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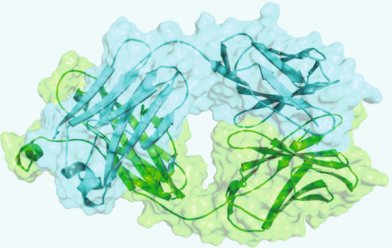
MODERN THERMODYNAMICS FOR CHEMISTS AND BIOCHEMISTS



DENNIS SHERWOOD AND PAUL DALBY

Modern Thermodynamics for Chemists and Biochemists

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Dennis Sherwood and Paul Dalby

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Foreword

Thermodynamics has evolved dramatically since the precursor of this book, Dennis Sherwood's *Introductory Chemical Thermodynamics*, was published in 1971. This development is completely reflected in the new text, which is really an entirely new book. The title has also very aptly been changed in order to emphasise that one of the most important new areas where thermodynamics can make a major impact is within the bio world: biochemistry and molecular biology. This is emphasised by chapters on the bioenergetics of living cells, macromolecular conformations and interactions, and even an outlook toward where thermodynamics seems to be headed in the future, such as the self-assembly of large complexes.

The sequence of chapters cleverly escalates from everyday experiences to precise definitions, to ideal modelling and then real adjustments. Spontaneity, time, order and information follow naturally, and from these the more complicated chemical and electrochemical reactions, ending up with reactions and structure formation in the living environment – a very long staircase, but with comfortable small steps.

While the content has been brought fully up-to-date and the focus adjusted to fertile modern areas, the old friendly writing style has been preserved. In particular in the beginning where the basic thermodynamic concepts are introduced, we find essentially no equations, only simple verbal explanations based on common observations so that the reader will build a clear intuitive understanding of the topic without the all too frequent mathematical barrier. This approach is especially important for readers in the bio field who often do not have the same strong background in mathematical thinking and modelling as those in the hard sciences and engineering. This is not to say that the book has left out all maths, it just comes later when the concepts have been understood. This is a unique pedagogical approach among thermodynamics textbooks, which undoubtedly will facilitate the reader's entry into thermodynamic thinking.

Every chapter starts with a summary of the concepts presented in that chapter, useful both before reading the chapter for giving direction and after reading it for wrapping up the new items into a whole. The exercises at the end of all chapters further emphasise understanding and relations. They are unconventional by not asking the student to calculate a certain quantity, but to explain an observed behaviour, relating different effects, predict a behaviour and find an error in an argument. In other words, they encourage thinking, rather than mechanical calculational skills. The concluding glossary of thermodynamics terms, and the introductory index of symbols, are very useful for the novice when the many new words and symbols become confusing.

I strongly recommend this introductory thermodynamics textbook for its inviting approach, focus on concepts and relationships, comprehensive coverage, and openness toward the biological sciences.

Bjarne Andresen
Niels Bohr Institute, University of Copenhagen

Oh, you can't pass heat from the cooler to the hotter
You can try it if you like, but you far better notter
'Cause the cold in the cooler will get cooler as a ruler
That's the physical law!

From *First and Second Law*, by Michael Flanders and Donald Swann, performed in their musical revue *At the Drop of Another Hat*, 1963

Preface

This book originated as a proposed second edition to *Introductory Chemical Thermodynamics*, published in 1971, with the specific intention of adding material relating to current-day applications of thermodynamics to biology, including topics such as bioenergetics, protein-folding, protein-ligand interactions, and protein aggregation. This has, indeed, been done, but we also took the opportunity to enrich and enhance the discussion of the fundamentals of thermodynamics, the Three Laws, and chemical applications. Accordingly, this book is structured as:

