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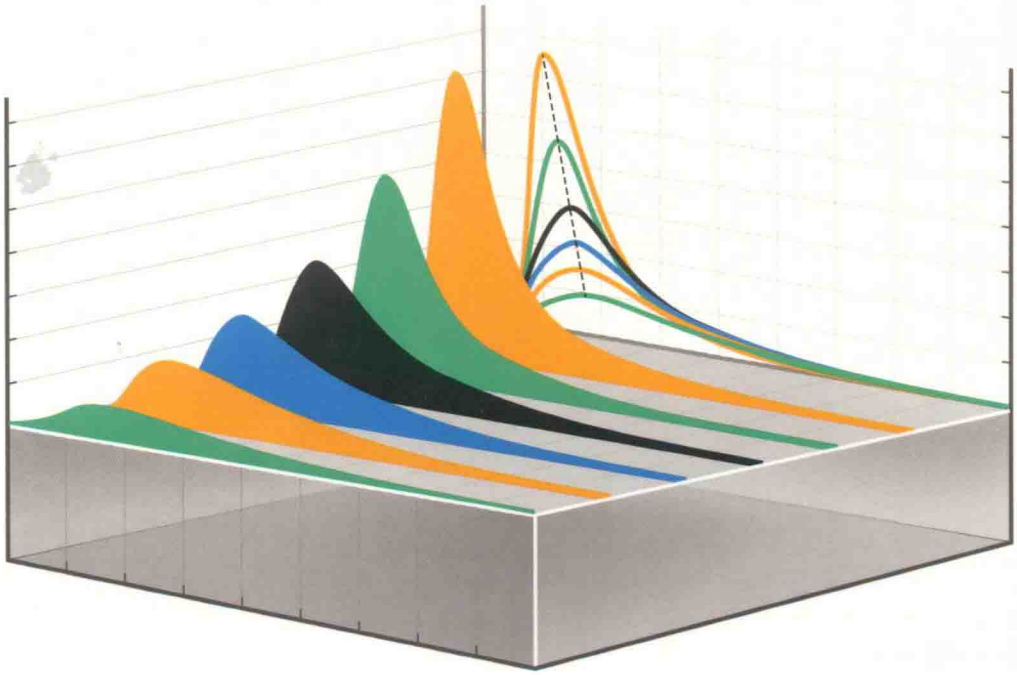

Andrew Maczek
Anthony Meijer

STATISTICAL THERMODYNAMICS

SECOND EDITION

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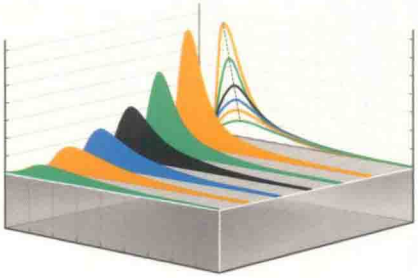

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Impression: 1

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Statistical Thermodynamics

Preface to 1st edition

Statistical Thermodynamics is, in its fullest sense, a *complete* subject. It spans the extremes from Classical Thermodynamics, which firmly avoids any reference to the underlying microscopic structure of matter, through Spectroscopy, whose interpretation requires a willingness to visualize matter in terms of atoms and molecules, to Quantum Mechanics, which illuminates the understanding of spectral behaviour. And it leads to such productive ends! It provides an ability to calculate equilibrium constants from spectroscopic data using Classical Thermodynamics and also (beyond the scope of this text) to the possibility of predicting the rate at which equilibrium is attained using Activated Complex Theory. It is, above all, a *unifying* topic in Physical Chemistry.

Some, coming to Statistical Thermodynamics for the first time, find its rigour, coupled to its simplicity, a little daunting. This book attempts to dispel such worries and to present the topic in a logical and manageable manner. From the outset, in Chapter 1, where the concept of the *most probable configuration* is introduced, to the conclusion, in Chapter 15, where the *position of equilibrium* in real systems is calculated, the reader is encouraged to approach the subject through a series of short, self-contained sections. It is hoped that this approach will make the subject more transparent and easier to understand.

