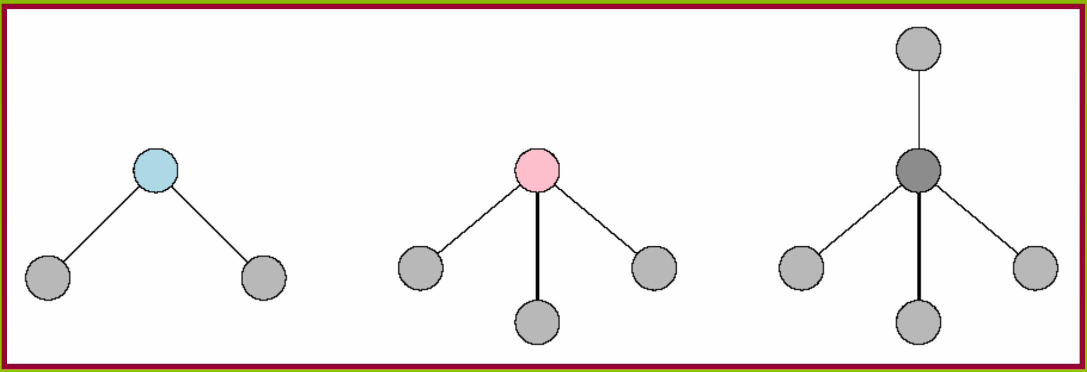
Basic Books in Science

Book 5

Atoms, Molecules and Matter: The Stuff of Chemistry



Roy McWeeny

BASIC BOOKS IN SCIENCE

– a Series of books that start *at the beginning*

Book 5

Atoms, Molecules, Matter – the stuff of Chemistry

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Books in the Series are available *–free of charge–*from the websites
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BASIC BOOKS IN SCIENCE

Acknowledgements

In a world increasingly driven by information technology no educational experiment can hope to make a significant impact without effective bridges to the 'user community' – the students and their teachers.

In the case of "Basic Books in Science" (for brevity, "the Series"), these bridges have been provided as a result of the enthusiasm and good will of Dr. David Peat (The Pari Center for New Learning), who first offered to host the Series on his website, and of Dr. Jan Visser (The Learning Development Institute), who set up a parallel channel for further development of the project. The credit for setting up and maintaining the bridgeheads, and for promoting the project in general, must go entirely to them.

Education is a global enterprise with no boundaries and, as such, is sure to meet linguistic difficulties: these will be reduced by providing translations into some of the world's most widely used languages. Dr. Angel S. Sanz (Madrid) is preparing Spanish versions of the books and his initiative is most warmly appreciated.

We appreciate the interest shown by universities in Sub-Saharan Africa (e.g. University of the Western Cape and Kenyatta University), where trainee teachers are making use of the Series; and that shown by the Illinois Mathematics and Science Academy (IMSA) where material from the Series is being used in teaching groups of refugee children from many parts of the world.

All who have contributed to the Series in any way are warmly thanked: they have given freely of their time and energy 'for the love of Science'.

Pisa 10 June 2007 Roy McWeeny (Series Editor)

BASIC BOOKS IN SCIENCE

About this book

This book, like the others in the Series[1], is written in simple English – the language most widely used in science and technology. It builds on the foundations laid in Books 1-4, which covered many parts of Mathematics and Physics.

But the approach will be a bit different. In Book 4, we were able to start from simple observations about the way things move when they are pushed or pulled; and then to introduce concepts, like force and mass, and finally to set up 'laws of motion' for simple systems consisting of a few point masses or 'particles'. From there we could pass directly into the foundations of Physics. But in the present book we're going to be talking about particles so small that nobody can ever even see them. All the things around us, sticks and stones, flesh and bones, and even the air we breathe, are made up from countless millions of such particles. They are called **atoms** and when they are put together they give us various forms of **matter**: sometimes the atoms stick together in small groups, called **molecules**; or in enormous groups (with the atoms arranged in a repeating pattern), forming **crystals** like salt or ice; sometimes the atoms stay apart and move around at high speed, as in air and other **gases**. All these forms of matter are studied in **Chemistry** and this interpretation of what matter consists of, going back to ancient times, is the **atomic hypothesis**

When different kinds of matter are put together they may **react**, giving new **products**, in which the atoms are differently arranged. Sometimes the **reaction** is *explosive*, sometimes it is slow and gentle, as in cooking food. And in Chemistry we want to know all about such reactions. The ancient philosophers didn't have much understanding of all these things: they worked almost entirely by 'trial and error' (sometimes you get it right, sometimes you don't) and Chemistry started as a purely experimental subject. It took many hundreds of years to make sense of everything that happened: but you can start from what we know *now*, essentially that **the atomic hypothesis is true**, and you can also make use of what you've learnt in Mathematics and Physics. That's the way we'll go in Book 5 – taking all the 'short cuts' we can find!

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[1] The aims of the Series are described elsewhere, e.g. in Book 1.

Looking ahead –

Like Physics, Chemistry is a big subject and you'll need more than one book; but even with only Book 5 you'll be able to lay the *foundations* which are needed in all parts of the subject – going from the structure of matter, in terms of atoms and molecules, to the way matter can be changed by *chemical reactions*, to the reactions among gases in the atmosphere, to those that go on in our bodies (the subject of the Life Sciences, like Biochemistry and Biology). The part of Chemistry dealt with in this book is mainly the part closest to Physics (Physical Chemistry), so Book 4 has given you many of the basic ideas. But what is new is that you can never actually *see* what's going on in Chemistry at the deepest level – of the atoms themselves. You have to *imagine* everything that happens, starting from the atomic hypothesis and using the laws of Physics to try to *interpret* what you can see in the laboratory.

Let's look at some of the main steps you'll take.

- In Chapter 1 you learn what **atoms** are. how small they are (so small that it takes around 10^{24} of them to fit inside a 1cm cube) and how they can come together to make **molecules** and other structures: they are the 'building blocks' of matter. You get first ideas about what they are made of: mainly **electrons** and **protons**, which have both mass and 'electric charge', and **neutrons** which have only mass. You know about mass and force from Book 4, but electric charge will have to wait until Book 10; it's enough here to know that it's what generates the *forces* between particles that carry a charge.

  The rest of the chapter is about what you can build from the atoms; first molecules and then matter 'in bulk', in the forms you know best as **solids**. **liquids** and **gases**.

- Chapter 2 builds on the Physics in Book 4, showing that the moving molecules in a gas must produce a **pressure** on the walls of the container that holds them. If the container is *heated*, the molecules move faster and their increasing **kinetic energy** measures the 'hotness' of the system. You learn about **temperature scales** and find the 'equation of state' (relating temperature (T), pressure (P) and volume (V) for this **ideal gas**

- In Chapter 3 we really pass from Physics into Chemistry, by including the **thermal motion** of the atoms and molecules (never even thought about in Book 4!). In **chemical reactions**, where molecules may be breaking up and forming new ones, the thermal energy is constantly changing. The whole system will have an **internal energy** (U), which may be changed by heating it (putting in **thermal energy** q), or by doing **work** (w) on it: the total change will be $\Delta U = w + q$ and this is the **First Law of Thermodynamics**. Energy is still never lost: it's just pushed around from one form into another!

  This key principle extends the idea of energy conservation (in Book 4) to systems in which heat flow takes place; and the nature of the matter itself is changing through chemical reactions among the molecules. You'll find how to deal with such changes, defining standard **heats of reaction**, **heats of formation**, and so on, which can be collected in Tables and used over and over again: this is **thermochemistry**.

- Chapter 4 goes deeper than Chapter 2, using the ideas of **probability theory** to think about the *distribution* of molecular speeds in an ideal gas. You'll meet the laws of Gauss and of Maxwell and find how **temperature** comes into the picture.

- In Chapter 5 there are many new ideas: energy is never *lost*, but it may be *wasted* – going into forms which can't be used in doing work or boiling water. This is because heat always flows 'downhill' from a hotter body to a cooler one, never the reverse. From this simple idea you come to the **Second Law of Thermodynamics** and discover a new quantity, the **entropy**. Anything that happens 'by itself' is **irreversible**: it will never run backwards! It must lead to **entropy increase**; and as far as we can tell this principle holds everywhere in the whole Universe! Here, on Earth, you need it in talking about almost everything to do with heat and energy – from **steam engines** to **refrigerators**.

- The next two chapters are about *understanding* where the laws of thermodynamics come from, at the level of the atoms and molecules. They build on the ideas of order and disorder, the laws of large numbers and **probability**. You'll find that increasing entropy corresponds simply to increasing *disorder* and that all of 'classical' thermodynamics (from the days before much was known about atoms) can be built up from what you know about probabilities. You'll find new bridges between theory and experimental chemistry.

- And in a final chapter you'll learn how to predict what will happen in simple chemical reactions: whether the reaction will probably go with a bang, with all the reactants used up; or whether it will go only halfway, with a lot of stuff left over; or whether it won't go at all!

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Notes to the Reader.

When Chapters have several Sections they are numbered so that “Section 2.3” will mean “Chapter 2, Section 3”. Similarly, “equation (2.3)” will mean “Chapter 2, equation 3”.

Important ‘key’ words are printed in **boldface**, when they first appear. They are to be collected in the Index at the end of the book, along with page numbers for finding them.

(The **Index** is still in preparation and will appear in the next updating. The same is true for the **Exercises**, which will appear at the end of every Chapter.)

Chapter 1

The structure of matter

1.1 Atoms – the building blocks of matter

Have you ever wondered what everything around you is *made of* – stone, metal, air and water, even living creatures? People started asking that question thousands of years ago. Nowadays we can give an answer: everything is built up from **atoms** and in our world we find less than a hundred different kinds of atom. Atoms of any one kind form a **chemical element** and when these elements are put together, in countless different ways, they give us all known forms of **matter**.

Each kind of atom has a definite **mass** (see Ch.1 of Book 4) and an approximate 'size' (approximate because the atoms are a bit 'soft' and may get 'squashed' by the other atoms around them). They have been given names and symbols (standing for their names): the atom of smallest mass is called Hydrogen, with symbol H; the next, in order of increasing mass, is Helium (He) and the next is Lithium (Li). Figure 1 will give a rough idea of the relative sizes of the first ten atoms, showing also their names and chemical symbols:

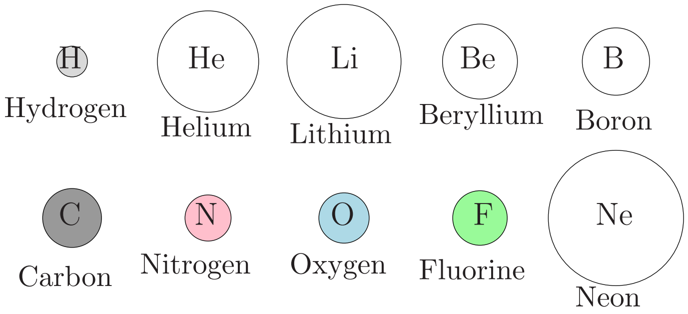


Figure 1. Relative sizes of the 10 lightest atoms

The atoms shown in colour (mainly, in fact, H, C, N, O) are the ones that make up more than 99 percent of your total body mass: they are the atoms that are vital to an understanding of the **Life Sciences** (like Biology and Biochemistry). And the science built mainly around these elements is **Organic Chemistry**. All the rest used to be called **Inorganic Chemistry**, but nowadays we don't make such sharp separations between the different areas of the subject. Chemistry is about atoms, how they can be built into more extended **structures**, like **molecules** and **solids**, and about how the new structures can be prepared by means of **chemical reactions**. But above all it is about *understanding* how atoms and molecules behave and what you can do with them.

One of the most amazing things about atoms is their *size*. Most books use the **Ångström**, with 1 Å$= 10^{-10}$m $= 10^{-8}$cm, when talking about atoms; and the centimetre (cm) is the 'everyday' sort of unit used in describing small objects. But if you want to measure quantities of the 'stuff' you're dealing with, then you'll be more interested in the *volume* of the bits of stuff (which we've called "atoms"); and a length unit of 10^{-8}cm corresponds to a volume unit of $(10^{-8}\text{cm})^3$. To fill a 1 cm cube wih atoms of that size, you'd need around 10^{24} of them! That's a quantity of stuff you can easily imagine – it would fit inside a small box. It's approximately what Chemists call a **mole** of stuff. In fact, a mole of atoms is just a bit less than 10^{24} of them. This number is called "Avogadro's number" and is usually denoted by L (after Loschmidt, who used it first); its more precise value is

$$L = 0.602 \times 10^{24}.$$

The reason for that strange definition is buried in history; but it's only a convention anyway and the important thing to remember is that a quantity of 1 mole contains L 'elementary units', whether they be atoms, molecules, or even bicycles!

The masses of the atoms indicated in Fig.1 are often expressed as multiples of an *atomic mass unit* $m_{\text{u}} = 1.661 \times 10^{-27}$ kg: the approximate numerical multipliers are collected in Table 1 for the first ten elements.

H	He	Li	Be	B	C	N	O	F	Ne
1.0	4.0	7.0	9.0	11.0	12.0	14.0	16.0	10.0	20.0

Table 1. Relative atomic masses for the first ten elements.

Thus, the mass of an atom of Lithium is $m_{\text{Li}} \approx 6.0\ m_{\text{u}}$. The *numbers* in Table 1 used to be called "atomic weights", but more corectly they are **relative atomic masses**, each being a ratio (atomic mass divided by atomic mass unit). We'll often just call them "atomic masses", the unit m_{u} being understood. You might have expected them to run from 1 up to 10, corresponding to the order of the atoms in the list, but in a later Section we'll discover why it's not so.