- **Part 1: Fundamentals**: introducing the concepts of work, temperature, heat and energy, state functions and path functions, and some of the mathematical principles that will be used throughout the book.
- **Part 2: The Three Laws**: the core of the book, in which we explore the First Law, internal energy and enthalpy; the Second Law and entropy; and the Third Law and the approach to absolute zero.
- **Part 3: Free energy, spontaneity, and equilibrium**: where we explain the central role of the Gibbs free energy as regards both the spontaneity of change, and also the nature of chemical equilibrium.
- **Part 4: Chemical applications**: covering how the principles discussed so far can be applied to phenomena such as phase equilibria; reactions in solution; acids, bases, and buffer solutions; boiling points and melting points; mixing and osmosis; and electrochemistry.
- **Part 5: Biochemical applications**: where we describe how biological systems capture the free energy within molecules such as glucose, or within light, store it temporarily within molecules such as ATP, and then use that free energy to drive, for example, the synthesis of complex biomolecules; we also explore how proteins fold, and interact with ligands, as well as how proteins self-assemble to form larger-scale structures.

Thermodynamics is notoriously difficult to understand, learn, and use, and so we have taken great care to explain as clearly as possible all the fundamental concepts. As a quantitative branch of science, thermodynamics necessarily uses mathematics to describe how physically measureable phenomena, such as the pressure exerted by a gas, or the concentration of a component within a solution, are related, and how they change as conditions such as the system temperature vary. Much of the required mathematics is explained, and developed, within the text. The only pre-requisites are some knowledge of basic algebra, and of differential and integral calculus (for example, if $y = 3x^2$, then $\mathrm{d}y/dx = 6x$, and $\int(1/x)\,\mathrm{d}x = \ln x$).

This book has not been written to support a specific curriculum; rather, it has been written to provide "everything a student needs to know about chemical and biochemical thermodynamics" in the context of passing undergraduate examinations, and providing a solid platform for more advanced studies. The content of the book is therefore likely to be broader, and in some respects deeper, than the precise requirements for any specific course. We trust, however that it includes all the required content for very many courses. As a consequence, the book will be of value to undergraduate students of chemistry and biochemistry, and related fields, as well as to students of higher-level programmes who seek a source of reference. Also, the exercises associated with each chapter have been designed to stimulate thinking, rather than as practice problems for a specific examination.

Many people have, of course, contributed to our thinking and to the knowledge we are sharing in this book, and we gratefully acknowledge all our own teachers and mentors. In particular, we wish to thank Professor Alan Cooper, of the University of Glasgow, and Professor Bjarne Andresen, of the Niels Bohr Institute at the University of Copenhagen, for their most helpful suggestions and insights. We also thank Harriet Konishi, Shereen Karmali, Megan Betts and Sonke Adlung at OUP, and also Marie Felina Francois, Indumadhi Srinivasan and everyone in the production team, with whom it has been a pleasure to work—and, of course, our wives and children, who have been remarkably patient, supportive, and understanding as we have been (from their totally legitimate standpoint) both distracted and obsessed by the intricacies of reversible changes, electrode potentials, and entropy.

We trust you will enjoy reading this book and will benefit accordingly. If you notice any errors, think any particular topic is poorly explained, or if you have any ideas for making the book clearer or more useful, please do let us know—our email addresses are dennis@silverbulletmachine.com and p.dalby@ucl.ac.uk. Thank you!

