncratic style by Richard Feynman in his famous *Lectures on physics*⁵:

There is a fact, or if you wish, a law, governing all natural phenomena that are known to date. There is no known exception to this law—it is exact as far as we know. The law is called the conservation of energy. It states that there is a certain quantity, which we call energy, that does not change in the manifold changes which nature undergoes. That is a most abstract idea, because it is a mathematical principle; it says that there is a numerical quantity which does not change when something happens. It is not a description of a mechanism, or anything concrete; it is just a strange fact that we can calculate some number and when we finish watching nature go through her tricks and calculate the number again, it is the same.

This might imply that the conservation of energy, which we now recognise as one of the most fundamental laws of physics, is little more than an accounting device. The power of the idea of the conservation of energy is that once it was realised

that energy could be converted between its different forms, but could never be created or destroyed, then scientists had a window into the most basic operation of the universe, and a powerful rule that has never been found to be broken⁶.

2.2 The First Law of Thermodynamics

The principle of the conservation of energy is now formalised as the First Law of Thermodynamics. A typical statement of the first law is:

Energy can neither be created nor destroyed, but only changed from one form to another.

No principle such as this ever springs fully formulated into the scientific consciousness, and the essential idea underpinning the first law was formulated by the Swiss-born Russian chemist Germain Hess in 1840. Hess recognised that the energy change for a reaction that takes place in a series of steps was identical to the sum of the energy changes at each individual step. Then in 1841, the German Julius Robert von Mayer enunciated one of the original statements of the conservation of energy, when he stated that *energy can be neither created nor destroyed*⁷.

The First Law has important consequences for ecologists concerned with the flow of energy through organisms or ecosystems: it tells us that the inputs and outputs must balance, exactly. If the energy inputs are not accounted for by the sum of all outputs, then something has been missed. This may well be a result of failing to track energy that changes in form within the organism, particularly energy dissipated to the environment as heat.

We now recognise that all conservation laws in physics are a reflection of fundamental symmetries in nature, a relationship known as Noether's theorem⁸. The conservation of energy is an inevitable consequence of the symmetry (or invariance) of the laws of physics with time. An example of this symmetry would be the physicist's familiar model of colliding billiard balls. If we were to film one ball striking another and then replay the film in reverse, it would look perfectly natural. Indeed without ancillary information it would be impossible to decide which of the two versions of the film was the original. This is because the equations that describe

how billiard balls interact are invariant with respect to time: Newton's laws of motion work just as well backwards as forwards. The same applies to motion such as the orbiting of the Moon about the Earth, or the planets around the Sun.

This is fine theoretically, but we are all familiar with processes in everyday life that are clearly irreversible and move only forwards in time, such as the burning of wood in a fire. Biological examples might be the development of an embryo into an adult organism, a cheetah eating a gazelle or the decay of a plant cut down and left to rot on the compost heap. These do not indicate, as was once thought, that there is something special about the energetics of living things. But they do exemplify what the physicist Arthur Eddington called the *arrow of time*, and they indicate that something else is involved⁹. Quite what that something is we will return to later.

2.2.1 Potential energy and kinetic energy

All forms of energy can be classified into one of two fundamental categories, potential energy and kinetic energy (Box 2.1). Potential energy is energy a body has by virtue of its position, for example a body's gravitational potential energy depends on

that body's position in the gravitational field. Kinetic energy is energy a body has by virtue of its motion.

This classification is useful in clarifying different forms of energy, but it still does not tell us what energy is. Neither does it resolve the nature of the relationship between energy and work, or tell us whether all forms of energy are the same thing. These are deep and troubling questions which go to the very heart of nature, for as we now know there are circumstances under which energy and matter can be converted and energy is linked intimately with the nature of time.

2.2.2 Interconversion of energy and mass

Our intuition might suggest that mass and energy are different things: a given amount of matter, say a lump of copper, should have a particular mass (the amount of copper) and contain a defined amount of energy. However, since the work of Albert Einstein we have known that mass can be converted to energy, and vice versa¹⁰. The mathematical relationship between mass and energy is captured in perhaps the most famous equation in all of science:

$$E = mc^2$$

Box 2.1 Potential and kinetic energy

Physicists divide energy into *potential energy*, which is energy a body possesses by virtue of its position, and *kinetic energy*, which is energy a body possesses by virtue of its motion. All the familiar forms of energy can be assigned to one of these two fundamental categories.

Kinetic energy	Potential energy
Kinetic energy	Gravitational energy
Radiation energy	Electrodynamic (magnetic) energy
	Electrostatic energy
	Chemical (bond) energy
	Elastic energy

This simple classification encapsulates some surprising ideas. For example, that the mechanics of light (photons) can

be treated identically to that of matter, and so radiation is a form of kinetic energy. Note that thermal energy is not listed explicitly, as this is a form of kinetic energy. Some physicists would also classify mass as a form of potential energy, but the interconversion of mass and energy is not relevant to ecology so we do not do so here.

In considering potential energy, it is also important to determine the limits to the system under consideration, if only to make the mathematics tractable. For example, in calculating the change in gravitational potential energy of a body taken to the top of a mountain, we focus on the gravitational field of the Earth, but ignore that of the Sun. This is because the change in potential energy from the Sun's gravitational field over this distance is very small. In contrast, for calculating the orbits of the planets or the trajectory of a spacecraft, then the gravitational field of the Sun is critical, as are those of the planets, but we can ignore that of the nearby stars.

where E is the energy, m is the mass and c is the velocity of light *in vacuo*¹¹. One consequence of this equivalence is that mass is sometimes regarded as a form of potential energy (Box 2.1).

The very large value of c means that a tiny amount of mass is equivalent to an enormous amount of energy. For example, the difference in mass between a helium nucleus and the two protons and two neutrons from which it is forged is extremely small, but the energy released in nuclear fusion when helium is formed from hydrogen is what makes the Sun shine, and thereby is the source of energy of most biological energy on Earth.

It is worth noting in passing that there can be very small changes in mass during chemical reactions, caused by the difference in bond energies between the initial reactants and the final products. Strictly, what is conserved in a chemical reaction is thus mass plus energy. However the changes in mass are so small that while important theoretically, they are of no practical relevance to the flows of energy involved in physiology or ecology, and we will ignore them from now on.