Now let's come back to the mole as a unit of quantity and ask what is the mass in kg of 1 mole of atoms with atomic mass x. The mass of a single atom, in kg, will be $x \times m_{\text{u}} = 1.661 \times 10^{-27}x$ kg: and the mass of a mole of those atoms will therefore follow on multiplying by L (given above). The resultant **molar mass** will thus be

$$\text{molar mass} = L(= 0.602 \times 10^{24}) \times 1.661 \times 10^{-27}x \text{ kg} = 1.000 \times 10^{-3}x \text{ kg}.$$

In other words,

> The molar mass of an element X will be the atomic mass of the X atom, expressed as that number of grams.

It's no accident that it's so easy! (Check the rule for yourself, using the definitions given above.) And now, if you have a Table showing the atomic masses (i.e. relative atomic masses) of the elements, you can write down immediately the masses of a mole of any element, in grams. For example, a mole of the metal lithium will have a a mass of almost exactly 7 g, while a mole of oxygen atoms will have mass 16 g, and one of hydrogen atoms will have mass 1 g. In later Sections we'll be dealing with **compounds**, built up by combining atoms of various elements, in a similar way.

1.2 But what are atoms made of?

Before starting to build molecules you'll be wondering what's inside the atoms themselves. (If you don't want to know yet, you can skip this Section and come back to it later.)

Just after Table 1 we noted that the atomic mass numbers of the elements were not simply related to the numbers 1, 2, ... 10, which gave the order of the elements in the list: they jumped around quite a lot – 1, 4, 7, 9, ... 20. Nowadays we know the reason for this; and it's quite simple.

All atoms contain one very heavy particle, called the **nucleus**, together with a number of much lighter particles (more than two thousand times less massive) called **electrons**. It's the number of *electrons* that corresponds to the order in which the elements are listed: this is called the **atomic number** and is always denoted by Z. The *chemical* properties of an atom are determined by Z, but the *mass* of an atom, which is almost equal to that of the nucleus alone (the electrons being so light), depends on which element you're talking about.

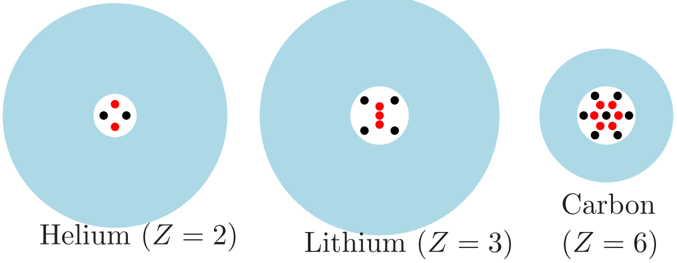


Figure 3. Constituents of He, Li, C (schematic)

The nucleus contains in fact *two* kinds of heavy particle. They are called **protons** and **neutrons**; and they have almost exactly the same mass. It's now clear why the atomic masses in Table 1 (which go 1.0, 4.0, 7.0, etc.) can be so different from the atomic numbers Z (which go 1, 2, 3, etc.): the mass of the nucleus must be simply the number of heavy particles (both types of '**nucleon**') which it contains. For example, the nucleus of the He atom must contain 4 nucleons, two of them protons, the other two being neutrons; and similarly the Li nucleus ($Z = 3$) must contain 3 protons, the remaining 4 being neutrons.

What about the much lighter particles, the electrons? It used to be thought that they moved around the nucleus in orbits, like the planets around the sun (studied in Book 4); but now it's known that they don't follow definite paths. Think of them instead as buzzing around the nucleus like a swarm of bees: the number of electrons is definite and is equal to Z; but you can never know exactly where they are! Figure 3 may help you to get a picture of what's inside an atom.

Remember this picture is very schematic: the light blue balls just indicate the regions in which the electrons are most likely to be found. The diameters of these atoms are of the order of 1 Å unit, 1 ten-millionth of a centimeter – so it's no surprise that you can't see them. And the diameters of their *nuclei* are roughly ten thousand times smaller still! So the white circles in Fig.3, really give no idea of nuclear sizes; they are there only to indicate the *contents* of the various nuclei. The red spots represent the protons and the black spots the neutrons; but again you mustn't think of them being placed at particular positions to form some kind of structure – like the electrons, they're always on the move and there's no way of knowing exactly where they are. In chemistry all that doesn't matter: what counts is the atomic number Z, the number of red spots in Fig.3, which determines all the chemical properties of the elements.

Before moving on to molecule building, just one last question: What holds all these particles together? There must be **forces** of some kind, which can pull them together or push them apart. In Chapter 1 of Book 4, you learnt about forces and especially the force 'due to gravity', which pulls any mass towards the centre of the Earth and makes it fall to the ground. The forces inside an atom are so much bigger that we can now forget about gravity. The electrons are attracted towards the nuclei because both carry an **electric charge**. This idea was not dealt with in Book 4 and will be treated in detail much later in the Series, but for what we have to do now it's easy to explain. The *gravitational* force F_{grav} between two *masses*, m_1 and m_2, is proportional to their product. and to the inverse square of the distance r between them. The force F_{elec} between two particles carrying *electric charges*, q_1 and q_2, is given by a very similar law. In fact

$$F_{\text{grav}} \propto \frac{m_1 m_2}{r^2} \quad (a), \qquad F_{\text{elec}} \propto \frac{q_1 q_2}{r^2} \quad (b). \tag{1.1}$$

But whereas masses are always *positive* quantities, and the force F_{grav} is an attraction, the charges can be either positive or negative: if both have the same sign F_{elec} is a repulsion (tending to increase the separation r); while if q_1 and q_2 are of opposite sign F_{elec} is an attraction (tending to reduce the separation r). In short,

> **Charges of the same sign repel one another, those of opposite sign attract one another.**

We can now answer the question we started from. Electrons are particles with a negative charge, written $-e$ (e being used for the *magnitude* of the electronic charge); protons are particles with a positive charge $+e$; and neutrons are particles with zero charge. It follows that:

> A nucleus, with positive charge Ze will repel any other nucleus, as also will any

two electrons, but that the nuclei will be attracted towards any ‘electron-rich’ region.

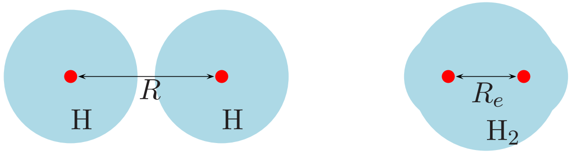
This simple principle holds the answer we needed: all the structures we meet in chemistry, however elaborate they may be, are held together by forces which are basically electrical in origin.

1.3 Building molecules

Now we know enough about atoms to start putting them together. The simplest structures we can imagine contain just two atoms; they are **diatomic molecules** and the simplest one of all is the hydrogen molecule, usually indicated by H_2. The subscript 2 shows there are *two* H atoms and therefore two nuclei, each being a proton with positive charge $+e$.

The hydrogen molecule

In the pictures below the nuclei are shown as red spots: the electrons are most likely to be in the regions shown in light blue – but we can’t say exactly where, so think of the blue as the picture you would get if you could photograph them with a long ‘time exposure’, giving you a blurred image. In Fig.4(a) the atoms are far apart, each with its own electron – shown as a blue ball, as if the electron were ‘smeared out’ into a ‘cloud’ of negative charge, with the nucleus at the centre.



(a) (b)

Figure 4. Formation of H_2.

In Fig.4(b) the two atoms have moved closer together and the two separate electron clouds have become one, showing an increased density *between* the nuclei: that’s where the electrons are most likely to be found. As the electrons carry negative charge and the nuclei (indicated by the red spots) are positive, the nuclei are both attracted towards the charge cloud (shown in blue) between them. But they move together only until the force of attraction is balanced by the force of repulsion between them. When the forces are in balance the system is in **equilibrium** and at that point the separation R_e is the **equilibrium bond length**. This is the origin of the chemical bond (more exactly the *covalent bond* which holds atoms together in a molecule: the cloud of electrons, or negative ‘charge density’, provides the ‘glue’. Later, we’ll find another kind of bond, very common in crystals, but for the moment let’s look at a few other molecules.

Lithium Hydride

When two *different* atoms come together they may also form a chemical bond, as in Fig.5. Here the atoms are lithium (Li) and hydrogen (H) and they give you “lithium hydride”, LiH. But as the atoms are different the molecule of this **compound** is 'lopsided' as in Fig.5(b).

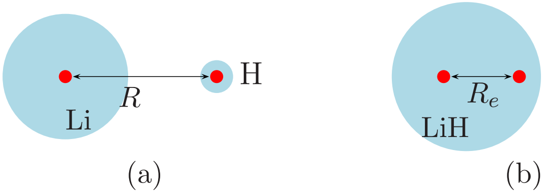


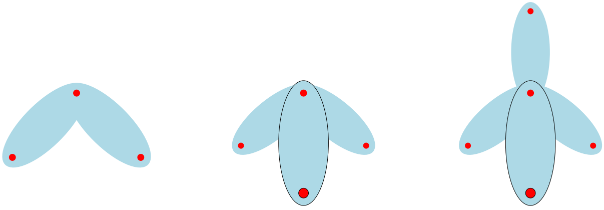
Figure 5. Formation of LiH.

That's because Lithium ($Z = 3$) is three times as strong as Hydrogen in attracting electrons and it grabs more than its fair share of the charge cloud. As a result the hydrogen nucleus is 'swallowed' by the Lithium. Instead of being shared more or less equally between the two atoms, the electronic charge cloud is pulled over towards the nucleus with the higher value of Z. It's as if the H has lost its electron, which now belongs to the Li. When this happens, the atom that loses the electron becomes a **positive ion**, while the one that gains it becomes a **negative ion**. The ions formed in this way are denoted by adding to the name of the atom a + or − sign to get, in this example, H^+ and Li^-. Of course the transfer of an electron isn't always complete – as you can see from Fig.5(b), the two nuclei are both sitting inside the same electron cloud – but this kind of bond is often described as *ionic*. And many people like to think of it as coming from the attraction between a positive ion H^+, which is just a 'bare' proton, and the negative ion Li^-, which is simply Li with an extra electron. In the present example, it looks as if the proton is 'embedded' in the lithium negative ion; but whatever description you like best, remember it's only an *approximation* which helps to give a simple picture of what's going on.

Some other small molecules, H_2O, NH_3, CH_4

From two atoms of hydrogen and one of oxygen it's possible to form the **triatomic molecule** H_2O, which is the elementary unit of water – which, as you know, is a liquid. The molecule has the shape of a letter V, with the angle H-O-H opened out to about 105°, and is one of the most plentiful and important molecule in the world (think of the oceans and the fact that most of your body is simply water!). This molecule is pictured in Fig.6(a)

But if you take the nitrogen atom, instead of oxygen, it can combine with *three* atoms of hydrogen to give the 'ammonia' molecule NH_3, which again forms a *gas*. The molecule has the form of a pyramid with the nitrogen atom at the top, as in Fig.6(b); and the gas, found during the decay of animal and vegetable waste (e.g. in stables), has a sharp smell that makes you catch your breath. So changing just one atom in the molecule can completely change the nature of a substance.

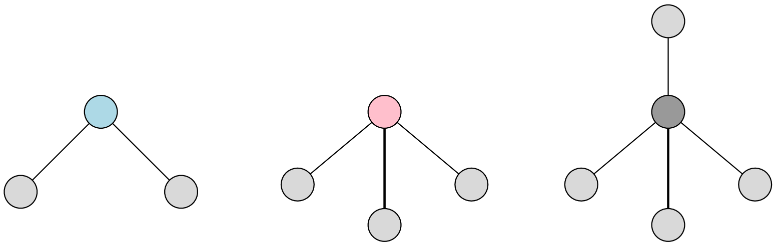


(a) H_2O (b) NH_3 (c) CH_4

Figure 6. Some simple polyatomic molecules.

(Note that, in the Figure, the bond that points towards you is outlined in black)

Pictures like these are often simplified by showing the various atoms as small balls connected by 'sticks'. In this way you get the 'ball-and-stick' molecular models shown below (Fig.7). (Bonds that point towards you are shown with a thicker line and the same colours are used for the atoms as in Fig.1)



(a) H_2O (b) NH_3 (c) CH_4

Figure 7. Ball-and-stick models.

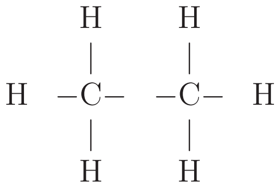
If you use the carbon atom (C), in place of O or N, it can combine with *four* H atoms to give the 'methane' molecule CH_4, which again forms a gas. The gas burns very easily and is used in stoves and lamps; it is also found naturally, underground, as 'natural gas' along with oil and petrolium products, and is very important in industry. The molecule has the form of a pyramid CH_3, with one extra H attached to the carbon atom at the top. Of course you can't always be drawing pictures of all the molecules you can make: the important thing is the **chemical formula**, which lists the atoms and shows how many of them you need and (roughly) how they are connected. Thus H_2O has two hydrogens joined to one oxygen; NH_3 has three hydrogens joined to one nitrogen; and CH_4 has four hydrogens joined to one carbon. (Note that we don't always add the word 'atom', the name of the element being enough; and that the *order* in which the symbols are written doesn't usually matter.)