To those who have encouraged me to write this book I am truly grateful. I owe most, perhaps all, to those of my students who, over the years, have reassured me by asking the right questions and giving the right answers. But also, I acknowledge two of my mentors, Peter Gray and Courtenay Phillips, who were the first to show me that it could all be such fun.

Department of Chemistry, University of Sheffield A.O.S.M.
October 1997

Preface to 2nd edition

Reading the preface to the first edition, it strikes us how many of the sentiments expressed there are still true. Statistical Thermodynamics, in our eyes, can still be seen as the apotheosis of Physical Chemistry, the one topic that combines all the things that have come before; it is amazing what can be achieved with the machinery it provides. However, for our students, Statistical Thermodynamics is still a little daunting (sometimes rather more than a little) for all sorts of legitimate reasons.

Therefore, we have decided in this second edition not to deviate from what made the first edition what it was. The reader is still encouraged to approach the subject through a series of short, self-contained sections. However, to aid understanding and to allow students to test their knowledge, we have added a series of self-test questions and some more exam-like questions at the end. In addition, some of the more mathematical aspects of Statistical Thermodynamics are dealt with in an 'Additional mathematical aspects' section, also at the end of the Primer. We hope that this will allow students with greater mathematical ability to get more out of this text, while not closing off the subject to those who are less mathematically inclined.

Department of Chemistry, University of Sheffield A.O.S.M & A.J.H.M.M.
May 2017

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1 The Boltzmann law

1.1 Introduction

The objective of this book to introduce the reader to the methods that link all the predictive potential of classical thermodynamics to an existing understanding of the quantum nature of matter. Classical thermodynamics, based as it is on working fluids which are featureless and lack internal structure, enables us to deduce hitherto unmeasured quantities for specified substances and to predict the position of the equilibrium they will eventually reach if mixed under specified conditions.

Thermodynamics is based on three *laws of experience*. Once these laws are accepted, the edifice it builds is totally self-consistent. If a given measurement has the value X under one set of conditions and the value Y under another, then a number of inescapable consequences follow. In particular, if we can gather together comprehensive lists of free energy data, as is done in thermodynamic tables, we can find ourselves in a position to be able to predict, in quantitative detail, much of what lies in the field we call *chemical change*.

A law of experience is one that is based on observation. It persists only as long as no evidence is found to refute it.

What is lacking, however, is any clear view of why free energies take the values they do. It would be immensely satisfying to be able to predict these values directly from known molecular properties, without having to repeat specific calorimetric measurements of the kind that have given validity to the laws of thermodynamics. It is this predictive power, the ability to link function to structure, that statistical thermodynamics addresses and, to a large extent, succeeds in achieving.

1.2 The Boltzmann factor

At the heart of much of physical chemistry lies the exponential factor

$$\text{Physical quantity} \propto \exp\left[-\frac{E}{\text{const} \times T}\right] \tag{1.1}$$

where the constant, with units *energy per unit of temperature*, is required to make the exponent dimensionless. This expression can be linked directly to the Boltzmann factor, $e^{-\varepsilon/kT}$ and, in turn, to the Boltzmann law (equation 1.2) for the population of quantized energy states, as shown in Fig. 1.1:

$$\frac{n_i}{n_j} = e^{-(\varepsilon_i - \varepsilon_j)/kT} \tag{1.2}$$

The Boltzmann law

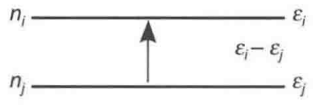

Fig. 1.1 Two quantum states with n_j particles in the lower state with energy ε_j and n_i particles in the upper state with energy ε_i.

In SI units, the temperature, T, is in kelvins and energies are expressed in joules. The constant of proportionality, the Boltzmann constant, k, takes the value 1.38×10^{-23} J K^{-1}.