Dennis Sherwood
Exton, Rutland

Paul Dalby
University College, London

Contents

Index of symbols

Roman upper case

Roman lower case

dm	Decimetre = 10^{-1} m, unit-of-measure of length	170
e	Base of natural logarithms, 2.71828...	68
e^-	Electron	596
f	Arbitrary path function	230
f	Frequency of simple harmonic motion	237
f	Fugacity	657
g	Acceleration due to gravity = 9.81 m sec^{-2}	21
g	Gas phase	154
h	Planck's constant, 6.6261×10^{-34} J sec^{-1}	738
h	Height	21
k	Arbitrary constant	238
k	Reaction rate constant	452
k_B	Boltzmann's constant, 1.381×10^{-23} J K^{-1}	70
$k_{H,i}$	Henry's law constant for component i	510
kg	Kilogram, unit-of-measure of mass	6
kJ	Kilojoule = 10^3 J, unit-of-measure of work, heat and energy	154
l	Liquid phase	155
l	Litre = 1 dm^3 = 10^{-3} m^3, unit-of-measure of volume	170
m	Mass	17
m	Metre, unit-of-measure of distance	21
mol	Mole, unit-of-measure of quantity	7
n	Mole number	7
n_e	Number of electrons	595
n^*	Critical number of monomers for nucleation	782
nm	Nanometre = 10^{-9} m, unit-of-measure of length	724
ox, red	Referring to a redox reaction	619
p	Partial pressure	49
p	Proton motive force, as in Δp	732
pX	= – $\log_{10}$ X (as, for example, pK_a = – $\log_{10} K_a$), or	539
	= – $\log_{10}$[X] (as, for example, pH = – $\log_{10}[H^+]$)	537
q	Heat	56
s	Solid phase	154
sec	Second, unit-of-measure of time	21
t	Temperature as measured in °C	6
v	Rate of reaction	450
w	Work	26
x	Arbitrary variable	77
x	Linear distance	133
x	Mole fraction	170
y	Arbitrary variable	77
z	Arbitrary variable	88
z	Charge number	667

Greek upper case

Greek lower case

Subscripts

Superscripts

Other symbols

Index of units-of-measure

List of Tables

PART 1

Fundamentals

1 Systems and states

Summary

Thermodynamics is the macroscopic study of **heat**, **work** and **energy**.

The domain of the universe selected for study comprises the **system**, and the rest of the universe constitutes the **surroundings**. The system and the surroundings are separated by the system **boundary**.

At any time, any system has a number of properties, known as **state functions**, which can be measured, and serve to define the state of the system at any time. **Extensive state functions**, such as mass, depend on the extent of the system; **intensive state functions**, such as temperature, are independent of the extent of the system. All extensive state functions per unit mass are intensive state functions.

Thermodynamic equilibrium is a state in which all state functions are constant over time, and for which all intensive state functions have the same values at all locations within the system.

If measurements are taken on an equilibrium system at different times, and if the value of at least one state function X has changed from an initial value X_1 to a value X_2, then the system has undergone a **change in state**. The corresponding change ΔX in the state function X is defined as

$$\Delta X = X_2 - X_1 \tag{1.2a}$$

in which the initial value X_1 is subtracted from the final value X_2. Mathematically, all state functions are defined by an **exact differential** $\mathrm{d}X$.

A consequence of equation (1.2a) is that the change ΔX in any state function X depends only on the values X_1 and X_2 of X in the initial and final states, and is independent of the path followed during the change in state. The value of ΔX therefore contains no information of how a particular change in state took place.

An **ideal system** – of which an **ideal gas** is one example – is a system in which, fundamentally, there are no intermolecular interactions. Any macroscopic properties, such as the thermodynamic state functions, are linear additions of the state functions of smaller sub-systems, and, ultimately, of the microscopic properties of the molecules themselves. In real systems, molecules do interact, and so ideal systems are a theoretical abstraction. They are, however, much simpler to describe and analyse, and so the study of ideal systems provides a very useful model, which can then be used as a basis of the study of more complex, real, systems.

1.1 Some very familiar concepts . . .

We all know that iced water feels cold, that freshly made tea or coffee feels hot, and that many of the meals we eat are warm – not as cold as the iced water, not as hot as the tea,

Modern Thermodynamics for Chemists and Biochemists. Dennis Sherwood and Paul Dalby.

but somewhere in-between. From a very early age, we learn that the degree of 'coldness' or 'hotness' we experience is associated with a concept we call 'temperature' – things that feel hot have a high temperature, things that feel cold have a low temperature.