The molecules indicated in Fig.6 and Fig.7 are all held together by **covalent bonds** in which a pair of electrons is 'shared' by the two atoms joined by the bond. In these examples, the number of hydrogens attached to another atom is called the **valence** of the atom: so oxygen in H_2O has a valence of 2, or is 'di-valent', while nitrogen in Fig.6b is tri-valent and carbon in Fig.6c is 'quadrivalent'. Hydrogen itself is 'mono-valent', attaching itself to only one other hydrogen. In the early days of chemistry, the valence number was thought of as the number of 'hooks' with which an atom could hold on to other atoms: the valence was thought to be a property of the element and whole books were written on the subject (more than 90 different elements are found in Nature!). But nowadays we think about this property in terms of shared electons, rather than mechanical hooks. And you'll have to wait for Book 10 before you can learn the whole story.

Methane is a key molecule in organic chemistry, being the first of a long series of molecules called the **paraffin series**: they can all be built from carbon and hydrogen alone simply by adding more and more CH_2 'groups' to form a chain

$$\mathrm{H} - (\mathrm{CH}_2) - (\mathrm{CH}_2) - (\mathrm{CH}_2) - (\mathrm{CH}_2) - \mathrm{H}$$

in which every carbon atom has two hydrogens and is also connected to the two carbon atoms in the groups that go before it and come after it; the end groups in the chain each take an extra hydrogen, so that every carbon is joined to four neighbours. As you can easily see, a paraffin chain with n CH_2 groups will have the general formula C_nH_{2n+2}. The formula isn't always enough to tell you which atoms are connected. In that case you may need to help it: for example, the second member ($n = 2$) of the paraffin series (called 'ethane') could be written as



$$\begin{array}{cccc} & \mathrm{H} & \mathrm{H} & \\ & | & | & \\ \mathrm{H} & -\mathrm{C}- & -\mathrm{C}- & \mathrm{H} \\ & | & | & \\ & \mathrm{H} & \mathrm{H} & \end{array}$$

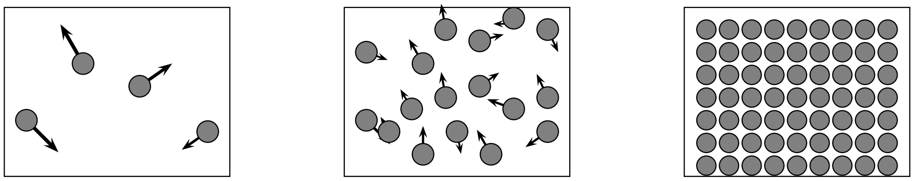
which shows how each carbon is connected to four neighbours. This shows the *topology* of the molecule, but not its *geometry* i.e. how the atoms are arranged in space. Here it's as if the molecule has been squashed flat, in the plane of the paper: squashing changes the geometry, but doesn't change the topology - things are still *connected* the same way.

One thing the formula *does* tell you, however, is what quantities of hydrogen and carbon are needed in making ethane. To get quantities big enough to see, and weigh, you need enormous numbers of atoms and molecules. But we know from Section 5.1 how to go from molecules to moles: the molecule C_2H_4 is the 'elementary unit' of ethane, the substance, and if we take L molecules we'll have $2L$ atoms of C (the elementary unit of carbon, which is a solid) and $4L$ atoms of H (the elementary unit of hydrogen, which exists as a gas of H_2 molecules). So to make 1 mole of ethane you'll need 2 moles of carbon and 4 moles of hydrogen – it's easy! And it's all you need in order to understand the 'cookbook' of chemistry.

But you'll want to know how to weigh out 2 moles of this and 4 moles of that – if you're dealing with a gas how do you go about it? So first you need to know a bit about the **states of matter**, gases and solids and their properties.

1.4 The states of matter.

There are three main kinds of matter: gases, liquids, and solids, all built out of similar elementary units – molecules (including of course atoms, which are monatomic molecules) They are called the **states** of matter: in a gas the molecules are, on the average, a long way apart and moving quite rapidly; in a liquid they are much closer and constantly bumping into each other – jostling in a crowd; in a solid they are packed close together so they can hardly move. The states are pictured in the Figure below. The molecules are shown as circles, with arrows attached to indicate how fast they are moving and in what direction (i.e. their **velocity vectors**; they are put in a two-dimensional box only because it's easier to draw them that way. In reality, the container will be three-dimensional and the number of molecules in unit volume will be the **number density**. This density increases as you go from gas, Fig.8(a), to liquid, Fig.8(b), to solid, Fig.8(c); and since each molecule has a *mass* the **mass density** of the material also increases.



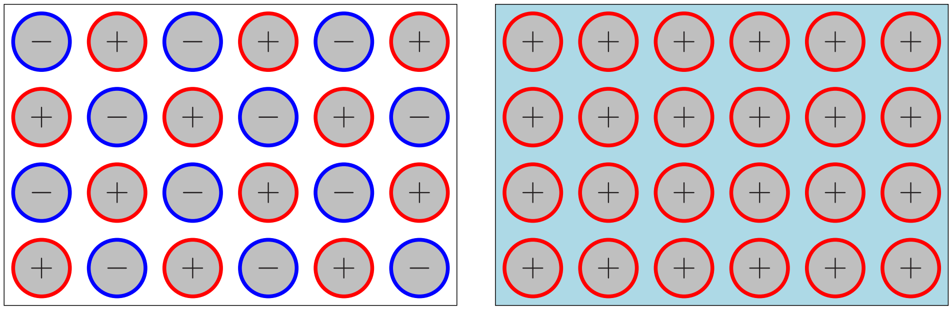
(a) Gas (b) Liquid (c) Solid

Figure 8. The states of matter

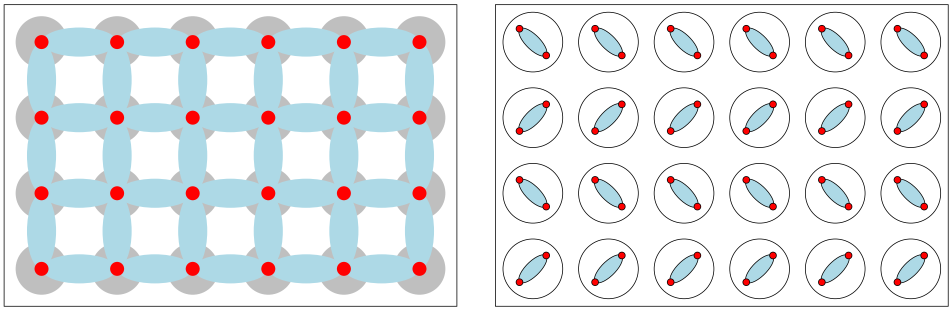
Now it's clear why gases weigh very little, while solids are dense and can be quite heavy, holding a lot of mass in a small volume. Gases and liquids are both **fluids** and take the shape of whatever container you put them into, but solids keep the shape you give them (by bending, cutting, or beating).

There are many different kinds of solid: Figure 9 just shows a few of the most common forms. The pictures are only 'schematic', but will be enough to show up the main differences between one type and another. Fig.9(a) indicates how an **ionic crystal** is built up: the basic units are not atoms or molecules, but positive and negative *ions*. So every unit carries a charge (the positive ions being shown outlined in red, the negative in blue) and the oppositely charged ions attract each other. The cystal holds together because ions of each kind have 'nearest neighbours' only of the opposite kind. Their attraction outweighs the repulsion coming from more distant ions of the same kind. The regular **lattice** of ions is what gives crystals like salt and ice their special shapes, but ionic crystals don't have strong bonds and they usually break easily.

Metals, on the other hand, can be very strong. They are usually built up from atoms that easily lose some of their electrons into a common 'pool'. In Fig.9(c) the pool of electrons is shown in blue (negative charge) and the positive ions they leave behind are circled in red, as in Fig.9(a); but there are no negative ions – the positive units are left alone, swimming in a sea of negative charge.



(a) Ionic solid (b) Metal



(c) Covalent solid (d) Molecular crystal

Figure 9. Some types of solid (schematic)

This simple picture helps us to understand many of the special properties of metals: they can be bent without breaking strong bonds, because the bonding is not ‘localized’ between pairs of atoms and if the positive units are moved they are still attracted towards the ‘sea’ that can flow around them; and the sea of electrons is easily moved if an electric force is applied from outside – metals are good **conductors** of electricity.

Some kinds of solid, however, still depend on covalent bonds like those in simple molecules. Fig.9(c) indicates the structure of a **covalent solid**, in which neighbouring atoms are held toether by a network of strong covalent bonds, not very different from those in diatomic molecules. It is the cross-linking of all the bonds that gives these solids their strength and hardness; you can’t push the atoms around without breaking large numbers of bonds. Crystals of diamond, for example, are among the hardest known materials: you even can cut steel with a wheel studded with tiny bits of diamond.

The last kind of solid in Fig.9 is a **molecular crystal**, Fig.9(d), in which the basic units are simply *molecules*, not held together by any bonds of the kind we’ve met so far. Often the molecules are quite big, but the interactions between them are very weak and it is easy to separate the molecules – which may come away as vapour, giving the material a particular smell. Camphor is one you may know, but new materials of this kind are constantly being produced in organic chemistry.

Exercises – to follow.

Chapter 2

Molecules in motion

2.1 The ideal gas: a simple model

The simplest system to start from is a ‘box’ containing only molecules, usually far apart and moving in all directions at high speed. Suppose, for simplicity, that each molecule consists of only one atom (i.e. is “monatomic”) and is therefore just a single particle, a **point mass**, which moves according to the laws of physics (Book 4). Suppose also that the

box has a movable wall, as in Fig.10(a), so that its volume can be changed by moving the wall.

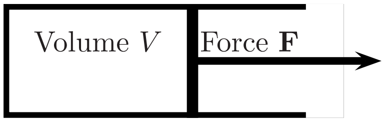


Figure 10(a)

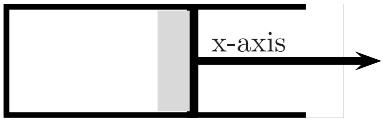


Figure 10(b)

That’s what happens in a **pump**, where the movable wall is called a **piston** and may have a handle – to which you can apply a **force** F. If the piston has a surface area A, the force per unit area F/A is the **pressure** exerted by the gas: we’ll denote the pressure by P and the volume of the box by V. (If you’ve forgotten all about volumes and forces and the laws of physics, you’d better look back at Books 2 and 4 as you’re going to need them!)

Most things that go on in Chemistry depend on pressure and volume, so we want to know how P and V are related and how they depend on molecular motion. In Book 4 we were usually dealing with only one or two particles at a time and we could find how they moved, when forces acted on them, by using Newton’s laws: but now we’re talking about a container in which there are millions and millions of particles! So we can only use general principles and think about what goes on “on the average”: for example, there may be n particles per unit volume and that number probably won’t change much as we go from one element of volume to another – the **average** number per unit volume will be everywhere $n \approx N/V$, where N is the *total* number of molecules in the container. In the same way we’ll suppose that they all move with about the same average speed. We know that when a particle hits the wall and bounces back its momentum will be changed; and that the *rate* of change of momentum, in any direction, will show up as a *force* in that direction. *One* particle will hardly do anything, but millions *will* – and to find the force exerted on the piston by the millions of hits we only need get the total momentum change per unit time in the x-direction in Fig.10(a). We do it as follows.

- In time t, a molecule with x-component of velocity v_x will move a distance $v_x t$ towards the piston. The shaded 'slab' in Fig.10(b), of thickness $v_x t$ and area A, will therefore contain $nv_x tA$ particles that will hit the piston:

  $$\text{Number of hits/unit time } = nv_x A.$$

- x-momentum change per hit is $mv_x - (-mv_x) = 2 \times mv_x$ (assuming perfectly elastic collision), so

  $$\text{Resultant force } = 2nAmv_x^2$$

- Pressure = Force/Area = $2nmv_x^2$ (v_x positive). On writing $\langle v_x^2 \rangle$ for the **average value** of v_x^2, this gives

  $$P = \tfrac{1}{2} 2nm\langle v_x^2 \rangle = nm\langle v_x^2 \rangle$$

- All components give same average value:

  $$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \tfrac{1}{3}\langle v^2 \rangle \quad (v^2 = v_x^2 + v_y^2 + v_z^2)$$

  and the pressure formula thus becomes

  $$P = \tfrac{1}{3} nm\langle v^2 \rangle.$$

- Multiplying by volume (V) and noting that $n = N/V$, this gives the **ideal gas law** which we write in the form

  $$PV = \tfrac{2}{3} N\langle \tfrac{1}{2} mv^2 \rangle = \tfrac{2}{3} U, \qquad (2.1)$$

  where U is the **total kinetic energy** of the gas molecules.

2.2 Temperature and thermometers

The gas law (**??**) simply states that, for N molecules in a container, "pressure × volume = constant", and that the 'constant' (C, say) measures the average kinetic energy per molecule. But the 'constant' is *really* constant only if we don't allow anything else to change – only P and V.

Suppose now you come back on a very hot day and make the same experiment, determining V for a series of values of the pressure P and finding $V = V(P) = C/P$. If you make a graph of V against P it should be a straight line of slope C, but the slope is not the same as it was on a cold day! In fact, the value of C depends on the *hotness* of the system, the container and the gas inside it. It would be nice if we could *measure* the hotness (from now on we'll call it **temperature**) in some way, but first we need to be sure of exactly what we mean by "temperature".