It is the objective of this chapter briefly to outline the basis of the Boltzmann law before applying it in subsequent chapters. At some stage in a scientific education, it is necessary to confront and to appreciate the origins of this law, but its application to the problems we meet depends less on how it is derived and much more on how it can be used. For those who have already met the derivation, it is perfectly reasonable to turn directly to Chapter 2 and seek such applications.

1.3 The average basis of the behaviour of matter

The first, and vital, step in linking the individual properties of molecules and the thermodynamic behaviour of bulk matter is to realize that thermodynamic properties are concerned with *average behaviour*. Properties such as temperature and pressure (and others), which are characteristic of large assemblies of molecules, are average properties. At any instant, the actual pressure exerted on a given wall may fluctuate a little from the average as slightly more or slightly fewer molecules happen to strike that wall. The actual temperature in one small part of the total volume may be a little higher than the average because of a fluctuation leading to more of the high speed molecules (which carry more energy and are 'hotter') congregating there. But such fluctuations turn out to be negligibly small compared with the established average, simply because the number of particles contributing to the average is so vast.

In this sense, the Boltzmann law (equation 1.2) is also a law that deals with averages. To be strictly correct, the occupation numbers of the two states should be written as averages $\langle n_j \rangle$ and $\langle n_i \rangle$, as in equation 1.3, since these numbers too are subject to infinitesimal fluctuations:

$$\frac{\langle n_i \rangle}{\langle n_j \rangle} = e^{-(\varepsilon_i - \varepsilon_j)/kT} \tag{1.3}$$

However, since the instantaneous values of the occupation numbers are never very different from the averages, we shall dispense with stressing their average nature in everything that follows.

1.4 Plan of attack

In order to gain an understanding of how the Boltzmann law can be reached, we need to use certain aspects of the laws of probability, to establish some assumptions and to understand some of the language that is in accepted use. The list below can serve as a route-map of the progress we hope to make, and each item is discussed in turn in the sections that follow:

- distinct, independent particles
- configurations: sharing out the energy

- statistical weights
- equal probability of configurations
- conservation of number and energy
- the predominant configuration
- maximization subject to constraints.

1.5 Distinct, independent particles

We start by assuming that we have an assembly of particles at *constant temperature*. These particles are *distinct* in the sense that we can always tell which is which They carry labels (a, b, c, . . ., etc). They are also *independent*. We also assume that they interact with each other minimally, just enough to interchange energy at collision. We say that they are *weakly coupled*, and this allows us to write the total energy E, at any instant, as the sum of the individual energies of these labelled particles, ignoring any mutual potential energies between them:

The traditional way of ensuring a constant temperature is to immerse our assembly in a heat bath that is large enough to ensure that there is no overall fluctuation in temperature.

$$E = \varepsilon^{a} + \varepsilon^{b} + \varepsilon^{c} + \varepsilon^{d} + \ldots = \sum_{i} \varepsilon^{i} \tag{1.4}$$

1.6 Configurations: sharing out the energy

Individual particles have access to a manifold of *energy states*, with energies ε_0, ε_1, ε_2, ε_3, . . ., etc. From now on we shall adopt the convention that the state with lowest energy is the zero of energy, that is, $\varepsilon_0 = 0$. This may mean that we have to add some constant value to *thermodynamic energy functions* such as U, H, A, . . ., etc, which are calculated by summing over all possibilities, but this is only a minor inconvenience.

Conventionally $\varepsilon_0 = 0$

Thermodynamic energy functions:
U, the internal energy
H, the enthalpy
A, the Helmholtz free energy
G, the Gibbs free energy

Over a period of time, particles interchange energies (always subject to a constant total energy) so that, at any instant, the distribution of particles among energy states may involve, say, n_0 with energy ε_0, n_1 with energy ε_1, n_2 with energy ε_2, and so on. We call this instantaneous distribution the *configuration* of the system. At the next moment the distribution will be different, giving a different configuration with the same total energy. These configurations identify the way in which the system can share out its energy among the available energy states. For a large number of particles, many different configurations are possible.