We also know that flames are very hot indeed, far too hot for us to feel directly with our hands. And when we put a saucepan containing cold water in contact with a hot flame – as we do when we're cooking – we know that the water in the saucepan gets steadily warmer: the proximity of the hot flame to the cold water heats the water up.

Putting something hot next to something cold is not the only way things can get warmer: another way is by working. Once again, we all know that when we work hard – for example, by vigorous physical exercise such as running hard, digging a hole, or carrying heavy weights – we quickly become very warm, just as warm as we would by sitting quietly by a log fire. And after we've worked hard for a while, we become tired, and we feel we've lost energy, as if the energy that was in our body earlier in the day has been used up because of the work we have done. So we rest, perhaps have something to eat, and after a while, we feel we have more energy, and can then do some more work.

This is very familiar to all of us – words such as cold, hot, temperature, heat, work and energy are part of our natural every-day language. They are also the fundamental concepts underpinning the science of **thermodynamics**, and to explore that science – as we will do in this book – we need to enrich our understanding of what words such as 'temperature', 'heat', 'work' and 'energy' actually mean, moving beyond subjective feelings such as 'hotness' and 'coldness' to well-formulated scientific definitions. So, our purpose in the first three chapters is to do just that, and to offer some deeper insights into these familiar every-day phenomena.

1.2 The macroscopic viewpoint

Thermodynamics is a very practical branch of science. It's development, during the nineteenth century, was closely associated with the need to gain a better understanding of steam engines, addressing questions such as:

- How much work can a steam engine actually do?
- How might we design better engines – engines that can perform more work for the same amount of coal or wood used as fuel?
- Is there a maximum amount of work a steam engine might do for a given amount of coal or wood? In which case, what might this optimal design be?

Given the importance of steam engines at that time – engines that provided mechanical power to factories, motive power to railways, as well as releasing ships from their reliance on the wind – this is practical stuff indeed.

As a consequence, thermodynamics is concerned with quantities that are readily measurable in real circumstances – quantities such as the mass of an engine, the volume of a boiler, the temperature of the steam in a turbine. These quantities all at a 'human scale', they are all **macroscopic**. Macroscopic quantities may be contrasted with **microscopic** quantities, where in this context, the term 'microscopic' does not relate to what you might observe in the optical instrument known as a microscope; rather, it refers to phenomena associated with the atomic and molecular structures of, for example, the engine, the boiler or the steam. We now know, without any doubt, that atoms and molecules exist, and we now have a deep understanding of their behaviour. But when thermodynamics was developed, the concepts of atoms and molecules were theoretical, and very much under exploration – there was at that time no direct evidence that these invisible particles actually existed, and there were no measurements of their properties.

One of the strengths of thermodynamics is that the intellectual framework, and very many of its practical applications, are rooted firmly in the macroscopic, directly observable, world. As a consequence, thermodynamics does not rely on any assumptions or knowledge of microscopic entities such as atoms and molecules. That said, now that we have some very powerful theories of atomic and molecular behaviour, it is often both possible, and helpful, to interpret the macroscopically observed behaviour of real systems, as expressed and understood by thermodynamics, in terms of the aggregate microscopic behaviour of large numbers of atoms and molecules – that's the realm of the branch of science known as **statistical mechanics**, which forms a bridge between the microscopic world of the atom and molecule, and the macroscopic world of the readily observable.

Accordingly, much of this book will deal with the macroscopic, observable world – but on occasion, especially when the interpretation of macroscopic behaviour is made more insightful by reference to what is happening at an atomic or molecular level, we'll take a microscopic view too.