When the gas in the container is *not changing* in any observable way, as time passes, it is said to be in **equilibrium**: it is in a **state**, corresponding to the values of the two variables P, V. Now forget about the system in Fig.10, with its movable piston, and think instead of *any* two systems, X and Y say, each comprising a given number of molecules in a container of fixed volume and each free to exchange thermal energy with the 'outside world'. This means the walls of the containers are **thermally conducting**. The state of each system may be prepared by putting it in a **'heat bath'** (e.g. a large tank of water), called a **thermostat**. If X has been in a bath of *cold* water and Y in one of *hot* water, until equilibrium is reached, then X will be at some temperature, T_1 say, and Y will be at temperature T_2. Now put them together, as in Fig.11(a), so they can exchange thermal energy, but wrap them up well with some material that does not allow such energy to escape from X + Y into the outside world: material of this kind is said to be **thermally insulating**. In Fig.11(a) the cold system is shown in blue, the hot system in red, and the insulating material in grey. But they don't stay that way for long, as thermal energy flows from the hot part Y to the cold part X; and after a while the system comes into a new equilibrium state, indicated in Fig.11(b).

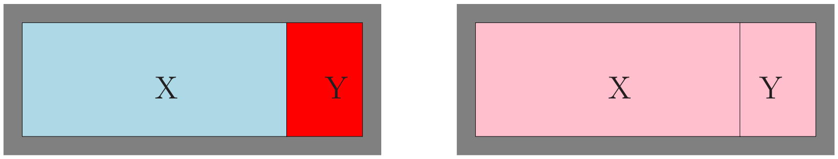


Figure 11(a)

Figure 11(b)

As far as we know, the only thing that can have changed – *at the level of the molecules* – is their total kinetic energy. *Heating a system* is simply another way of putting energy into it: the energy put in is described as **thermal energy** and its effect is to increase the average speed of the molecules. In equilibrium, the energy exchange has stopped and X and Y are said to be "at the same temperature": in Fig.11(b) they are shown in the same colour, pink. To summarize:

> **Two systems in thermal contact, free to exchange energy only with each other, will be in equilibrium only when their temperatures reach a common value.**

Next we'll need to set up a **temperature scale** by first defining two 'fixed points': Point 1, 'cold'= temperature (T_1) of melting ice, Point 2 'hot'= temperature (T_2) of boiling water): these points will be identified by the corresponding values, x_1 and x_2 of some easily measured temperature-dependent quantity x. The temperature interval, $T_2 - T_1$, is then conveniently divided into a hundred parts, called "centigrade degees" – and you have a temperature scale! Instead of writing that every time you just write $T_1 = 0$ °C, $T_2 = 100$ °C, and similarly for other temperatures. This is an 'empirical' scale, determined purely by experiment, and we make it *linear* by writing (see Book 3)

$$T = a + bx, \tag{2.2}$$

where the constants a, b are chosen to make $T_1 = a + bx_1$ and $T_2 = a + bx_2$.

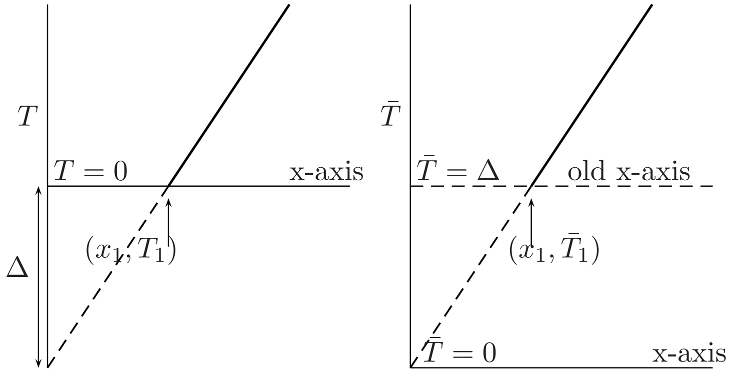


Figure 12(a) Figure 12(b)

This relationship is shown in Fig.12(a). Here the independent variable x is plotted along the horizontal x-axis, as usual, and the dependent variable T upwards, along the y-axis. The experimentally fixed temperature range, going from T_1 (ice temperature) to T_2 (steam temperature) corresponds to the solid line. But if the line is continued (shown as a broken line) it crosses the temperature-axis at $T_0 = a = -\Delta$. In fact, it comes out that $T_0 \approx -273°\mathrm{C}$ and this used to be called the "absolute zero" of temperature, the lowest you could ever reach; but its exact value depends quite a lot on what property x measures and we'll find a better definition later.

If the x-axis in Fig.12(a) is shifted down by $\Delta \approx 273°\mathrm{C}$, you find the 'Kelvin scale' indicated in Fig.12(b): temperatures on the new scale are then

$$\bar{T} = T + \Delta = bx, \tag{2.3}$$

and the ice temperature becomes $\bar{T}_1 \approx 273$ °K$\approx$ 0°C. To express a temperature in degrees centigrade on the Kelvin scale you just add on 273.

Now let's think about the property we've called x. At the beginning of this Section we noted that, for an ideal gas, pressure and volume were related by $PV = C$; but that the 'constant' C depended on how hot the system was. So why don't we use the value of C as the temperature-dependent quantity, in place of x? In that case, for gas at a constant pressure, we will have $PV_1 = C_1$ for ice and $PV_2 = C_2$ for steam. And the *ratio* of the two volumes will give the ratio of the two temperatures:

$$\frac{V_2}{V_1} = \frac{C_2}{C_1}. \tag{2.4}$$

But (**??**) tells us that (writing C in place of x)

$$\frac{\bar{T}_2}{\bar{T}_1} = \frac{C_2}{C_1} = \frac{V_2}{V_1} \tag{2.5}$$

– *provided the temperatures are measured on the Kelvin scale.* This will all be clear from Fig.12(b), where the temperature ratio equals the volume ratio only when the temperatures are measured from the 'absolute zero': you must use $\bar{T}_1, \bar{T}_2$, not the arbitrary temperatures T_1, T_2. From now on, we'll drop the 'bars' and always assume the the Kelvin or 'ideal gas' scale is being used.

An instrument for measuring temperature is called a **thermometer**. But the apparatus pictured in Fig.10 would not be easy to carry around and use. To make something simpler you can use the fact that most things get bigger, they expand, when they are heated. Any liquid in a small container (Fig.13) will expand on heating and the expansion is easy to measure: any increase in volume of the liquid in the glass bulb on the left is 'magnified' by letting it pass into the very narrow tube on the right. If the liquid just reaches a point at distance x from the bulb, you can use the value of x as a measure of the temperature.

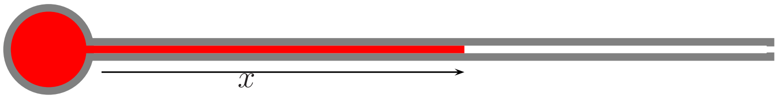


Figure 13

In the thermometer shown, the liquid used is coloured red so you can see it easily and measure x against a scale set alongside the tube. Usually, in a small 'everyday' thermometer, this is marked in millimeters and x may run from x_0 (ice) to x_{100} (boiling water), the actual distances depending on what liquid is used. The two points will be marked 0 °C and 100 °C, corresponding to the usual centigrade scale (the Kelvin scale is hardly ever used except in science). Your body temperature will normally be a bit less than 40 °.

2.3 The equation of state

In the last Section we started from the ideal gas law (**??**), written in the form $PV = C$, where the 'constant' C depends only on how 'hot' the system is; and we decided to use the value of C as a measure of the *temperatue* such that, according to (**??**), $C \propto T = RT$. If we are dealing with 1 mole of gas then R is called the "gas constant per mole", but since C is the *kinetic energy of the molecules* then it must depend also on how many of them there are i.e. on the quantity of gas: so for n moles of gas we should replace R by nR. Properties that depend on quantity in this way are called **extensive properties**. The ideal gas law for n moles of gas will therefore be written

$$PV = nRT, \tag{2.6}$$

which is called an **equation of state**.

Remember that all physical quantities have **dimensions**, showing how they depend on mass, length and time, and that we must take care in using the proper **units**. (You might want to look back at such things in Books 1-4, starting perhaps with Chapter 1 of Book 4). In Chemistry the 'mole' has been brought in as a general 'unit of quantity' for any kind of material; and now we have the 'degree' for things that depend on temperature. Both sides of (**??**) are *energies*: on the left, pressure is force (dimensions MLT^{-2}) divided by area (L^2), so that gives ML^{-1}T^{-2}, with dimensions of energy, so that's OK. On the right of (**??**) we have R, which on multiplying be a quantity (in moles) and a temperature (in 'deg' or °K) must give an energy; so the dimensions of R must be [energy] mole^{-1} deg^{-1} and since energy is expressed in Joules (see Book 4) R will be expressed in units of J deg^{-1} mole^{-1}. The actual value is

$$\text{R}= 8.315 \text{ J deg}^{-1} \text{ mole}^{-1}.$$

Of course you can write (**??**) in other ways, each expressing one of the variables P, V, T in terms of the other two:

$$P(V,T) = \frac{nRT}{V}, \qquad V(P,T) = \frac{nRT}{P}, \qquad T(P,V) = \frac{PV}{nR}, \tag{2.7}$$

where P, for example, is used not only for the pressure (which is something you *measure*) but also for the name of the *function* i.e. the rule for calculating P when you are given values of the independent variables V and T. As you will know from Book 3, this is just a simple way of naming the different functions and saying which variables are to be varied independently and which one they determine (the 'dependent' variable. Here, in fact, we're dealing with relationships among *three* variables: each has a definite value when we are given the values of the other two, and so is a function of more then one variable. We found how to handle these things in Chapter 6, Section 6.1, of Book 3, so you only need a quick reminder.

When you have a function of, say, two variables $f(x, y)$ defining a quantity $z = f(x, y)$ for every pair of values of x, y, you can think of z as the height of a point on a surface above the plane of the x- and y-axes. This is indicated in Fig.50 of Book 3, repeated here (below) as Fig.14:

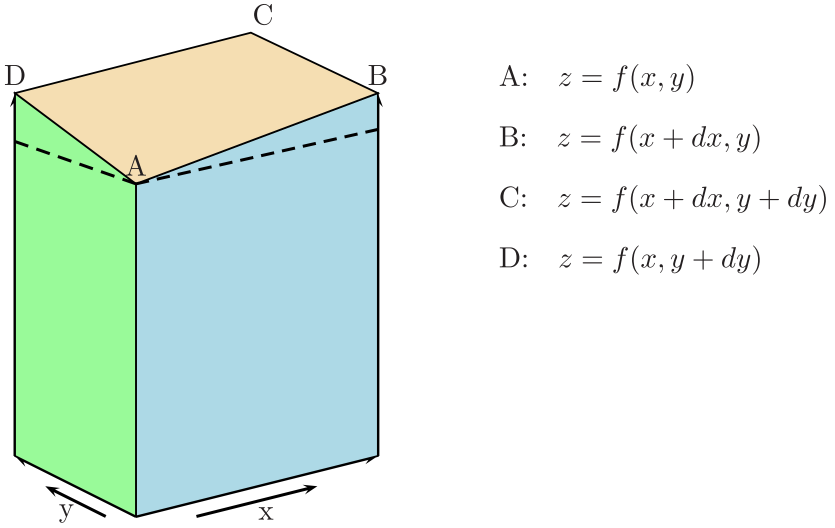


Figure 14

When we want to know how fast z changes when we vary only the value of x, by a small amount dx, we hold the other variable y fixed and differentiate the function $z = f(x, y)$

with respect to x *alone*. And the result is written $\partial z/\partial x$ and called a *partial* derivative: it's simply the slope of the surface, at the point with coordinates x, y, as you go in the x-direction. We also found the result of making small changes $\mathrm{d}x, \mathrm{d}y$ in *both* variables, finding

$$\mathrm{d}z = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y, \tag{2.8}$$

which is called the **total differential**.

Partial derivatives have a very important meaning in chemistry and physics. Let's take a first example, putting V in the second equation of (**??**) in place of z and the variables P, T in place of x, y. In this case

$$\mathrm{d}V = \left(\frac{\partial V}{\partial P}\right)\mathrm{d}P + \left(\frac{\partial V}{\partial T}\right)\mathrm{d}T.$$

On keeping the pressure constant ($\mathrm{d}P = 0$), while raising the temperature of the system, it follows that

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)\mathrm{d}T.$$

And if both sides are divided by V we get the *fractional* increase in volume ($\mathrm{d}V/V$), per unit rise in temperature, at constant pressure:

$$\frac{\mathrm{d}V}{V} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)\mathrm{d}T = \alpha \mathrm{d}T.$$

The coefficient of $\mathrm{d}T$, usually denoted by α, is called the **coefficient of volume expansion at constant pressure**:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{2.9}$$

The subscript P is added to the derivative only to remind us that this is the variable we're holding constant when changing T; but it's not really needed when there are only two independent variables (it just means "the other one").

Two other derivatives are important enough to be mentioned in passing. They are (with their usual names) as follows: the first is

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{2.10}$$

– the **compressibility at constant temperature**, which gives the fractional *decrease* in volume when you 'squeeze' the system by making unit increase in the pressure. (Note that $-\mathrm{d}V/V = \kappa \mathrm{d}P$ shows that positive κ means $\mathrm{d}V$ will be negative for squeezing.)

The last one is

$$\beta = \frac{1}{P}\left(\frac{\partial P}{\partial T}\right)_V \tag{2.11}$$

and is called the **temperature coefficient of pressure increase at constant volume**. It gives the fractional increase in pressure ($\mathrm{d}P/P$), for unit rise in temperature, when you heat the system in a closed container: $(\mathrm{d}P/P) = \beta \mathrm{d}T$.