2.2.3 Energy and work

If we are to understand the nature of energy in relation to organisms, it is necessary first to have a clear idea of the various forms of energy, the nature of work and how these are related.

A simple introduction to the concept of work is to consider what is involved in lifting a heavy object. Here work is being done against gravity, and the amount of work done is calculated simply by multiplying the weight of the object by the height through which it was lifted. Since weight is a force this relationship can be generalised: work is done when any kind of force is exerted through a distance, and the work can be calculated as the product of the force and the distance. For our example of a heavy object being lifted, the work done is given by:

$$W = mg\Delta h$$

where m is the mass of the object, g the acceleration of free fall and Δh the height through which the body was lifted. Note the mathematical convention here: Δ symbolises a finite, measurable, difference,

so Δh is the difference between the height of the object before being lifted and its height afterwards¹².

Whenever a body does work on its surroundings, that body loses energy equivalent to the work done. Equally when a system does work on a body, that body gains energy equivalent to the work done. Work and energy thus have the same dimensions and units. In lifting a heavy object such as a suitcase against gravity, we have done some work. This work has been done on the suitcase, and the suitcase has thereby gained potential energy. Recall that potential energy is energy that an object has by virtue of its position in a field, in this case the Earth's gravitational field. So here the change in potential energy, ΔE_p , is a function of the gravitational field (mg) and the change of position within that field (Δh):

$$\Delta E_p = mg\Delta h$$

It is immediately obvious from these two equations that the gain in potential energy of the suitcase is identical to the work done in lifting it against gravity.

Let us change the example slightly and consider lifting a ball from the floor. As with the suitcase example above, here we have done work on the ball, lifting it against the force of gravity, and the ball has gained potential energy equivalent exactly to the work done. If we then allow the ball to fall to the ground, it gains energy of a much more obvious kind: it starts to accelerate and gains kinetic energy (Figure 2.1). As the ball falls it loses potential energy, because it is moving through the gravitational field of the Earth, but gains kinetic energy in exact proportion. Total energy is conserved (the First Law), but the nature of that energy has changed. The kinetic energy, E_k , is given by:

$$E_k = \frac{mv^2}{2}$$

where m is the mass of the ball and v its velocity.

When the ball hits the ground the kinetic energy is converted briefly to elastic potential energy, which is then immediately converted back to kinetic energy as the ball bounces. The ball slows as it rises, with kinetic energy being converted back to gravitational potential energy. Were this a perfectly elastic collision, the ball would return exactly to the

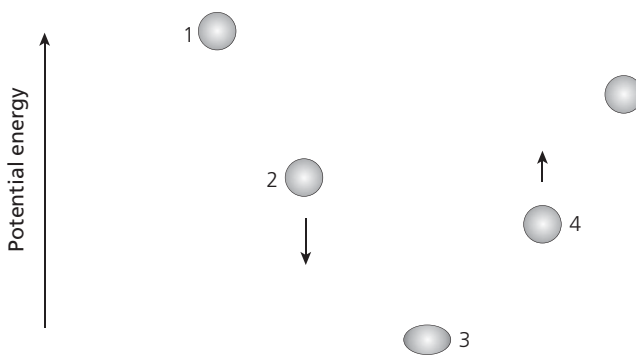


Figure 2.1 A bouncing ball shows the interconversion of potential energy and kinetic energy. At 1 the ball is stationary with a potential energy dictated by its height above the ground. On being released the ball gains kinetic energy as it accelerates down (2), in direct proportion to the decrease in potential energy. When the ball hits the ground (3) the kinetic energy is converted briefly to elastic potential energy, with some also going to other forms of energy such as sound and frictional heat. The ball then rebounds (4) as the elastic potential energy is converted to kinetic energy but the ball never reaches the original height (5) because of the conversion of some of the kinetic energy to sound and heat.

height from which it was released. In reality some of the kinetic energy is also converted to heat and sound, and so at each successive bounce the ball rises to a lower height. Although the conversion of kinetic energy to heat and sound is sometimes described loosely as a loss of energy, the First Law is not being broken. It is simply that in the real world the energy is partitioned into a wider range of forms than in an idealised thought experiment. The First Law remains intact.

This simple illustration contrasts very nicely the two fundamental types of energy, potential and kinetic energy, which together these make up the total energy of a body:

$$E = E_k + E_p$$

where E is the total energy, E_k the kinetic energy and E_p the potential energy.

Although we have established the basic principles with simple physical examples, it is worth using these principles to see what is happening in a more complex biological example, namely a bird such as a hawk taking off. Here the bird is doing work against gravity, and the energy for that work comes from chemical energy in the muscles. As the hawk rises its potential energy increases in proportion to the work done. If it spots a prey item, this potential energy is converted to kinetic energy as the hawk stoops. However, as with the bouncing ball, none of these conversions is perfectly efficient and some energy will be dissipated as sound and heat: many birds make noise in flight and in all organisms muscular activity generates heat. The First Law tells us that a budget calculated for the hawk taking off and stooping on prey will only balance if

all of these forms of energy are accounted for. Some of these are very difficult to measure, and this is why it is so difficult to make energy budgets for organisms or ecosystems balance.

2.2.3 Work, energy and heat

For centuries scientists and philosophers had struggled to understand the nature of heat. Although Isaac Newton had suggested in the early eighteenth century that heat was comprised of small particles in motion, the idea that came to dominate science was that heat was a fluid, *caloric*, which was released when heat moved from one body to another. This was proposed by Antoine Lavoisier in 1789 as an alternative to the long-held idea that combustion involved the release of the hypothetical substance *phlogiston*. Lavoisier was an exceptionally careful experimenter, and he gave particular attention to weighing all of the reactants and products in the processes he was studying. Lavoisier became convinced that *phlogiston* did not exist, and instead he proposed that heat was an invisible, tasteless, odourless, weightless fluid, and he called this *caloric fluid*. He postulated, not unreasonably, that hot bodies contained more of this fluid than did cold ones, and that a given body contained a set amount of heat¹³.