A configuration is a specific distribution of particles over energy levels. It does *not* specify which particle is in which state. If one specifies exactly which particle is in which state, then this is often referred to as a *microstate* of the system. The corresponding term macrostate refers to observable quantities of the system, such as pressure, volume, etc.

1.7 Statistical weights

A given configuration can be reached in a number of different ways, that is, each configuration contains a certain number of *microstates*. We call this number of ways, Ω, the *statistical weight* of that configuration. It represents the *probability* that this configuration can be reached, from among all other configurations, by totally random means.

A useful analogy here is to make reference to coin-tossing. If we were to toss a hundred coins successively a huge number of times, then clearly the configuration 'all heads' (or 'all tails') would occur significantly less often than the configuration '50 heads, 50 tails'. The importance of the analogy, however, is that we know how to calculate the probability (statistical weight) of any given configuration, '72 heads, 28 tails', say. For N particles arriving at a configuration in which there are n_0 particles with energy ε_0, n_1 with energy ε_1, n_2 with energy ε_2, and so on, the statistical weight is

The factorial function:
$x! = x(x-1)(x-2)(x-3)(x-4)\ldots$ 3.2.1
By definition, $0! = 1$.

$$\Omega = \frac{N!}{n_0!n_1!n_2!n_3!\ldots} \tag{1.5}$$

which is essentially the number of ways we can create a given configuration by relabelling particles.

Statistical thermodynamics, like much of physical chemistry is best learned by doing problems or actually working through material by yourself. So, we have included self-test questions in the back of the primer to help you with this.

However, you should also do this throughout the primer. Here, rather than accept that the configurations and weights for $E = 4$ and $N = 4$ for a system with equi-energy gaps between levels are given by Fig. 1.2, try to derive this result yourself. How does the result change, if $E = 5$ and $N = 5$ or $E = 3$ and $N = 3$? (See the primer's website for the answer to these questions.)

The configurations and weights for $E = 4$ and $N = 4$ for a system with constant energy gaps between the levels are given in Fig. 1.2. For one of the configurations, we have also enumerated all the microstates.

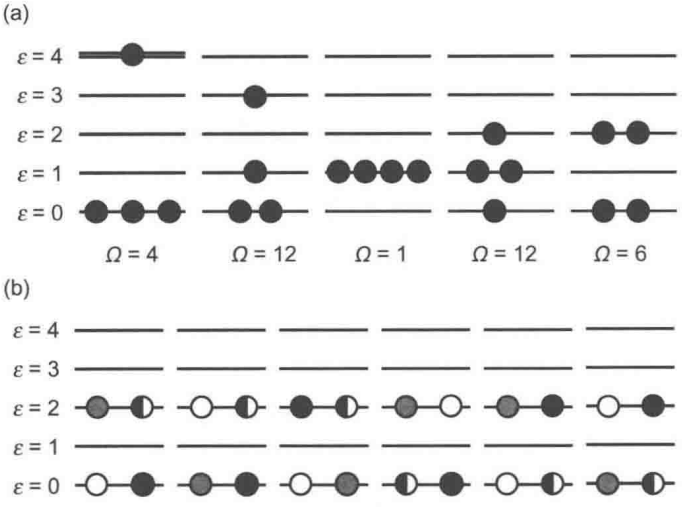

Fig. 1.2 Configurations and microstates for a system with constant energy gaps between levels. Panel (a) shows the configurations and their statistical weights for $E = 4$ and $N = 4$. Panel (b) shows the different microstates that make up the configuration that lies at the far right of panel (a).

1.8 Equal probability of microstates

We assume that there is no bias towards any microstate a system can adopt, that it is free to roam unhindered through all possible microstates. We call this the *principle of equal a priori probabilities*. As a consequence, in the course of time (perhaps infinite time) each configuration will be visited exactly in proportion to its statistical weight. We shall need to use this further down.

The principle of equal a priori probabilities indicates that all microstates are equally probable.

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