1.3 The system, the surroundings, and the system boundary

Our universe is huge and complex, and however much we may wish to understand the universe as a whole, we often choose to examine only a small portion of it, and seek to understand that. The areas of study that different people might select can be very diverse in scope, and of very different scales: so, for example, a sociologist might seek to understand the social interactions in a city; an astrophysicist, a star; a biochemist, the structure of a protein. We use the term **system** to define the domain of interest in any specific circumstance, so, for the sociologist, the relevant system will be a chosen city; for the astrophysicist, a particular star; for the biochemist, a specific protein. Everything outside the defined system constitutes the **surroundings**, and the system and the surroundings collectively make up the **universe**. Given the distinction between the system of interest and the surroundings, we use the term **system boundary** to refer to the system's outer perimeter, defining precisely where the system meets the surroundings: everything within the system boundary comprises the system, everything beyond it, the surroundings. The system boundary may be rigid if the system is of fixed size and shape, but this is not a necessary condition – many systems of interest can change their size or shape, changing the boundary accordingly.

1.4 State functions

That said, our study of thermodynamics will start with a system that does have a rigid boundary – a system comprised of a homogeneous **gas**, within a sealed container, the walls of which are assumed to be rigid (for example, steel), rather than flexible (for example, a rubber, inflatable, balloon). The interior surface of the container wall forms the system boundary, as shown in Figure 1.1, with the container itself being in the surroundings.

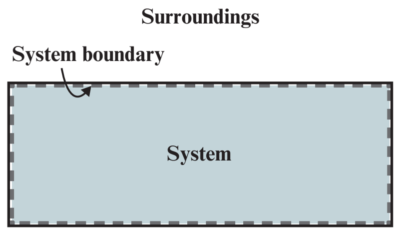

Figure 1.1 A system. This system is a gas within a sealed, rigid, container, with the system boundary being the interior wall (as shown by the somewhat exaggerated dashed line). The gas within the container may be associated with a number of properties, such as its mass M kg, its volume V m^3 and its temperature t °C.

At any time, any system will be associated with a number of relevant properties. So, for example, the system of a homogeneous gas within a container will have a mass M kg (that's the mass of just the gas, not including the mass of the container that holds the gas), the gas will occupy a volume V m^3, and the gas will have a temperature t °C. Properties of a system that can be measured at any single point in time – of which mass, volume and temperature are three examples – are known as **state functions**. The simultaneous values of all the state functions relevant to any particular system collectively define the **state** of the system at the time of measurement, and a state may be represented by specifying the appropriate state function values within square brackets as $[M, V, t, \ldots]$.

1.5 Extensive and intensive state functions

All state functions may be classified as either **extensive** or **intensive**, according to whether or not a measurement of that state function depends on the size and scale of the system.

So, for example, a system's volume clearly depends on how big the system is, and if an imaginary partition is drawn half-way across a system of volume V, this would result in two sub-systems, each of volume $V/2$. Volume is therefore classified as an extensive function, as is mass M, and to determine the value of any extensive state function, we need to make a measurement on the system as a whole.

In contrast, an intensive state function does not require a measurement to be taken on the system as a whole: rather, a meaningful measurement can be taken at any location within a system. One example of an intensive state function is temperature; another is density = mass/volume, where we see that the intensive state function, density, is the ratio of two extensive functions, mass and volume.

In general, extensive state functions are additive, whereas many intensive state functions are not. To illustrate this, consider two systems: the first a solid of a given material of mass M_1 kg, volume V_1 m^3, density $\rho_1 = M_1/V_1$ kg/m^3 and temperature t °C; and the second, a solid of a different material of mass M_2 kg, volume V_2 m^3, density $\rho_2 = M_2/V_2$ kg/m^3 and at the same temperature t °C. If the two systems are combined, then, according to the Law of the Conservation of Mass, the mass of the resulting system is $M_1 + M_2$ kg, and we would expect the volume to be $V_1 + V_2$ m^3. The density of the combined system, however, is $(M_1 + M_2)/(V_1 + V_2)$ kg/m^3, which is not in general equal to the sum $\rho_1 + \rho_2 = M_1/V_1 + M_2/V_2$; furthermore, given that both systems were at the same temperature t °C, the temperature of the combined system is also t °C, and not the sum of the temperatures $2t$ °C. Extensive functions are therefore additive, but many intensive functions are not.