The first indication that there was something incomplete in these ideas came from the work of Benjamin Thompson (later Count Rumford, the name by which he is usually known). Rumford spent time in Germany, where he was given the task of supervising the improvement of munitions at the arsenal in Munich. At that time cannons

were produced by casting a solid block of metal and then boring this out (hence the modern term bore for the size of a rifle or artillery piece). Rumford was intrigued by the immense amount of heat produced during the boring process, and he set about measuring this. He devised a deliberately blunt boring tool to maximise the amount of friction, and immersed the cannon in water to measure the heat released. He was surprised to find he could boil the water, and intrigued that the cannon appeared to be the source of an inexhaustible amount of heat: the longer the boring went on, the more heat was produced. Thompson quickly realised that Lavoisier's idea that the cannon contained only a fixed amount of heat, because it contained only so much caloric fluid, could not possibly be correct. He recognised that what was going on was the conversion of work into heat. He was even able to estimate the amount of heat produced by a given amount of work¹⁴.

Very soon afterwards this was followed by the seminal work of James Joule. In a series of very careful experiments, Joule was able to make accurate and precise estimates of both the amount of work involved and the quantity of heat produced, and thereby estimate what he called the *mechanical equivalent of heat*. The apparatus consisted of a paddle wheel which was driven by weights which were allowed to fall through a set distance. The paddle was designed very carefully to move past a series of baffles so that the work was used to heat up the water and not simply move it around, and great care was taken to minimise the loss of heat to the surroundings. What Joule had measured was how much energy it takes to increase the temperature of water, what we now call the heat capacity of water¹⁵.

This early work looked at the world macroscopically, that is at the everyday scale of cannons, billiard balls and hawks. This is the realm of classical thermodynamics and while this is appropriate for exploring the thermal ecology of organisms, it lacks any underlying mechanism. In essence, using the equations of classical thermodynamics we can describe what is going on, and do so in very precise mathematical terms, but we do not know why. To explain what is going on, and provide a mechanism, we need to move to the atomic scale.

2.3 Energy at the atomic scale

An understanding of the mechanisms that explained the properties of bodies described by classical thermodynamics only came with the recognition of the existence of atoms, coupled with the development of the kinetic theory of gases and statistical mechanics (Box 2.2).

Statistical mechanics explains how the concepts of classical thermodynamics, such as temperature or heat, arise from the behaviour of atoms when the number of atoms is so vast that we cannot know what each and every atom is doing individually. Instead we use probability theory to predict the bulk properties that emerge, an approach usually termed statistical thermodynamics.

In any body at a temperature above absolute zero the atoms and molecules that make up that body are in constant motion. For a monoatomic gas such as argon at room temperature, the energy of the gas is essentially all in translation (that is, movement of the atoms in space). For a molecule containing more than one atom then there is also energy of rotation (the molecules are spinning) and of vibration (the two atoms in the molecule are moving closer together and then further apart, as if on a spring, and there are also bending motions). Because of these complications, the basic theory was worked out for what physicists term an *ideal gas*. This is a purely theoretical ideal, where the atoms are point-like and of zero size, undergo perfectly elastic collisions and do not interact (that is, van der Waals forces are ignored).

Because the gas molecules are moving rapidly, and continually colliding with other gas molecules, it might be thought that given sufficient time the energy of the molecules in a gas would even out such that all the molecules have more or less the same energy. Perhaps surprisingly, this is not so. The distribution of molecular speeds in an ideal gas was determined in 1860 by James Clerk Maxwell¹⁶. The distribution is:

$$f(v) = 4\pi \left[\frac{m}{2\pi k_B T} \right]^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}}$$

Here $f(v)$ is the fraction of molecules with speed v , m is the mass of the atom, T is the absolute

Box 2.2 Atomic theory and thermodynamics

Although a number of ancient civilisations appear to have speculated that everyday objects are composed of tiny discrete and indestructible units, the birth of atomism is traditionally ascribed to the Greek philosophers Leucippus and Democritus. Democritus is said to have considered the problem of whether an object could be cut into ever-smaller pieces, or whether there was a point beyond which no further subdivision was possible. He concluded there must be a limit, defined by the Greek adjective *ατομος* (atomos), meaning uncuttable, thereby giving us the word atom. This is captured in his famous statement (one of very few direct quotations from Democritus that survive):

by convention sweet and by convention bitter, by convention hot, by convention cold, by convention colour; but in reality atoms and void

Here Democritus is offering a profound philosophical view of the world, arguing that there is a difference between what our senses tell us and the underlying reality (which remains an important message for any scientist working today). Although Democritus believed that the existence of atoms explained many features of the natural world that were otherwise difficult to understand (such as the ability of salt to dissolve in water, or of fish to swim through the sea), atomism largely disappeared as a view of the world for over two millennia¹⁷.

It was John Dalton, widely regarded as the father of atomic theory, who placed the existence of atoms on a firm theoretical basis with his analysis of the proportions in which elements and chemical compounds combine. His atomic theory comprised five key propositions:

1. Elements are made of extremely small particles (atoms).
2. Atoms of a given element are identical in size, mass and other properties; atoms of different elements differ in size, mass and other properties.
3. Atoms cannot be subdivided, created or destroyed.
4. Atoms of different elements combine in simple whole-number ratios to form chemical compounds.
5. In chemical reactions, atoms are combined, separated or rearranged.

Apart from the slight complications introduced by the existence of isotopes and nuclear processes (notably radioactivity), Dalton's atomic theory remains a cornerstone of chemistry¹⁸.

While a few physicists remained unconvinced of the existence of atoms (most famously Ernst Mach), for the majority the crucial empirical evidence for their existence came from Albert Einstein's 1905 explanation of the Brownian motion of suspended pollen grains as being caused by the impact of rapidly moving water molecules.

temperature and k_B is what we now call Boltzmann's constant. The distribution is determined completely by m and T .

Although the distribution of molecular speeds in oxygen at 20°C looks fairly symmetrical (Figure 2.2), there is a long tail produced by a small fraction of molecules with high speeds. As a result the mean speed (440 m s⁻¹) is slightly higher than the most probable (modal) speed (390 m s⁻¹). However the high frequency of collisions and the consequent small mean free path length (~70 nm for dry air at sea-level) mean that the rate at which an individual molecule covers the linear distance between two fixed points is much slower. This is why it takes time to smell the food after an oven door has been opened¹⁹.