All that we've done so far, in this Section, relates to an ideal gas – represented by a 'model' in which the molecules have no size (they are *point* masses and possess only kinetic energy. But *real* chemistry is not like that! The molecules may be 'big', with extra kinetic energy coming from the motion of the atoms inside them; and they will certainly *interact*, so the energy of interaction (which is *potential* energy) should also be considered. If you look back to Fig.8 it will be clear that such effects will often be large, especially for dense gases and liquids (where the molecules are close together and constantly colliding) and for solids (where they may be packed tightly and hardly able to move at all). So for much of what we want to do the equation of state (**??**) may be too unrealistic to be useful. However, it can be changed in a very simple way which brings it much closer to reality. The equation of state proposed by van der Waals has the form (for one mole of substance)

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT, \tag{2.12}$$

where V_m is the molar volume, while a, b are adjustable constants – chosen to get good agreement with experimental data for whatever substance is used. It has no proper theoretical basis, but often works surprisingly well.

On the other hand, the fact that an equation of state *exists* (i.e. that there is a function of the three variables P, V, T such that choosing any two of them tells us what the third must be) is enough to give certain results that are valid for any substance. This is because the equations in (**??**) are all equivalent to a single condition

$$f(x, y, z) = 0, \tag{2.13}$$

where x, y, z means V, P, T in any order. This condition in turn leads to

$$\left(\frac{\partial z}{\partial x}\right)\left(\frac{\partial x}{\partial y}\right)\left(\frac{\partial y}{\partial z}\right) = -1. \tag{2.14}$$

On replacing x, y, z by V, P, T this gives

$$\left(\frac{\partial T}{\partial V}\right)\left(\frac{\partial V}{\partial P}\right)\left(\frac{\partial P}{\partial T}\right) = -1 \tag{2.15}$$

and the experimentally observable quantities α, κ β, defined above in (**??**), (**??**), and (**??**), must therefore be related by

$$\kappa\beta P = \alpha \tag{2.16}$$

– as you can check for yourself by substituting from their definitions. This is a general result, which holds for any substance and any equation of state.

Knowing that the 'ideal gas' gives us a surprisingly good description of many systems in physics and chemistry, we'll use it again and again in later chapters as a simple model to start from.

Exercises – to follow.

Chapter 3

Chemical Reactions

3.1 Work, Heat, and Energy

In Chapter 1 we started thinking about the structure of matter and how everything can be built up out of atoms; first molecules – usually with just a small number of atoms – and then gases, liquids and solids – substances containing vast numbers of atoms and molecules, big enough to see and study in the laboratory. We went on, in Chapter 2, to study a very simple 'model' of a gas of N atoms in a container of volume V, introducing the Kelvin temperature T as a measure of the 'hotness' of the system. The **state** of the system could then be defined by giving the values of any *two* of the three variables P, V, T. If you know, say, V and T, then the pressure exerted by the gas on the walls of the container is determined as a function $P = P(V, T)$: pressure, volume, and temperature are related by an **equation of state**, $f(P, V, T) = 0$. For an ideal gas, this equation is very simple: $PV = RT$, for one mole of gas, or $PV = nRT$ for n moles. For other systems, like a mixture of gases, the equation may be more complicated and you will have to say how many moles there are of substance A, of substance B, and so on; so you'll need more variables (n_A, n_B, etc.). But for now we'll just be talking about a system in which such variables are not changing and needn't be considered.

Whatever system we're thinking about, however, must contain **energy**, as well as atoms and molecules, and in the last Chapter we extended the idea of energy (which you first met in Physics, in Book 4) to include **thermal energy** – which has to do with the motion of the atoms and molecules, not included in the 'classical' Physics of two centuries ago because nobody knew about them! In Chemistry, on the other hand, we have to deal with systems in which substances are constantly changing as their molecules change in **chemical reactions**. So to understand what's going on we *must* take into account changes of thermal energy when the *composition* of the system is also changing.

In the last Chapter the kinetic energy (KE) of the molecules in the container was denoted by U and was also a function of state: $U = U(V, T)$ if volume and temperature are chosen as independent variables. We noted that U could be changed in two ways; firstly by doing work on the system (squeezing it into a smaller volume) and secondly by *heating it.* In the first way, force was applied to the piston and the gas was compressed. The work done

w went into the gas, increasing the thermal motion of its molecules, and was kept there by using a container with insulating walls to prevent the heat escaping: such a change, in which $\Delta U = w$, is called **adiabatic** compression.

In the second way, the volume of the system is not changed, so no mechanical work is done on it, but the insulating material is taken away and the system is heated. We say that **thermal energy** flows into the gas, calling it q, and that the change $\Delta U = q$ is *equivalent* to w when it brings the system to the same final state. In other words: *Heat is a form of energy.*

In general, when we don't worry about insulating the system or keeping its volume constant, both kinds of change can take place at the same time and the result is

$$\Delta U = w + q. \tag{3.1}$$

The heat absorbed by a system from its surroundings is naturally measured in units of work or energy, the **Joule**. But before the equivalence of heat and energy was discovered q was measured in **calories**: 1 calorie is the amount of heat needed to raise the temperature of 1 g of water from 14.5 °C to 15.5 °C, without doing any mechanical work ($w = 0$). To change from heat to energy units all you need remember is that 1 cal $\approx$ 4.2 J. The main unit used in Chemistry is the 'kilogram calorie' which is 1 kcal = 1000 cal.

The principles introduced so far apply to any kind of system. To summarize:

> There exists an energy function U, which depends only on the *state* of the system – *not on how the system gets there* – and equation (**??**) holds for any change that may take place.

This statement is usually called the **First Law of Thermodynamics**. It is so general and useful that values of ΔU for many 'standard' chemical reactions, such as the formation of molecules from the atoms they contain, have been measured and are kept in tables for future use.

To deternine ΔU experimentally, for a given reaction, a **bomb calorimeter** can be used. This is usually a strong steel cylinder, with a screw top, inside which the reaction is started (e.g. by using an electric spark or a small heater, or 'detonator'). As the reaction goes on, the **reactants** are changed into **products** and, as the volume is fixed, $\Delta U = q$. This is the amount of thermal energy liberated (if ΔU is negative) or absorbed (if ΔU is positive), which passes through the conducting walls of the cylinder and into (or out of) the temperature bath in which it is placed. To measure q, and hence ΔU, you only have to observe how much energy is needed to bring the bath (or 'thermostat') back to its original temperature. The people who do such experiments are very clever in designing the apparatus so as to get highly accurate results.

In general, however, chemical reactions usually go ahead under conditions of constant *pressure*, that of the atmosphere around us, and part of ΔU goes into mechanical work w as the system changes its volume. For that reason it's usually more convenient to think in terms of the function

$$H = U + PV \tag{3.2}$$

instead of the internal energy U. Various names have been used for H: we'll use **heat content**, which tells you what it is, but some books use **enthalpy** (so watch out!). For a reaction at constant pressure it follows that

$$\Delta H = \Delta U + P\Delta V, \tag{3.3}$$

where ΔV is just the volume change resulting from the reaction. Clearly, like the internal energy U, the heat content H is also a function of state, not depending on the 'path' you take to reach the given state. Such state functions are often called 'potentials'. They are similar to the potential energy (PE) which you met in Book 4 except that they apply to systems in which heat exchange and changes of composition can take place. (Even though U measures mainly the *kinetic* energy of molecular motion, its importance is due to the fact that it depends only on the *state* of the system and has the 'potential' for being released again in doing mechanical work.)

3.2 Energy changes in reactions

Let's start by writing down the chemical formulas describing three important reactions:

(i) $2H_2\ (g) + O_2 \rightarrow 2H_2O\ (l)$,

(ii) $C\ (s) + 2\ O_2\ (g) \rightarrow CO_2\ (g)$,

(iii) $CH_4\ (g) + 2O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$.

What do they mean? The terms on the left of the arrow stand for the **reactants**, while the terms on the right stand for the **products** into which they change as a result of the reaction. The arrow itself can be read simply as "go to". The letters H,O,C stand for the elements (hydrogen, oxygen, carbon) as in Section 3.1 and compound names, like H_2O, indicate molecules and show the atoms from which they are built, subscripts telling you how many atoms of each kind. So H_2O is a water molecule, formed from 2 atoms of hydrogen and 1 atom of oxygen (the 1 not being shown). The big numbers, standing in front of the atom and molecule names, show *how many* of them must be used; and finally the letters s,l,g show the **phase** (solid, liquid, or gas) in which the atoms or molecules are present.

Take the three reactions in turn:

- Reaction (i) states, in words, that 2 molecules of hydrogen (H_2) and 1 molecule of oxygen (O_2) go to 2 molecules of water (H_2O), hydrogen and oxygen being in the 'gas phase' and water in the 'liquid phase'. If we take L molecules of everything, instead of just 1, we'll be talking about *moles* of each substance, as explained in Section 3.1, and the reaction formula then says that "2 moles of hydrogen plus 1 mole of oxygen go to 2 moles of water".

  This is a very violant reaction, releasing a lot of energy, and is used as a basis for rocket fuels. It also leads to 'clean' fuels, whose main reaction product is water, which is harmless to everyone. It will be used more and more (with proper controls), instead of oil and petrol (which are 'dirty' fuels, causing much damage to the environment)

- Reaction (ii) takes place in the burning of coal and other ‘fossil fuels’, which all depend on carbon. When such things burn they take oxygen from the air and, besides producing a lot of energy, liberate large quantities of carbon dioxide (CO_2). This is one of the main causes of **climate change**, the gas accumulating high above the Earth and reacting with the ‘ozone layer’ which for thousands of years has sheltered us from too much sunshine. Reaction (ii) couldn’t be simpler: one atom of carbon joins on to the two atoms of oxygen in the O_2 molecule to give CO_2 – which we don’t want!

- Reaction (iii) is another **oxidation reaction** in which the hydrocarbon methane (CH_4 - see Fig.3) is burnt by adding on two molecules of oxygen to give two molecules of water (harmless enough) and one of carbon dioxide – which agin we don’t want. The heat of reaction in such processes is also called a **heat of combustion**; it is set free whenever you burn anything.

Before studying the energy changes in reactions we must learn how to get the numbers right when we write down the formulas. We know that the numbers of atoms of each kind, on the left and right of the ‘go to’ arrows (→) must agree. Because we never lose atoms (the ‘building blocks’) or make any new ones – we only move them around into different molecules. So, if you don’t know how many oxygen molecules you’ll need in burning one molecule of methane, you only have to ‘balance the equation’ by counting the numbers of atoms of each kind on the left and right and making them agree: if you’re looking for H_2O among the products you’ll need to take 2 molecules in order to match the 4 H atoms in the CH_4 on the left. With a bit of jiggling everything soon falls into place.

Turning next to the energy changes, note that the formulas used in describing the reactions are not *exactly* like the equations in Mathematics and Physics – where the things on the two sides of an equals sign (=) must have the same numerical value. They are not quantities but bits of ‘stuff’ formed out of atoms and molecules. On the other hand, each has a certain internal energy (U) or heat content (H) and these can be added and compared just as we do in Mathematics. So let’s look again at Reaction (i), writing it in terms of molar energies.

Suppose 1 mole of H_2 has heat content H_{H_2}, and similarly 1 mole of O_2 has H_{O_2}, and 1 mole of H_2O has H_{H_2O}. Then

Heat content of reactants is $H_{\mathrm{R}} = H_{\mathrm{H}_2} + H_{\mathrm{O}_2}$

Heat content of products is $H_{\mathrm{P}} = H_{\mathrm{H}_2\mathrm{O}}$.

The increase of H in going from reactants to products is thus $\Delta H = H_{\mathrm{P}} - H_{\mathrm{R}}$ (final value minus initial value) and the experimental value of this quantity is found to be -571.6 kJ. The heat content thus goes *down* – the products have lower energy than the reactants. The heat-content equation for Reaction (i) can therefore be written as

$$H_{\mathrm{H}_2} + H_{\mathrm{O}_2} - 571.6\mathrm{kJ} = H_{\mathrm{H}_2\mathrm{O}} \tag{3.4}$$

where the ‘go to’ arrow in the ‘chemical equation’ has been replaced by the heat content change in reading along the line from left to right, reactants to products. You won’t get the signs wrong if you remember that simple rule.

Now we know how to translate reactions into heat-content equations we can handle them using the simple rules of algebra. To see how it works look at Reactions (ii) and (ii). Putting in the experimental values for heat-content changes, which are −393.5kJ for Reaction (ii) and −890.3kJ for Reaction (iii), we get

$$H_{\mathrm{C}} + H_{\mathrm{O_2}} - 393.5\mathrm{kJ} = H_{\mathrm{CO_2}} \tag{3.5}$$

for Reaction (ii) and

$$H_{\mathrm{CH_4}} + 2H_{\mathrm{O_2}} - 890.3\mathrm{kJ} = H_{\mathrm{CO_2}} + 2H_{\mathrm{H_2O}} \tag{3.6}$$

for Reaction (iii).