1.6 The mole number n

An extensive state function that will feature strongly throughout this book is the **mole number** n, which specifies the number of **moles** of material within any given system. By definition, 1 mol of material comprises a fixed number of particles, which may be atoms, molecules or ions, depending on the nature of the system in question. The "fixed number" is defined by the **Avogadro constant** N_A = 6.022141 particles mol^{-1}. The mole number n defines how much material is within any given system, so for example, the total mass M_i of a system of n_i mol of any pure substance i is given by $M_i = n_i\, m_i$, where m_i is the mass of a single particle, this being an atom, molecule or ion as appropriate.

As we have just seen, the value of any extensive function for any system depends on the extent of that system, where 'extent' is determined by how much material is contained within the system. For a system comprised of a single pure substance i, all extensive functions therefore depend linearly on the mole number n_i. Accordingly, the mass M of any system is related to the mole number n as

$$M = n\,\boldsymbol{M}$$

in which $\boldsymbol{M}$, the **molar mass**, is the mass M of a system comprising precisely 1 mol of material, where, as before, the 'material' refers to the particles from which the system is composed, these being atoms, molecules or ions as appropriate.

Our example so far has referred only to the mass M; in fact, for any system of n mol, any extensive state function X is related to its molar equivalent by an equation of the form

$$X = n\,\boldsymbol{X} \tag{1.1a}$$

from which

$$\boldsymbol{X} = \frac{X}{n} \tag{1.1b}$$

Equations (1.1a) and (1.1b) have a particularly important implication. Since any molar state extensive function $\boldsymbol{X}$ is defined for a specific, fixed, quantity of material, 1 mol, then the value of any molar extensive function $\boldsymbol{X}$ cannot depend on the extent of the corresponding system – that extent is totally defined as 1 mol. Any molar extensive state function $\boldsymbol{X}$ is therefore itself an *intensive* state function. It is therefore always possible to convert any extensive state function X into its intensive counterpart $\boldsymbol{X}$ by dividing X by the appropriate mole number n.

1.7 The 'ideal' concept

In the previous paragraphs, we used our words carefully: so, for example, we said "in general, state functions are directly additive ...", "according to the Law of the Conservation of Mass ..." and "we would expect the volume to be $V_1 + V_2$ m^3". These words might appear to be superfluous: of course adding a mass M_1 kg to a mass M_2 kg results in a combined mass of $(M_1 + M_2)$ kg; of course adding a volume V_1 m^3 to a volume V_2 m^3 results in a system of volume $(V_1 + V_2)$ m^3. Both of these statements are often true, but not always. So, for example, at room temperature, if 1 m^3 of pure ethanol C_2H_5OH is added to 1 m^3 of pure water, the resulting volume is not 2 m^3 – rather, it is about 1.92 m^3. And if two masses of 0.75 kg of uranium-235 are added, the result is not a mass of 1.50 kg – it is a nuclear explosion.

Being able to add the values of extensive state functions is very useful, and so two substances are said to be **ideal** if the value of any extensive state function – such as the mass or the volume – of any mixture of those two substances is the sum of the appropriate values of the corresponding state functions of each substance in its pure state. This concept also applies to a pure substance too, for a system comprising any given mass M kg of a pure substance is, in principle, a mixture of two half-systems, each of mass $M/2$ kg. All extensive state functions of ideal substances are therefore linear with the quantity of matter, usually measured in terms of the mole number, the number of moles of material present, as represented by the symbol n.

As will be seen throughout this book, ideal behaviour is much easier to analyse, and to represent mathematically, than real behaviour. And although ideal behaviour is fundamentally a theoretical abstraction, the behaviour of many real systems approximates to the ideal closely enough for ideal analysis to have real practical value. Also, the theoretical foundations of ideal behaviour act as a very sound basis for adding the additional complexities required for a better understanding of real behaviour. We will identify some further properties of ideal systems elsewhere (see, for example, page 17); in general, throughout this book, unless explicitly stated otherwise, all systems will be assumed to be ideal, and associated with linearly additive extensive state functions.