In air the nitrogen molecules are moving slightly faster than the oxygen molecules, and the carbon dioxide molecules slightly slower. The slight differences

in speed are caused solely by the small difference in mass; their kinetic energies are similar because they are continually exchanging energy as they collide.

Maxwell's distribution of molecular speeds was extended to consider the distribution of molecular energy by Ludwig Boltzmann²⁰. Boltzmann's derivation was explicitly statistical and showed that the distribution of energy among identical particles at thermal equilibrium depends only on the mass of the molecule and the temperature of the body. Specifically $f(E)$, the probability that a particle will have energy E , is given by:

$$f(E) = Ae^{-\frac{E}{k_B T}}$$

where A is a normalisation factor (such that $f(E)$ varies between 0 and 1), k_B is the Boltzmann constant and T is the absolute temperature. What this equation tells us is that the higher the temperature,

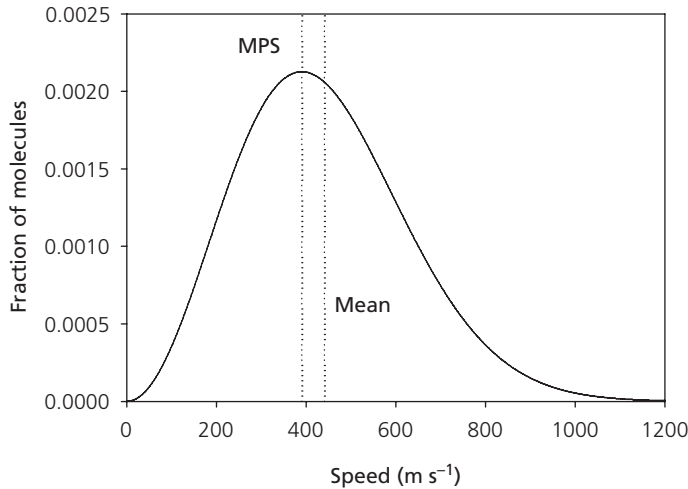


Figure 2.2 The Maxwell–Boltzmann distribution of molecular speeds for oxygen at 20°C. The plot shows the fraction of oxygen molecules that have a speed at, or very close to, a given speed. The dotted lines show the most probable speed (MPS) and the mean speed. Note that the mean speed is slightly higher than the most probable speed because of the long tail comprising a small fraction of molecules with high speeds.

the greater the probability that a particle will have energy E . The Maxwell–Boltzmann distribution of molecular energies is a result of profound importance to thermal ecology.

Statistical approaches are so much a part of the modern ecologist’s toolkit that it is easy to underappreciate just how radically Maxwell and Boltzmann changed our view of the universe. The giants of classical physics, Johannes Kepler, Galileo Galilei and Isaac Newton, had built a view of the universe that was resolutely deterministic (A causes B), and the metaphor they used was that of clockwork. Maxwell and Boltzmann showed that the outcome of any physical process is purely statistical (that is we can only ascribe a likelihood that A will result in B). For the processes dealt with by classical thermodynamics the number of particles involved is so vast that the likelihood is overwhelming, and to all intents and purposes the outcome is deterministic. For some biological processes, however, the number of particles or entities can be sufficiently small that behaviour is far less predictable (an example here would be the number of free protons in the intracellular milieu of the smallest cells).

2.3.1 Characteristic energy, thermodynamic beta and the Boltzmann factor

One important aspect of the Maxwell–Boltzmann distribution is that the average energy of a particle is approximated by $k_B T$. This is sometimes called the

characteristic energy; at 25°C its value is 4.11×10^{-21} J ($= 0.026$ eV), or in macroscopic systems 2.479 kJ mol $^{-1}$. This tells us something important about the nature of Boltzmann’s constant: it is simply the conversion factor between energy and temperature. Its numerical value is set by the units of energy we select and the value we assign to the fixed point that defines the absolute temperature scale.

The inverse of the characteristic energy, β , is of profound significance to thermodynamics. It is sometimes referred to as *thermodynamic beta*, and it captures the relationship between temperature and energy (indeed as we shall see in Chapter 3, it is regarded by some physicists as a more useful indication of the temperature of a system than temperature itself):

$$\beta = \frac{1}{k_B T}$$

The exponential factor in the Boltzmann distribution is particularly important in thermal physics, and it is often referred to as the *Boltzmann factor*:

$$\text{Boltzmann factor} = e^{-\frac{E}{k_B T}}$$

A Boltzmann factor appears in any fundamental equation involving temperature and energy. We will encounter both thermodynamic beta and the Boltzmann factor again in Chapter 7 when we look at temperature and its effect on physiological reaction rates.

We now have enough background to start exploring in more detail the nature of energy in objects such as organisms. The first concept we need to explore is that of *internal energy*.

2.4 Internal energy

The internal energy of a body is the sum of all the kinetic energy and potential energy associated with the atoms and molecules that make up that body. It is usually designated U , and is one of the most important measures for keeping track of the energy changes in a system.

An organism, even an apparently simple one such as a bacterium, is an extremely complex object. So to get a handle on the concept of internal energy we should start with a much simpler example, such as oxygen or nitrogen gas. Here each molecule consists of two atoms linked by a covalent bond, and the molecules are moving around at great speed (Figure 2.2) so they have significant kinetic energy. However the molecules are also vibrating and tumbling around, so the internal energy of the gas is distributed among the component molecules in three types of movement: translation, vibration and rotation. For a more complex molecule, such as a cellular metabolite or a protein, there are a range of further bond motions and molecular flexions that contribute to internal energy.

By convention, internal energy comprises only those forms of energy that can be modified by heat, work or chemical reactions. That is, classical thermodynamics deals with only two of the four fundamental forces of nature, namely gravity and electromagnetism. The other two, the strong and weak nuclear forces, operate only over distances too small to be of relevance to the bulk flow of energy; internal energy thus does not include nuclear energy.

Internal energy is an *extensive* property; that is, its magnitude depends on the mass of the body: a larger animal or plant has more internal energy than a smaller one (see Box 2.3). Unfortunately, while we can define internal energy, we cannot measure it. There is no instrument known in which we could place our lump of copper (or indeed any other object) and obtain a measurement of its internal energy. Neither can we calculate the internal energy from first principles, it is just too complicated.