Notice that you can move things around in the usual way, without getting lost. In the last equation, for example, you can carry things across the = provided you change the sign (just as you learnt long ago in Book 1). So if you want to get ΔH by itself you can move the things in front of it to the other side, as long as you change their signs. The three heat-content equations above can therefore be written instead as:

$-571.6\mathrm{kJ} = H_{\mathrm{H_2O}} - H_{\mathrm{H_2}} - H_{\mathrm{O_2}}$
$-393.5\mathrm{kJ} = H_{\mathrm{CO_2}} - H_{\mathrm{C}} - H_{\mathrm{O_2}},$
$-890.3\ \mathrm{kJ} = H_{\mathrm{CO_2}} + 2H_{\mathrm{H_2O}} - H_{\mathrm{CH_4}} - 2H_{\mathrm{O_2}}.$

They say exactly the same thing, but express ΔH – which is called the **heat of reaction** – as H[products] − H[reactants]). (Don't get mixed up by calling $-\Delta H$ the heat of reaction – if you get the algebra right the signs will look after themselves!)

Now you can do something very nice: you can use the results you already have to get the heats of reaction for *other* reactions - which you don't yet know anything about! Provided temperature and pressure are the same, of course, for all the reactions you're talking about, you can simply combine their heat-content equations using the ordinary rules of mathematics. For example, just add together the first two heat-content equations above and subtract the last one. You'll get

$$-74.8\mathrm{kJ} = -H_{\mathrm{C}} - 2H_{\mathrm{H_2}} + H_{\mathrm{CH_4}}$$

and this is the heat-content equation for the *new reaction*, C (s) $+2\mathrm{H_2} \rightarrow \mathrm{CH_4}$, since it corresponds to H[products] −H[reactants] = heat of reaction (-74.8 kJ). In this case ΔH is a **heat of formation** of the molecule $\mathrm{CH_4}$ from its elementary units, the atoms of carbon and hydrogen in their normal states (solid and gas phases) at the given temperature and pressure. The heat of formation of methane, which is fairly small, has thus been found from a knowledge of heats of *combustion* which are larger and more easily determined. Heats of formation of many thousands of the molecules in organic chemistry have been found in this way.

It used to be thought that knowing ΔH for a reaction was enough to decide if it would actually take place: if ΔH was *negative*, the reaction would go ahead naturally liberating heat (i.e. it would be *exothermic*), but with ΔH positive it would not happen except when heat was put in (being *endothermic*. But later it was discovered that this is not always true and that other factors must be recognized – but we'll come to that part of the story in later Chapters.

Exercises – to follow

Chapter 4

A deeper look at the ideal gas

A note to the reader

Some parts of this Chapter, and others that follow, are difficult; but don't be put off – on first reading don't try to understand everything. You'll find new and fairly simple ideas keep coming in and as you go further you'll see how they all start coming together. You're going to use a lot of things from Books 1-4: so go back to them whenever you get stuck. If you do so you'll soon be in good shape for going on to the end of the book.

4.1 Back to basics: the laws of large numbers

We've got used to the idea that all the things we meet in daily life are built up from vast numbers of tiny particles – atoms and molecules – and that the numbers involved are so enormous that we have to write them in 'exponential form'. The number of particles in 1 mole of matter (Section 1.1), a quantity you can actually see and weigh out in the laboratory (or the kitchen!), is of the order 10^{24} (24 being the 'exponent'– the power to which you have to raise the 'base' 10 to get the number you want). Talking about "ten to the 24" is certainly much easier than saying "a million million million million" every time you use it. So we expect chemistry to be full of *exponentials*, e^n when we use the 'natural' base $e \approx 2.718$ instead of 10, and indeed it is.

Another way of putting this (look back at Book 1, Chapters 4, 5) is to say that if $N = 10^{24}$ then $24 = \log_{10} N$: the enormous number N has the *logarithm* 24. (Here we've shown the base (10) only because the *natural* base e is the one we usually have in mind when we talk about exponentials and logarithms: when the base is not shown you can be sure it's e). In general, remember, if $y = e^x = \exp x$ then $x = \log y$ – the logarithm is the *inverse* of the exponential function (Book 3, Section 1.4).

When we come down to 'basics' a large part of chemistry depends very directly on the properties of the logarithmic function, as we'll see in later Chapters. But whenever we're dealing with large numbers of any kind – of people or of particles – we need new ideas. We start talking about the "chance" of something happening, or the "probability" of finding this or that when we observe something, and we may say that " on the average" this is what we'll find. We might even say "nine times out of ten it will be so" – which is beginning to be more mathematical. What we have to do now is to express such ideas in a precise and usable form.

Suppose we are observing some quantity, let's call it A. which can take numerical values $A_1, A_2,\ ...\ A_k,\ ...$. It could, for example, be the number of people on a bus, or the ages of people in a population. We focus on one particular result, $A = A_k$ say, which we'll call 'favourable', and count the number of times we get it (N_k say) in a large number (N) of observations. The **relative frequency** N_k/N of finding the 'favourable' result $A = A_k$ is then found to approach a definite **limiting value** (p_k, say) as N is taken larger and larger. This limit is called the **probability** of finding $A = A_k$ under the given experimental conditions (e.g. number of people = 30 on a certain city bus during the 'rush hour' when people are going to work). We write in general

$$p_k = lim_{N\to\infty}\left[\frac{N_k(\text{number of favourable results})}{N(\text{number of observations})}\right]. \tag{4.1}$$

This way of getting a set of probabilities is called "making a statistical analysis" and it's very easy to do. An example you can try for yourself needs only a 'die' of the kind you use in playing dice (a small cube with six faces, marked with the numbers 1,2, ... 6). The Table below contains values of $p_k = N_k/N$ resulting from N throws of the die, the first line from 10 throws, the second from 100 throws, the next from 1000 throws. In each case N_1 is the number of times the top face shows "1", N_2 the number of times you get "2", and so on.

N	N_1/N	N_2/N	N_3/N	N_4/N	N_5/N	N_6/N
10	0.2	0.1	0.0	0.2	0.2	0.3
100	0.16	0.20	0.14	0.20	0.18	0.22
1000	0.155	0.175	0.165	0.171	0.155	0.179
10000	0.1604	0.1690	0.1668	0.1681	0.1555	0.1802
$N\to\infty$	p_1	p_2	p_3	p_4	p_5	p_6

Table 1. Relative frequencies of getting 1,2,...6 in N throws.

In this case it seems that the "6" comes up more often than you'd expect – it has a *higher probability* than any of the other numbers. Perhaps the die is 'loaded', to give it a better chance of falling that way up? If all the faces had equal probabilities of coming up, as you'd expect from a 'fair' die, the numbers in the Table would approach the same value; and since there are six of them that value would be 0.1666...(1/6).

There are two ways of defining the probability of an event: the definition used in the Table, giving p_k as a relative frequency N_k/N, is based on *observation* – not on counting the number of events that we believe should be equally probable. The latter definition (which is '*mathematical*') brings in the idea of **equal *a priori* probabilities** ('*a priori'* meaning we accept something as 'true', even though we can't prove it!). Generally, when we have no reason to think one event more likely to be found than another, we suppose the alternatives will have equal *a priori* probabilities. This makes life much easier because we don't have to do thousands of experiments! In the case of the die we only need look at it and note that any particular 'favourable event' (call it a 'yes-event'), like throwing a '3', say, can only appear once out of six possible events – giving $p_3 = 1/6$.

To see how things work out, suppose you have a bag containing coloured beads, 3 red, 5 green, and 2 blue. You put your hand in and pull one of them out. What is the probability that if will be blue? The number of yes-events in this case is 2, but there are 3+5+2 =10 possible events: so the blue bead will have a probability $p_b = 2/10 = 0.2$. This also means that if you do the experiment a thousand times the *relative frequency* of getting a blue bead will be something close to 200/1000, every bead coming out roughly 100 times and a blue one (no matter which) twice that – 100 for each of the two. The 'experimental' and 'mathematical' definitions should give more or less the same results if you make enough experiments. Not *exactly*, as Table 1 suggests, because there may always be a slight 'scatter' around the values you expect; but as $N \to \infty$ the *percentage* scatter $\to 0$.

We can now state some very general conclusions:

- The probability p of any event is a positive number in the range 0 to 1: the value 0 means *impossibility*, no chance of observing the event, while the value 1 means *certainty*, you get the same result every time you look. (Example. If there are no black beads in your bag, then p for finding a black bead is 0. But if there are only blue beads in the bag, then p for a blue bead is 1.)

- The probability p of finding *either* of two events (no matter which), with separate probabilities p_1 and p_2, is the *sum* $p = p_1 + p_2$. (Example. The probability of pulling out either a blue bead or a green bead is $p = (5/10) + (2/10) = (7/10)$ – there are 7 yes-events, 5 for getting a green bead, 2 for getting a blue one, out of a total of 10 possible events.)

- The probability p of finding *both* of two events, in two separate experiments, is the *product* $p = p_1 \times p_2$ – provided the events are *independent*. (Example. To pull out a green bead in the first experiment you have 5 yes-events out of 10 possible. But to be sure the result of the second experiment is not affected by the first you must put back the bead you took first – for, if not, you'll be using a different system (with one bead missing). After putting it back, the bag of beads is exactly as it was at the start; and the probabilities of all events will be unchanged by what happened in the first experiment. That's what is meant by "independent". In this case there are *always* 5 ways of finding a green bead in the first experiment and 2 ways of getting a blue in the second; so if you do the 'double-experiment' there will be 5×2 yes-events out of 10×10 possible events (any of the 10 beads in the first experiment with any of the 10 in the second). And you will say the probability of getting green plus blue is

  $$p_{gb} = \frac{5 \times 2}{10 \times 10} = \frac{5}{10} \times \frac{2}{10} = p_g \times p_b$$

  – illustrating the product law for combining the probabilities of **statistically independent** events.)

Mathematical statistics is a big subject if you want to make proper proofs of eveything you say. But that's work for professional mathematicians; what's been done here will be enough for us.

4.2 Probability densities

Suppose we're making measurements of a quantity x which can take *continuously* variable values within a certain range and we want to get the probability that x will be found in the small interval $\mathrm{d}x$. This will be a positive number, with limits 0 and 1, which can be written $p(x)\mathrm{d}x$ where $p(x)$ is a continuous function of x and is called a **probability density**, a probability per unit range of x. (The probability itself must be proportional to the interval $\mathrm{d}x$, because if $\mathrm{d}x$ is doubled then the probability must also be doubled – being the sum of the ($\approx$ equal) probabilities of finding x either in the first half of the interval or in the second half.)

Probability densities have properties similar to those we found in the last Section. Thus (as we've just seen) the probability of finding a result in either the first half of a small interval or the second half will be the *sum* $p = p_1 + p_2$ of probabilities for the separate events; and this means that if p_1, p_2 each have the form density×range then the value of each can be represented as the area of a strip of height $p(x)$ and width $\mathrm{d}x$. (Look back at Book 3, Chapter 2, if you've forgotten your Calculus!). So if you know the density function $p(x)$ you can get the probability of finding a value of x anywhere in the range from x_1 to x_2: it will be the integral

$$\int_{x_1}^{x_2} p(x)\mathrm{d}x$$

– the sum of the areas of all the narrow strips between $x = x_1$ and $x = x_2$ i.e. the area under the curve $p(x)$ between ordinates at those limits.

An important application of this result follows from the fact that finding *any value of x whatever* in the range $x_1 = -\infty$ to $x_2 = +\infty$ must be unity (certainty). Therefore

$$\int_{-\infty}^{+\infty} p(x)\mathrm{d}x = 1. \tag{4.2}$$

A probability density satisfying this condition is said to be **normalized**.

There's one special form of the density function $p(x)$ that comes up again and again in many parts of Science: it is

$$p(x) = Ce^{-\alpha x^2} \tag{4.3}$$

and is called a *Gaussian function.* Whenever you try to measure something, x say, and get results x_1, x_2, x_3, which may be a bit too big, or a bit too small, you'll usually find your values form a **Gaussian distribution** like (**??**). The function looks like a bell (Fig.15) whose width depends on the numerical constant α: the *smaller* it is the wider the bell. And the constant C is usually chosen to give a *normal distribution* satisfying (**??**).

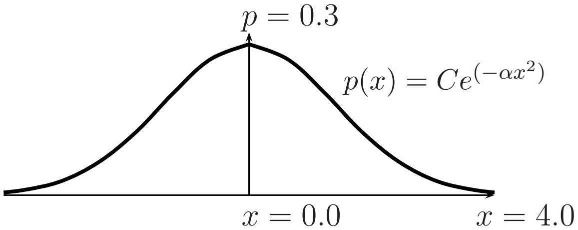


Figure 15. The Gaussian curve

At some time you've probably played the game of "darts", where you throw a dart at a target (usually it's a circular board, marked out in numbered circles, the small one in the middle carrying the biggest number). You score by adding the numbers on the areas you hit with your dart. As a simpler form of the game let's suppose you try to hit a vertical line, throwing your dart from a distance of, say, 2 metres. If you do this 100 times you'll find a 'scatter' of points where the dart landed, making a picture of 'hits' like the one on the left in Fig.16.