1.8 Equilibrium

Suppose we observe a system over a time interval, and measure all the system's state functions continuously. If all the state functions maintain the same values throughout that time, then the system is stable and unchanging – it is in **equilibrium**. Then, as time continues, if the value of even just one state function changes, the system is said to have undergone a **change in state**. Once again, that's all obvious – but there is a subtlety: we haven't specified how long that 'time interval' is. If the time interval is long – say, hours, days or years – and the values of all the state functions maintain the same values, then words such as 'stable', 'unchanging' and 'equilibrium' all make sense. But if the time interval is very short – say, nanoseconds – then we would expect many systems to be 'stable' over this very short timescale, but not over a somewhat longer timescale, say, a few milliseconds or seconds. This implies that, if the time interval over which measurements are made is short enough, *all* systems will be identified as stable, unchanging, in equilibrium – at which point, these concepts become unhelpful.

To avoid this problem, this book will make the assumption that the time interval over which any system is being observed is 'long' – that means seconds at the very minimum, and often in principle hours and days – rather than 'short' (picoseconds, nanoseconds, milliseconds).

A special, and limited, case of equilibrium is **thermal equilibrium**, as happens when two systems, or different component parts within a single system, are at the same temperature. **Thermodynamic equilibrium** is a broader concept, requiring all thermodynamic state functions to be in equilibrium. It is therefore possible for a given system to be in thermal equilibrium, but not in thermodynamic equilibrium – as, for example, happens when a gas expands, so changing its volume, but keeping its temperature constant.

A further feature of an equilibrium state is that, at any time, the values of all intensive state functions are the same at all locations within the system, whereas in a non-equilibrium system, it's likely that at least one intensive state function will have different values at different locations. As an example, consider a system composed of a block of metal at a higher temperature, placed in direct physical contact with a block of an equal mass of the same metal at a lower temperature, as shown in Figure 1.2.

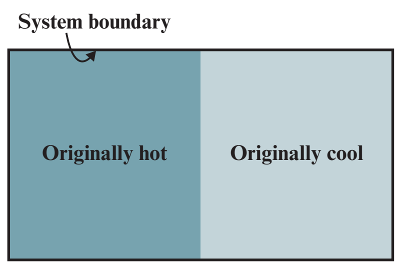

Figure 1.2 A system which is not in equilibrium. This system comprises a hotter block of metal (on the left) in contact with a cooler block of the same mass of the same metal (on the right). Over time, although the mass and volume of this system both remain constant, the temperature at any specific location in the system will change as the originally hotter block becomes cooler, and the originally cooler block becomes hotter. Furthermore, at any one time, the temperature will be different at different locations. Ultimately, both blocks will assume the same temperature, and that temperature will be uniform throughout the system: the system will then be in equilibrium.

An observer of this system would notice that, as time passes, the hotter block becomes cooler, and the cooler one hotter. Although the mass of the system remains constant, as does the volume (assuming that any thermal expansion or compression is negligible), the temperature at any single location within the system changes over time; furthermore, at any one time, the temperature will be different at different locations within the system. These observations verify that the system is not in equilibrium. Ultimately, the system arrives at a state in which, at any location, the temperature no longer changes over time; furthermore, throughout the system, the temperature has the same value. Thermal, and thermodynamic, equilibrium have now been achieved.

Equilibrium is an important concept since it underpins measurement: if a system is not in equilibrium, then the values of at least one state function will be changing over time; furthermore, at any one time, it is also likely that at least one intensive state function will have different values in different locations within the system. Under these conditions, it is impossible to make statements of the form "the value of [this] state function is [this number]", and so