Box 2.3 Extensive and intensive properties

An *extensive* property of an object depends on its size (extent), which must therefore always be given. Examples of extensive properties include mass and internal energy. A 2 kg lump of pure copper has exactly twice the number of atoms, and twice the internal energy, as a 1 kg lump of pure copper at the same temperature and pressure. An *intensive* property is independent of the size of the object. Examples here would be temperature or molar heat capacity.

A simple way to visualise the difference is to imagine the block of copper as being divided into two halves. Each half-block contains exactly half the number of atoms and exactly half the internal energy (extensive properties), but each is at precisely the same temperature (an intensive property).

This might suggest that internal energy is not a very useful concept. The reason this is not so is that we can measure a *change* in the internal energy of a body very precisely indeed, and this makes the concept extremely valuable. So much so that internal energy is central to understanding the interaction between a body and its surroundings. The change in internal energy (ΔU) is the difference between the internal energy at the start (U_1) and the end (U_2) of the process:

$$\Delta U = U_2 - U_1$$

The change in internal energy of a body is given by:

$$\Delta U = \Delta Q + w$$

where ΔU is the change in internal energy, ΔQ is the change in energy content resulting from a gain or loss of energy and w is the work done on the body (for example increasing its potential energy by lifting it). By convention, energy flow into a body and work done on that body are regarded as positive. Equally, loss of energy and work done by the body on the environment are negative.

To take a biological example, a lizard basking in the sun is increasing its internal energy by absorbing radiant heat (Plate 1). This extra energy causes all the component molecules of the lizard to move around more rapidly, and we can measure this greater motion as an increase in temperature (we

will explore the relationship between thermal energy and temperature in Chapter 3). If the lizard climbs a rock to bask, it also increases its potential energy.

2.4.1 Enthalpy

An important property of a system is its enthalpy, usually designated H . It is a state function (Box 2.4) and closely related to internal energy.

Enthalpy is a measure of the total energy content of a system; it includes the internal energy together with the amount of energy required to displace the environment and thereby establish the system's volume and pressure. Thus:

$$H = U + PV$$

where H is the enthalpy of the system, U its internal energy, V its volume, and P the pressure at the boundary between the system and its surroundings. One way to visualise the difference between enthalpy, H , and internal energy, U , is that U represents the energy required to create the system and PV represents the energy required to create room for the system in an environment of pressure P .

Enthalpy is sometimes referred to as the total heat content of the system. Although a useful shorthand, this statement is not strictly true, and things are not helped by the etymology of the term: enthalpy derives from the Greek *ενθαλπος* (enthalpos), which translates as 'put heat into'²¹.

As with internal energy, the enthalpy of a system cannot be calculated from first principles, nor can it be measured directly. The change in the enthalpy of a system is, however, exactly equal to energy added to or taken from the system as heat, provided that the system is at constant pressure and the only work done involves a change in volume. Since under almost all ecological conditions pressure is effectively constant, but volume is allowed to change, enthalpy is an immensely useful state function for understanding heat flow and energetics in ecology.

2.5 Energy and heat

We can see that the list of state variables of importance to thermal ecology (Box 2.4) includes internal energy and enthalpy, but not heat. So what exactly is heat?

Box 2.4 State functions

A *state function* (also called a *state variable*) is a physical property of a system that depends only on the present state of that system, and is independent of the path by which that state was reached. The state functions of importance to thermal ecology are:

State function	Symbol	SI unit
Volume	V	litre, l (or sometimes L)
Pressure	P	Pascal, Pa
Temperature	T	Kelvin, K (not °K)
Amount	n	mol
Internal energy	U	Joule, J
Enthalpy	H	Joule, J
Entropy	S	J K ⁻¹ (occasionally called 'entropy units')
Gibbs (free) energy	G	Joule, J

State functions are usually represented by a capital letter. The essential feature of a state function is that if a system is taken through a cyclic process and returned to its initial conditions, then the net change in all state functions is zero ($\Delta V = 0$, $\Delta T = 0$, $\Delta H = 0$ and so on). The opposite of a state function is a *path function*. Here the final state of the system depends on the route (path) by which that final state was achieved; an example of a path function would be work.

Perhaps surprisingly, it was only in the late nineteenth century that the Scottish physicist James Clerk Maxwell was finally able to make a clear statement of the nature of heat, developing the pioneering work of Rumford and Joule described in section 2.2.3, and based on the kinetic theory of gases (see Box 2.5).

A century on, and physicists now view heat in slightly more rigorous terms. Heat is the spontaneous transfer of energy through random molecular motion: energy is what is being transferred, and heat is the process. Energy can also be transferred through work, and a molecular view allows us to distinguish work and heat. The thermal motion of atoms is random and chaotic, and heat is the transfer of this energy through random atomic motions. In contrast, work is the transfer of energy through a coherent movement of atoms (Figure 2.3).

Box 2.5 James Clerk Maxwell and the nature of heat

In 1716 Jakob Hermann proposed that the heat content of a body was proportional to its density and *the square of the agitation of its particles*. Hermann spent some time in St Petersburg, where he undoubtedly encountered his compatriot Daniel Bernoulli who published his influential book *Hydrodynamica* in 1738. In this book Bernoulli ascribes the pressure of a gas to *very minute corpuscles, which are driven hither and thither with a very rapid motion*. Using this idea, Bernoulli was able to derive the relationship between pressure and volume of a gas (which we now know as Boyle's Law), and also proposed that as temperature is raised, the speed of the particles increased, and thereby the pressure²².

Although the prevailing view at the time was that heat was a form of fluid, Isaac Newton subscribed to the view that heat consists of the internal motion of the constituent particles, as did Henry Cavendish. In a recently discovered unpublished work on heat, probably written in 1787, Cavendish speculates that the heat content of a body consists of an

active component (the term current at the time was *vis viva*) which affects a thermometer, and an inactive component which resulted from the relative positions of the particles and was a measure of the 'latent' heat of the body. This hints clearly at the then unknown concept of entropy and was a remarkably prescient remark for the late eighteenth century²³.

It was James Clerk Maxwell who finally defined the nature of heat in rigorous terms, listing four key features²⁴:

Heat is something that can be transferred from one body to another.

Heat is a measurable quantity, and hence can be treated mathematically.

Heat cannot be treated as a material substance.