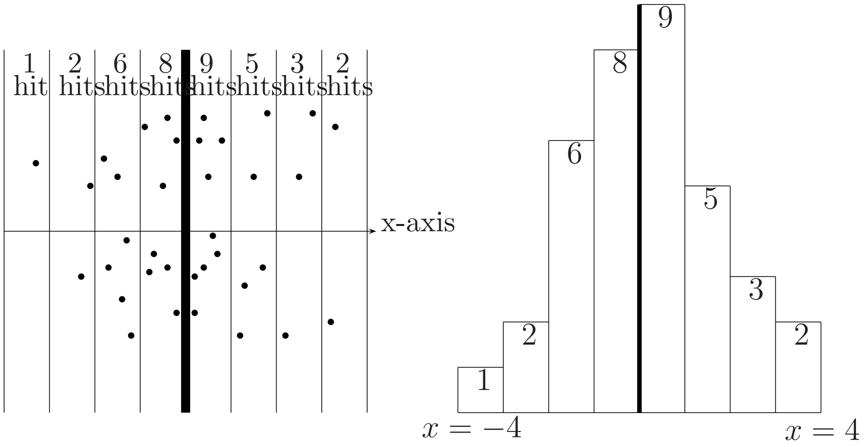


Figure 16. Making a histogram

Here the 'target-line' is shown bold and on either side of it are strips of unit width, with numbers at the top which show the number of hits in each strip. The strips closest to the target-line get the greatest number of hits (8 and 9) because you were aiming at the the vertical line with $x = 0$; but as you go out to a distance of $x = \pm 4$ units the numbers quickly go down. The distribution of numbers in an experiment of this kind is often represented graphically as in the **histogram**, shown on the right in Fig.16. Here each strip has a height equal to the number of hits and the histogram shows how the results of your 36 throws are distributed. If you increase the number of throws to 100, 1000, and so on, making the strips narrower and narrower, your histogram will begin to look more and more like a Gaussian. From the way it's been constructed, the area of the histogram in the Figure will be 36. So if you divide all your hit numbers by 36 the histogram will be *normalized*. Remembering your calculus (Chapter 2 of Book 3) you will guess that, as the number of throws tends to infinity and the width of the strips tend to zero, your histogram turns into a Gaussian distribution! We're going to use it now to find (with a bit of guess-work) one of the most important distribution laws in Physics and Chemistry.

4.3 Maxwell's distribution law

Let's think again about the ideal gas, consisting of N point particles (monatomic molecules) moving about in a container. In Chapter 2 we used this simple model to find the pressure exerted by the gas on the walls of the container. We introduced the idea of *temperature* and found that it measured the average *kinetic energy* of the moving molecules. Now that we know something about probability and the laws of large numbers we all set to do something a bit better: there are millions and millions of molecules rushing about in all directions with all sorts of speeds, so perhaps we should try to be more realistic.

Every particle will have a **velocity vector** with three components (see Book 2) along the x- y- and z-axes in space; let's call them v_x, v_y, v_z. Even if we focus on only one direction, along the x-axis say, the speed v_x of a particle can be positive (along the positive axis) or negative (the opposite direction) and it seems equally likely that it is moving one way or the other. (Note: the "speed" is a *scalar* quantity – we give it a sign only when it is a *vector component*. However, when the meaning is clear, it doesn't matter which word you use.) If the probability of finding a particle with a certain speed is to be independent of sign we can just as well say if depends on speed^2; and since speed is a continuous variable we'll also have to talk about probabitiy *density*, saying $p(v_x) = f(v_x^2)$. This is beginning to remind us of the example in the last Section! Could it be that the dependence on v_x is similar to that of the variation of the observed values of x, the distance of a 'hit' from the target value $x = 0$? Let's suppose it is and see what we get if try the functional relationship

$$p_x(v_x) = Ce^{-\alpha(v_x)^2}, \tag{4.4}$$

where the 'parameters' C and α don't depend on velocity. Remember this is a probability *density*, so that the actual probability of finding a molecule with x-component of velocity between v_x and $v_x + \mathrm{d}v_x$ will be $p_x(v_x)\mathrm{d}v_x$; and in the same way the actual *number* of molecules in this velocity range will be expressible as $n_x(v_x)\mathrm{d}v_x$, where n_x is also a number per unit range – a number *density*. And, since the probability is also the number in that range divided by the total number of molecules (N), it follows that

$$\left(\frac{n_x}{N}\right) = Ce^{-\alpha(v_x)^2}. \tag{4.5}$$

When plotted against the speed v_x, this function will give a bell-shaped curve of the kind introduced in Fig.15

We're nearly through! The last step (again almost a 'guess' but a very obvious one) is to note that what's good for the x-direction is sure to be true for any other direction: in other words, assuming (**??** applies for all three directions,

$$p_x(v_x) = Ce^{-\alpha(v_x)^2}, \qquad p_y(v_y) = Ce^{-\alpha(v_y)^2}, \qquad p_z(v_z) = Ce^{-\alpha(v_z)^2}.$$

But, since we're taking observations for the different directions to be **statistically independent** events (see Secton 4.1), the product law tells us that

> Probability of finding, simultaneously, v_x in range v_x to $v_x + \mathrm{d}v_x$, v_y in range v_y to $v_y + \mathrm{d}v_z$, v_z in range v_z to $v_z + \mathrm{d}v_z$
>
> $$= \quad p_x(v_x)\mathrm{d}v_x \times p_y(v_y)\mathrm{d}v_y \times p_z(v_z)\mathrm{d}v_z.$$

This product will give the probability of finding a molecule with velocity components falling in a small box of 'volume' $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$ at a point with 'coordinates' $v_x\ v_y\ v_z$. It has the form of a probability *density* $p(v_x, v_y, v_z)$ multiplying the volume element $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$. On multiplying together the three exponential functions you find (remembering that $e^x \times e^y = e^{x+y}$)

$$p(v_x, v_y, v_z) = C^3 \exp -\alpha(v_x^2 + v_y^2 + v_z^2) = C^3 \exp -\alpha v^2, \tag{4.6}$$

where $v^2 = v_x^2 + v_y^2 + v_z^2$ is just the molecular speed squared.

But why does this equation suggest a most probable speed of zero? The bell-shaped function certainly has its greatest value when $v = 0$ and the exponential factor becomes 1. The reason is not hard to find if you look at Fig.17 below:

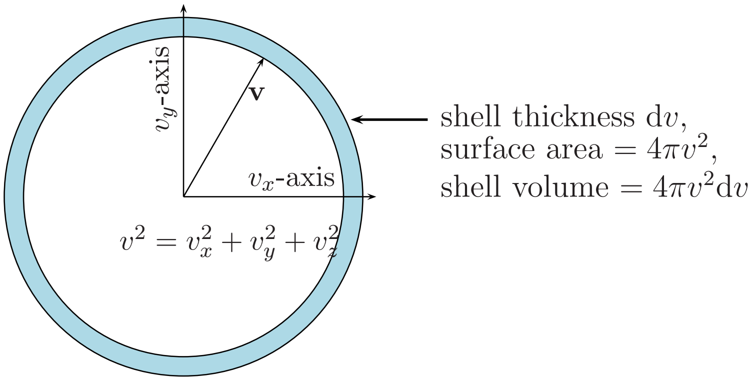


Figure 17. Volume element (spherical shell)

The reason is this: $p(v_x, v_y, v_z)$ is a probability *per unit volume* and doesn't give you an actual probability until you multiply it by a volume element like $\mathrm{d}v_x\mathrm{d}v_y\mathrm{d}v_z$; and when you do you'll get the probability of finding a molecule in that infinitesimal region. But what you really want is the probability that it has a given speed v; and the square of the speed is the sum of the squares of the velocity components, $v^2 = v_x^2 + v_y^2 + v_z^2$. In Fig.18 the components are represented as distances measured along the x, y, z axes and the velocity vector $\mathbf{v}$ has a constant magnitude v (represented as a length) when its end just reaches the spherical surface, shown in blue (see Section 5.2 of Book 2). So a molecule will have the same probability per unit volume in 'velocity space' for all points within the very thin spherical *shell* of thickness $\mathrm{d}v$. If we add the probabilities for all volume elements in the shell we'll get the total probability of finding a molecule with its velocity components lying within the blue shell: it will follow on multiplying the probability per unit volume in (**??**) by the spherical volume element $4\pi v^2 \mathrm{d}v$. The result is Maxwell's distribution law:

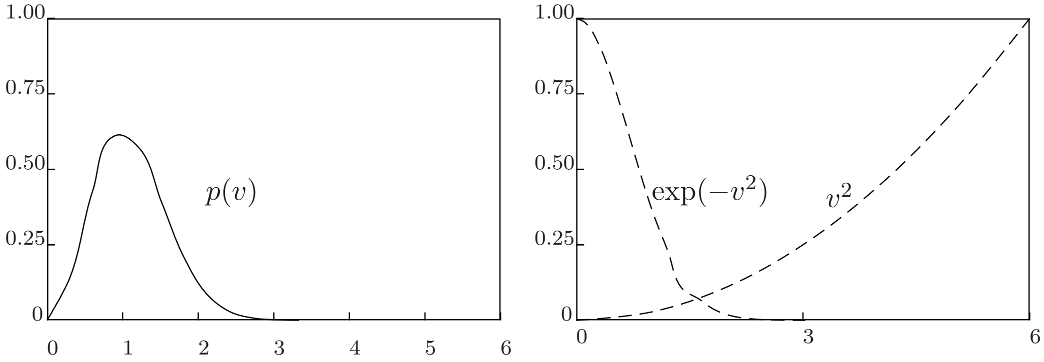
Probability of an ideal gas molecule having speed in the range v to $v + \mathrm{d}v$

$$= 4\pi C^3 v^2 e^{-\alpha v^2} \mathrm{d}v.$$

The probability density function is

$$p(v) = 4\pi C^3 v^2 e^{-\alpha v^2}, \tag{4.7}$$

which is plotted against v in Fig.18a for $\alpha = 1$. The factor v^2 is what pushes the maximum in the Gaussian curve (Fig.15) away from zero: there is now a peak at a finite **most probable speed** and the position of this peak depends on the constant α which determines how fast the exponential factor goes to zero. The first graph in Fig.18 shows the **normalized** distribution law, $p(v) = 4\pi C^3 v^2 e^{-\alpha v^2}$, in which the second constant (C) is chosen so as to make the probability of finding v *somewhere* between 0 and ∞. We'll find this 'scale factor' in the next Section.



(a) $p(v) = Av^2 \exp(-v^2)$ (b) The factors $\exp(-v^2)$ and v^2

Figure 18. The Maxwell distribution $p(v)$

The next graph, in Fig.18(b), shows the separate factors, $e^{-\alpha v^2}$ (which falls rapidly to zero as v increases), and v^2 (which rises rapidly, after starting at zero). Now you see how the peak is the result of the competition between the two; in the end, as v becomes large, the exponential always wins and $p(v) \to 0$.

4.4 What else can we get from Maxwell's law?

In fact we can find almost anything we need to know about the properties of an ideal gas. But first we have to look at the two parameters, C and α and try to connect them with what we know already – especially with temperature and with the equation of state.

First we can eliminate C, as suggested above, simply be normalizing the distribution, so that the probability of a molecule having *some* speed between zero and infinity will be 1 (certainty). The condition for this is that, using (**??**),

$$\int_0^\infty p(v)\mathrm{d}v = 4\pi C^3 \int v^2 e^{-\alpha v^2} \mathrm{d}v = 4\pi C^3 I_1 = 1, \tag{4.8}$$

where I_1 denotes the integral (with *one* factor of v^2 in the integrand):

$$I_1 = \int_0^\infty v^2 e^{-\alpha v^2} \mathrm{d}v.$$

The easiest way of getting an integral of this kind (the standard integrals listed in Book 3 won't help you!) is to start from the simpler one

$$I_0 = \int_0^\infty e^{-\alpha v^2} \mathrm{d}v, \tag{4.9}$$

noting that the result is just a function of the parameter α and can therefore be differentiated. Thus

$$\frac{\mathrm{d}I_0}{\mathrm{d}\alpha} = \int_0^\infty (-v^2) e^{-\alpha v^2} \mathrm{d}v = -I_1, \tag{4.10}$$

where we've differentiated the *integrand* first, before doing the integration, when we should really be doing it the other way round. (Here we accept that this is allowed, though a professional mathematician would want to *prove* it.)

So all we have to do is evaluate (**??**) and then differentiate the result. In one of the Exercises at the end of the Chapter you'll learn how to get I_0 and then you only need differentiate to get I_1. The results are

$$I_0 = \sqrt{\pi/2\alpha^2}, \qquad I_1 = \sqrt{\pi/2\alpha^4}. \tag{4.11}$$

The normalizing condition (**??**) then shows (substituting for I_0 in the last step) that $4\pi C^3 = \sqrt{2}\alpha^2/\sqrt{\pi}$. On putting this value into (**??**) we get the final result (check this)

$$p(v) = \sqrt{2\pi}\alpha^2 v^2 e^{-\alpha v^2}. \tag{4.12}$$

Now we have Maxwell's law for the distribution of molecular speeds we can find other things we'd like to know: for what value of v does the probability density have its maximum value? and what is the average value of the kinetic energy (KE) of a single molecule?

To get the maximum on the $p(v)$ curve you just have to differentiate with respect to v and set the result equal to zero (you've done it many times in Book 3). What comes out is

$$\text{Most probable speed} = 1/\sqrt{\alpha}$$

.

To find the mean KE you have to average the values of $\frac{1}{2}mv^2$, knowing that the fractional number of molecules with speeds in the range v to $v + \mathrm{d}v$ will be $p(v)\mathrm{d}v$: each one carries energy $\epsilon = \frac{1}{2}mv^2$ (using a Greek letter 'epsilon' so as not to get mixed up with the total energy E. So the mean molecular KE will be

$$\bar{\epsilon} = \int_0^\infty (\tfrac{1}{2}mv^2) p(v) \mathrm{d}v = \tfrac{1}{2}m\sqrt{2\pi}\alpha^2 \int_0^\infty v^4 e^{-\alpha v^2} \mathrm{d}v. \tag{4.13}$$

The integral looks like the I_1 in (**??**), except that there is a factor v^4 instead of v^2. But to get I_1 from I_0, in (**??**), you only had to differentiate it with respect to α; and you can use the same trick to bring down another factor of v^2. Try it! You'll find that

$$\bar{\epsilon} = \int_0^\infty (\tfrac{1}{2}mv^2)p(v)\mathrm{d}v = 3m/4\alpha. \tag{4.14}$$

The next thing we need to do is to make a connection with what we did in Sections 2.1 and 2.2, where we introduced the idea of temperature and found the equation of state for an ideal gas. We're now doing things at a deeper level and can feel much safer.