Heat is one of the forms of energy.

He also laid to rest the old idea of heat as a fluid with characteristically ruthless brevity:

Heat may be generated and destroyed by certain processes, and this shows that heat is not a substance.

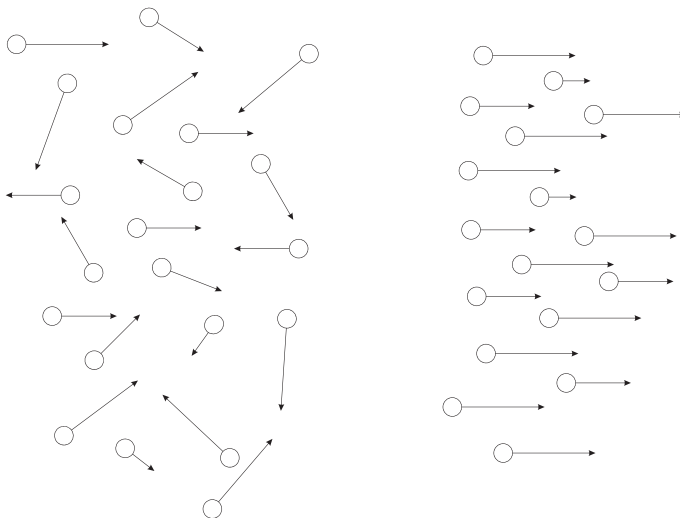


Figure 2.3 Molecular motion in thermal energy (left) and work (right).

Biologists are less rigorous in their terminology, and the thermal energy of a body is often referred to as its heat content. Moreover we often speak of heat being transferred between an animal and its environment, when strictly we should be saying that energy is being transferred through heat. In this book I will try to be rigorous, except when it would otherwise lead to convoluted or tortuous language, in which case I will slip into more

informal language (though never without pointing out what I have done).

2.6 Thermodynamic systems

So far we have been considering objects that exchange energy with their environment, or have work done on them. At this point we need to introduce an important thermodynamic convention,

defining the nature of the body under consideration in terms of precisely how that body interacts with the environment around it.

The first convention is that we divide the universe into two compartments: the system under consideration and everything else (its surroundings). We then consider the nature of the exchanges between the system and its surroundings:

An *open* system exchanges both matter and energy with the surroundings.

A *closed* system exchanges only energy with the surroundings.

An *isolated* system exchanges neither matter nor energy with the surroundings.

These are illustrated in Figure 2.4.

Since energy can be exchanged between the system and the surroundings by both heat and work, we can also define an *adiabatic* system (from the Greek *ἀδύβατος*, impassable); this is a closed system where the exchange of energy with the surroundings is through work alone.

A moment's reflection should convince you that all of ecology deals exclusively with open systems: all living things have to exchange both energy and materials with their surroundings.

2.7 Work and energy revisited

Although the concepts of work and energy were developed from mechanics, a molecular view of work shows us that in bioenergetics, work encompasses a wide range of physiological processes. Some examples of relevance to thermal physiology are shown in Table 2.1.

Table 2.1 Some examples of physiological work.

Type of work	Examples
Mechanical work	Movement of bulk material, such as in locomotion, or the movement of cilia or flagella, or of macromolecules within cells
Osmotic work	Movement of molecules and ions across a membrane against a concentration gradient
Electrical work	The directed movement of electrons or ions to create a difference in electric potential
Chemical work	Driving chemical reactions that would not happen spontaneously

Earlier in this chapter we saw that Count Rumford demonstrated that work could be converted completely to heat. The development of steam engines showed that heat could be converted to work, and Sadi Carnot had shown that the efficiency of this conversion was dependent on the temperature difference involved (see Box 2.6).

It was Rudolf Clausius who first recognised that this indicated a fundamental asymmetry in nature: while work can be converted completely to heat, the reverse is not true. There is some fraction of the energy of a body that can never be recovered as useful work. To explain why this is so, he introduced the concept of *entropy*²⁵.

2.8 Entropy

Entropy is one of the most important concepts in thermodynamics, but it is subtle and elusive and difficult to define precisely in simple language. Maybe because of this, or perhaps because many

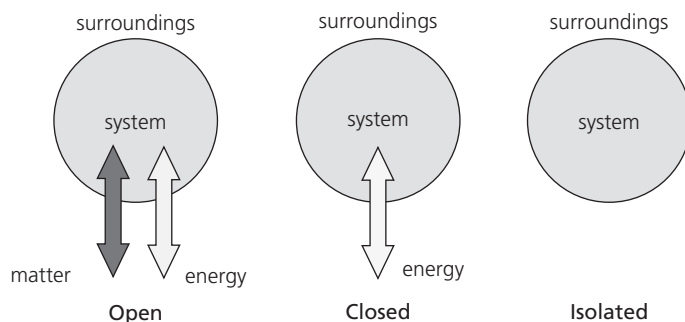


Figure 2.4 Thermodynamic systems.

Box 2.6 Carnot and efficiency

Carnot showed that for a heat engine taking energy from a hot reservoir at temperature and moving this to a cold sink at temperature to generate work, the maximum efficiency that could be achieved, η , is given by:

$$\eta = 1 - \frac{T_c}{T_h}$$

where T_h is the absolute temperature of the hot reservoir and T_c that of the cold sink. This formalises the engineering principle known to James Watt that for a steam engine, the hotter the steam the more efficient the conversion to work. Carnot recognised that this was a theoretical maximum, achievable only for a fully reversible process operating infinitely slowly (that is, doing no work!). For a heat engine where the processes of heat transfer are not reversible the maximum achievable efficiency, η^* is:

$$\eta^* = 1 - \sqrt{\frac{T_c}{T_h}}$$

discussions of entropy are couched in terms unfamiliar to non-physicists, few ecologists are conversant with it. Indeed, despite the central importance of entropy to biological energetics, few physiology texts even mention it. When entropy is discussed, it is usually through analogies such as randomness or disorder which do little to help understanding and may even mislead.

Although the concept of entropy is sometimes difficult to grasp, it is a precisely measurable quantity, just like length or mass. It is also of profound importance to thermal ecology, though this importance is sometimes hidden. A useful indication of the importance of entropy is to see how much of physiology and ecology is influenced by it; some examples are given in Table 2.2. This list should be enough to convince you that entropy is of fundamental importance to physiology.

Perhaps the best way to introduce entropy is through a few examples. All of these involve spontaneous change, that is a change which has a natural tendency to occur and which happens without the need for work to bring it about.

Table 2.2 Some biological processes where entropy plays an important role.

Process
<i>Physiological processes</i>
Formation of membranes
Protein folding
Binding of RNA and proteins to DNA
Binding of cofactors to proteins
Enzyme function (indeed all cellular chemical reactions)
Heat generation in endotherms
<i>Evolutionary processes</i>
Adaptation of enzymes to temperature, pressure and pH
<i>Ecological or environmental processes</i>
Heat generation in a compost heap
Melting of snow and ice

Consider a volume of gas allowed to expand isothermally into a vacuum (Figure 2.5). As soon as the barrier is removed (say by opening a stopcock) the very rapid random movements of the gas molecules mean that the gas rapidly fills the vacuum and re-equilibrates. The change in state variables is described by the ideal gas equation (Box 2.7):

$$PV = nRT$$

Since there has been no change in energy (no heat has flowed, and no work done on or by the gas since the movement of the molecules has been entirely random), then T remains the same: the distribution of speeds among the gas molecules is exactly the same as it was before. Since the amount of gas (n moles) also remains the same, the increase in volume (V) is offset by a decrease in pressure (P).

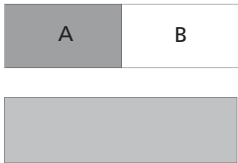


Figure 2.5 A spontaneous process: the expansion of a gas into a vacuum. In the upper diagram a volume of gas under pressure (A) is separated from an evacuated container (B) by an impermeable barrier. In the lower diagram the barrier has been removed and the gas now fills both spaces; the temperature remains the same but the pressure is lower and the entropy greater.

What else has changed is that the gas can now do less work. Consider using the gas to inflate a balloon, and it is easy to see that a larger balloon could be inflated by the gas before opening the stopcock than after. The energy content is the same, but for some reason the gas can now do less work.

A second example might be the release of a small amount of sugar or a highly coloured compound such as potassium permanganate, KMnO_4 , into water: the sugar or KMnO_4 diffuses slowly until the distribution is uniform. A final example would be

Box 2.7 The Ideal Gas Law

The Ideal Gas Law developed from a number of separate relationships established in the seventeenth century.

Robert Boyle established that the pressure, P , of an ideal gas is inversely proportional to its volume, V :

$$PV = \text{constant}$$

Boyle was a careful experimentalist, and recognised the need to control the temperature during measurements, and to allow for atmospheric pressure. This relationship is now known as Boyle's Law²⁶.

A short while later, in 1699, Guillaume Amontons showed that different volumes of air have their pressure increased equally by the same rise in temperature, and in a later paper showed that this relationship is independent of the initial pressure. Almost a century later, the French chemist Joseph Louis Gay-Lussac showed that when pressure is held constant, the relationship between volume and temperature, T , is similar in several gases:

$$\frac{V}{T} = \text{constant}$$

When he published his results, Gay-Lussac generously acknowledged that similar results had been established earlier by the French scientist and entrepreneur Jacques Charles, but were unpublished. This relationship is now known as Charles' Law, and Gay-Lussac is remembered today through his Law of Combining Volumes.

Boyle's Law and Charles' Law were combined by Émile Clapeyron, to produce the first formulation of the Ideal Gas Law²⁷. The modern representation of this law is:

$$PV = nRT$$

The constant of proportionality, R , is known as the *universal gas constant*, and has a value of $8.314 \text{ J (mol K)}^{-1}$; n is the number of moles.

bringing together two identical blocks of metal, say one at 200°C and the other at 100°C . Once they are in thermal contact one block warms and the other cools until both are at 150°C .

In all of these cases the process always goes in one direction: the gas always fills the vacuum, the sugar or KMnO_4 always spreads out by diffusion and the two metal blocks always come to the same temperature. We have an individual explanation for each of these (pressure always equalises, substances always diffuse to equilibrium, heat always flows from hot to cold), and so it was a major conceptual leap to recognise that there was a single deeper principle behind all of these. That step was taken by Rudolf Clausius in his recognition of entropy.

At this point it is helpful to take a final example, this time one where energy is changing. Consider a mass of ice at subzero temperature, and track its temperature as heat is supplied at a constant rate (Figure 2.6). First the ice warms, and then there is a plateau during which heat is continually being supplied but there is no change in temperature, which remains at the melting point of 0°C . Once all the ice has melted, the water then warms (though more slowly because the thermal capacity of water is greater than that of ice) until once again a plateau is reached. Here again, heat continues to be supplied, but the temperature remains constant, this time at the boiling point of 100°C . Once all the water has been vapourised to steam, the steam then starts to warm (or as an engineer would say, to superheat).

What is happening at the two plateaux, when energy is being supplied but there is no change in temperature? The original explanation was that the energy was providing latent heat, that is heat which is in some way hidden, and to distinguish this from energy supplied when the temperature changed, which was sensible heat (because it could be sensed, such as with a thermometer)²⁸.

This is perfectly correct, but a better way to look at it is that during the phase change from ice to water, and then from water to water vapour (the plateaux in Figure 2.7), the energy supplied is being used entirely to meet the difference in entropy between ice and liquid water, or between liquid water and water vapour. This tells us something important: entropy is real, and the change in entropy is a

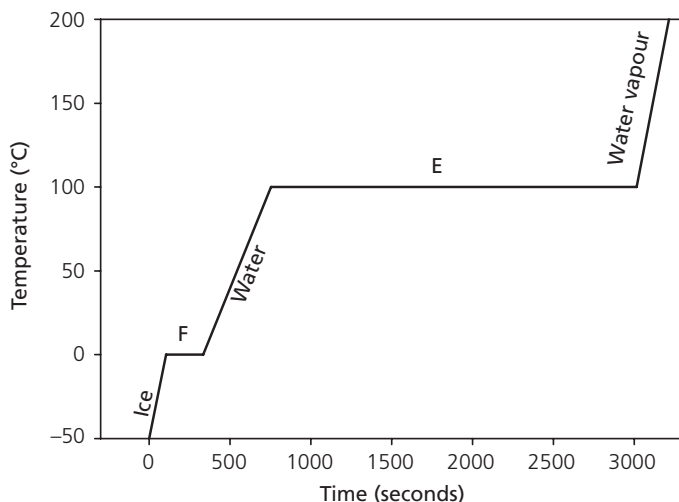


Figure 2.6 A heating curve for water. The plot shows the change in temperature of 1 kg of water, initially ice at -50°C , as energy is supplied at a rate of 1 kW, and the sample remains at atmospheric pressure. The two plateaux represent the entropy change at melting (F , the latent heat of fusion) and evaporation (E , the latent heat of evaporation).

precisely measurable property. Its definition is simple and explicit:

$$\Delta S = \frac{\Delta Q}{T}$$

where ΔS is the change in entropy, ΔQ is the energy supplied and T is the absolute temperature. This relationship was established by Clausius, and as always with equilibrium thermodynamics, it is assumed that the energy is supplied reversibly, that is very slowly and in very small amounts such that each step is, at least theoretically, perfectly reversible. It is important to note that entropy is not energy: its units are J K^{-1} .

It is only during phase changes (ice to liquid water, liquid water to water vapour and vice versa) that the energy supplied is utilised entirely by the change in entropy. At all other times, when the ice, liquid water or water vapour is also increasing in temperature, the energy input is increasing both the entropy and the temperature.

This is all very well, but we still have not said what entropy actually *is*. The explanation came from Ludwig Boltzmann, who considered the enormous number of ways that a given amount of energy could be divided within a system and used probability arguments to deduce the most probable distribution of energy across all the component entities (typically atoms or molecules). The details need not concern us here, but the outcome was that

Boltzmann linked entropy to the number of available microstates, W (or sometimes Ω) in the system. The modern formulation of this relationship is:

$$S = k_B \ln W$$

where S is the entropy and the constant of proportionality and k_B is Boltzmann's constant. Since W (Ω) is a pure number, the dimensions and units of S and k_B are identical. This version of entropy is sometimes called statistical entropy (or Boltzmann entropy), but for an ideal gas it is identical to the entropy defined in terms of classical thermodynamics by Clausius²⁹. This equation is carved on Boltzmann's memorial in Vienna, although Boltzmann never expressed his relationship in this way, and the inclusion of what we now refer to as Boltzmann's constant is down to Max Planck.

We now recognise that microstates are descriptions in terms of quantum mechanics of the different ways that molecules can differ in their energy distributions in a macroscopic system. When a macroscopic system is warmed, a great many additional microstates become available: its entropy increases. An element of this is captured by the change in molecular speed distribution of a gas when warmed; the broadening of the speed distribution indicates the greater range of microstates available at the higher temperature (Figure 2.7). There is a similar increase in available microstates when the volume of a gas is increased.

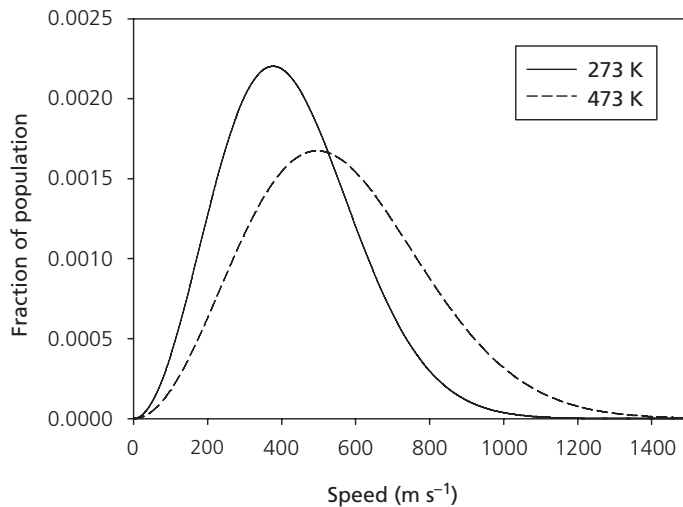


Figure 2.7 The distribution of molecular speeds in oxygen at 0°C (273 K) and 200°C (473 K). Note the broadening of the speed distribution at the higher temperature, reflecting the larger number of microstates available (greater entropy).

A simple analogy that captures the relationship between statistical likelihood and the number of microstates is the rolling of a pair of dice. Here the macrostate is the total score and the microstates are the faces of each die. A score of 2 or 12 is least likely because in each case there is only one way of achieving that score (1,1 and 6,6 respectively). In contrast a score of 7 is much more likely because this can be achieved in six different ways (1,6; 2,5; 3,4; 4,3; 5,2; 6,1). In this example of two dice there are 36 (6^2) possible microstates and the general result is that for n dice, the most probable number (represented by the greatest number of different microstates) is $3.5n$. If you pour 100 dice onto a table, the total face value will be close to 3500; the most probable total (macrostate) is that with the greatest number of microstates (that is, the highest entropy). It is just the same for the entropy of a gas (or any other system).

Most formal definitions of entropy are daunting for an ecologist or physiologist, so at this point I will suggest a working description as a basis for exploring the role of entropy in ecology:

Entropy is a measure of the way energy is distributed within a system that captures how much of the total energy is available to perform work.

This is not a formal definition of entropy; it is a broad-brush description that attempts to capture its essential features in a way that relates directly

to thermal ecology. The important caveats are that the system must be in thermal equilibrium and the work isothermal, but this simple description conveys the key features important for understanding the role of entropy in ecology.

In some of our examples of spontaneous change discussed earlier, for example the diffusion of sugar in water, there has clearly been a change from a highly ordered state to a less ordered state and an increase in entropy is often described in terms of an increase in disorder. However in other processes, such as the expansion of a gas into a vacuum, it is difficult to explain what has happened in terms of order or disorder: the distribution of molecular speeds of the gas molecules is exactly the same before and after. A better general description is that the energy has become more spread out or dispersed in space. Although both of these analogies are common in the literature, neither is precise nor always easy to visualise. Perhaps the best simple description is that in the absence of any constraint the energy in a system always moves to the most probable distribution across the component atoms and molecules. This explanation leads directly to a simple statement which forms the basis of the Second Law of Thermodynamics:

In an isolated system, entropy always tends to the maximum.