Let's go back to Section 2.1 and go through the steps leading up to equation (**??**), but now talking about the *probable* number of molecules hitting the piston with a velocity component v_x. Instead of Step 1 we'll write an expression for the *probable* number of hits from particles with v_x in the small interval $\mathrm{d}v_x$; and then we'll go on with Step 2 etc. as follows:

- Step 1: probable number of hits/unit time $= n(v_x)\mathrm{d}v_x \times v_x \times A$, where the old factor n (number of particles per unit volume in ordinary space) has been dropped, as we can put it in at the end. $n(v_x)$ is now the probability *density* for finding one of those particles with velocity component v_x; and it has the value $n(v_x) = Ce^{-\alpha v_x^2}$.
- Step 2: force due to particles of given $v_x = 2n(v_x)\mathrm{d}v_x \times Amv_x^2$
- Step 3: pressure due to particles of *all* v_x

  $$= m\langle v_x^2\rangle = m\int_0^\infty v_x^2 \times Ce^{-\alpha v_x^2}\mathrm{d}v_x$$

- Step 4: all components have the same average value

  $$\langle v_x^2\rangle = \tfrac{1}{3}\langle v_x^2\rangle$$

  and the pressure formula becomes

  $$P = \tfrac{1}{3}m\langle v^2\rangle.$$

- Step 5: on putting in the particle number per unit volume (N/V which we dropped at the beginning) and multiplying both sides by volume (V), we obtain the ideal gas law

  $$PV = \tfrac{2}{3}N\langle\tfrac{1}{2}mv^2\rangle = \tfrac{2}{3}N\bar{\epsilon} = \tfrac{2}{3}U,$$

  in agreement with (**??**), $U = N\bar{\epsilon}$ being the total energy of the gas molecules.

Now for 1 mole of gas $N = L$, Avogadro's number; and the equation of state has been written $PV = RT$, where T is the temperature on the ideal gas scale and the proportionality constant R is called the **molar gas constant**. It follows that, in terms of temperature,

$U = L\bar{\epsilon} = \frac{3}{2}RT$: but we also know from (**??**) that $\bar{\epsilon} = 3m/4\alpha$. And the parameter α in Maxwell's law is thus directly related to the temperature of the system:

$$\bar{\epsilon} = 3m/4\alpha = \tfrac{3}{2}(R/L)T = \tfrac{3}{2}kT,$$

which gives

$$\alpha = \frac{m}{2kT}, \qquad \alpha v^2 = \frac{\epsilon}{kT} \tag{4.15}$$

The constant k is the gas constant *per molecule* and is usually called **Boltzmann's constant**. It is an important fundamental constant in terms of which:

Mean KE per molecule, in an ideal monatomic gas at Kelvin temperature T, is

$$\bar{\epsilon} = \tfrac{3}{2}kT$$

.

Finally, let's write down the distribution law for finding a molecule with energy $\epsilon = \frac{1}{2}mv^2$, in an ideal gas. Since $\alpha v^2 = \epsilon/(kT)$, from (**??**). the distribution law (**??**) can be rewritten as

$$p(\epsilon) \propto \epsilon \exp(-\beta\epsilon), \tag{4.16}$$

where the parameter α has been replaced by $\beta = 1/kT$. The proportionality factor is most easily evaluated by requiring that $p(\epsilon)$, integrated over all ϵ, gives unity (see Exercise xx) The result is remarkably simple:

> Probability, per unit energy range, of a molecule of an ideal monatomic gas having kinetic energy ϵ is
>
> $$p(\epsilon) = \beta^2 \epsilon \exp -\beta\epsilon$$
>
> where $\beta = 1/kT$ (T being the Kelvin temperature).

We'll find similar laws for the probability of finding *any* kind of system (not just a single atom in a gas!) with any energy we may choose (E say). If the possible states of the system are numbered 1,2,3, ... i ...

; with energies $E_1, E_2....E_i, ...$, then the probability of finding it in state i will turn out to be

$$p(E_i) \propto \exp(-\beta E_i), \tag{4.17}$$

where the parameter β is still related to the Kelvin temperature T at which the sytem is kept, through $\beta = 1/kT$.

You may have noticed that the distribution of *energy* no longer follows a Gaussian law, but shows instead a simple exponential dependence on the energy. This came about when we stopped thinking about the components of *velocity* and focussed instead on the kinetic energy of the particles: this led in a simple and natural way to the the exponential law (**??**), which is in fact much more general – as we'll see in the next Chapter.

Before closing the present Chapter, stop for a moment and think what we've done. We've found how the kinetic energy in a gas is divided out among all those millions of moving molecules, getting a simple mathematical formula that tells us what fraction of them will be found in any given energy range; we've found how the picture changes as we put *heat* into the gas and how the parameters in the distribution function depend on the *temperature* of the gas. And all this seems to have come out of almost *nothing*.

We started with a few simple ideas and experiments about throwing dice, or darts, and how a long series of results could be described mathematically; and then found how they could usually be fitted with a 'gaussian' curve. It seemed possible that the distribution of particle speeds around a 'most probable' value might follow a similar law; so we tried it as a 'hypothesis' – and it worked! The only other things we had to assume were that particles moving to the left or to the right would be equally likely to have a given speed; that this would still be so if we had chosen any other direction in space; and that different (x, y, z) components of velocity could be treated independenty.

You might think we were just lucky to hit on the gaussian function: but that's not quite true – because that's *the only function* that fits the conditions just stated. What's really amazing is that such simple ideas could take us so far.

Exercises – to follow

Chapter 5

The Second Law

5.1 When the First Law is not enough – what then?

In the last Chapter we extended the idea of potential energy (which you first met in Physics (Book 4) to include **thermal energy** and its transfer from one system to another. This is the subject of **thermodynamics**. And the First Law of Thermodynamics, formulated in Section 3.1, simply stated that heat is a form of energy very similar to 'mechanical' potential energy, which can be *stored* in a system and depends only on the *state* of the system (described by variables such as pressure, volume, temperature, composition) and *not on how that state is reached*. If an amount of work w is done on the system, i.e. put *into* it, along with an amount of heat q, then its internal energy increases by $\Delta U = w + q$.

The First Law is so general that it applies to *any* kind of change; and in Chapter 3 we even admitted chemical reactions in which the composition of the system was changed, going from 'reactants' (in the initial state) to 'products' (in the final state). If such changes take place at constant volume, $w = P\Delta V = 0$ and q measures directly the change of internal energy in the reaction, $\Delta U = q$; and if ΔU is negative, then q is also negative – meaning that heat flows *out of* the system. But more usually reactions take place at constant pressure, and then the heat of reaction is not ΔU but instead $\Delta H = \Delta U + P\Delta V$. It was therefore found useful to consider the **heat content** (or 'enthalpy') instead of ΔU, thus allowing for changes of volume during the reaction. The heat content

$$H = U + PV \tag{5.1}$$

is clearly another function of state.

You might think the heat of reaction ΔH would be a good measure of the **affinity** of the reactants (how much they 'like' each other), a large negative value meaning they would come together with explosive violence (as in the hydrogen-oxygen reaction on p.xxx). But many reactions take place even when ΔH is slightly *positive*. How can this be explained? To do so we need a quite new idea, related to the idea of the *probability* of something happening, which we first met in the last section: perhaps it could be that the molecules of the products have a higher probability of being found than those of the reactants. We'll look at this possibility in a later Section, but first we'll use a simple example (again the ideal gas!) to show that another function of state can be found. It's called the **entropy**: and it's importance goes far beyond chemistry, into the design of engines of all kinds (those for doing work, producing power, and those for using power to extract heat – as in refrigerators); and even into understanding the structure of stars!

5.2 Reversible changes: an example

So far we've been talking about a system in a given state, with thermodynamic functions (e.g. U, H) depending on the state variables (e.g. T, P), and with the changes that follow on giving the variables new values. But the system has always been considered to be *in equilibrium*: so how can we change its condition without contradicting this idea? All we can do is to change the variables so slowly that the system 'doesn't notice': if the changes are infinitely slow we can suppose the system is always in equlibrium. Such changes are called **quasi-static** ('almost stationary') or **reversible** – since, at equilbrium, a small enough change of variables can be made and then 'un-made' without disturbing the equilibrium.

Let's take 1 mole of an ideal gas, in a container of volume V in a thermostat at temperature T, and plot corresponding values of T, P as points in a T-P diagram (T along the x-axis, P along the y-axis). By changing the variables in infinitesimal steps we can describe any path in 'T-P space', leading from a point with 'coordinates' (T_1, P_1) to another point (T_2, P_2).

First, we need to state the properties of the system. For 1 mole of an ideal gas they are as follows:

- There is an equation of states $PV = RT$, R being the 'molar gas constant' with the value $R = 1.987$ cal deg^{-1}.
- The system has an internal energy $U = U(T)$, depending only on temperature.
- The system has a **heat capacity** C such that, when it takes in thermal energy q and its temperature rises by dT, then $q = C\mathrm{d}T$ (heat intake per unit rise of temperature). In general C will depend on conditions (e.g. pressure kept constant), which must also be stated.

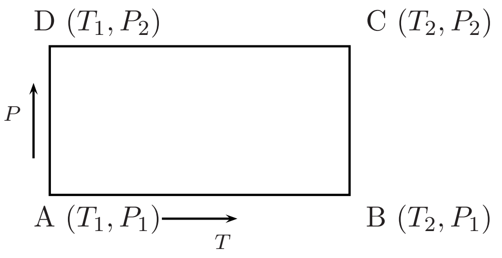


Figure 19. Reversible cycle

There are two important heat capacities: C_V denotes that at *constant volume* and C_P that at *constant pressure*. Since $\mathrm{d}U = q + w = C\mathrm{d}T + w$ and $w = P\mathrm{d}V$ it follows that $C_V = (\partial U/\partial T)_V$; and since, when P is kept constant but V is allowed to vary, $C_P\mathrm{d}T = \mathrm{d}U + P\mathrm{d}V = \mathrm{d}H$ it follows that $C_P = (\partial H/\partial T)_P$. Both C_V and C_P are measured in units of energy per degree rise in temperature:

$$C_V = \frac{\partial U}{\partial T}, \qquad C_P = \frac{\partial H}{\partial T}, \tag{5.2}$$

and for an ideal gas both are constants. (If you need to be reminded of partial derivatives, like $(\partial H/\partial T)$, turn back to Section 6.1 of Book 3.)

Turning to Fig.19, let's consider two paths leading from point A in the T-P diagram, with 'coordinates' (T_1, P_1), to point C (T_2, P_2). We're interested in functions of state, like U and H, which depend only on the values of the independent variables (in this case T and P), but not on the path we take to arrive at those values.(This should make you think of potential energy in Physics (Book 4), where thermal effects were not present and the work done on a particle all went into taking it slowly (so as not to give it *kinetic* energy) from one position to another.) Here, the paths we'll consider lead from A$(T_1.P_1)$ to C(T_2, P_2), but we may choose the path ABC, or the path ADC, or the diagonal path AC, or any wiggly path we may choose. We'll make a series of infinitesimal steps, in which work w is done on the system and heat q goes into it, and add all the little bits together to get, for example, the total work done in going from the beginning to the end of the path, calling it Σw. We can get Σq in the same way to find the total heat intake; and we can do the same for any quantity relating to work done or heat intake along any chosen path. The last one we're going to choose is the sum of heat intake (q) divided by temperature (T), for all the infinitesimal steps along the path. So we'll evaluate

$$\Sigma w, \quad \Sigma q, \quad \Sigma(q/T), \tag{5.3}$$

for paths such as ABC, ADC in Fig.19

Path ABC

Along AB the pressure is constant, with the value P_1, and the work done *on* the gas in a volume change ΔV is $w = -P_1\Delta V$. But as the temperature increases, so does the volume: at A we have $P_1V_1 = RT_1$, while at B $P_1V_\mathrm{B} = RT_2$; so the volume change is $\Delta V = V_\mathrm{B} - V_1 = R(T_2 - T_1)/P_1$ and the total work input along AB is

$$(\Sigma w)_\mathrm{AB} = -P_1\Delta V = -R(T_2 - T_1).$$

(Notice that ΔV doesn't have to be *small*, as long as pressure is constant, because all the little bits $w = -P_1\mathrm{d}V$ can then be added together to get $-P_1\Delta V$ without the trouble of integrating.)

What about the total heat intake along AB? It will be $(\Sigma q)_\mathrm{AB} = \Delta U - \Sigma w$, where, from (**??**),

$$\Delta U = C_V \times (\text{temperature increase})$$

. Again, since C_V is a constant, the *whole* temperature increase $T_2 - T_1$ can be used and the total heat intake is thus

$$(\Sigma q)_\mathrm{AB} = \Delta U - \Sigma w = C_V(T_2 - T_1) + R(T_2 - T_1) = C_P(T_2 - T_1),$$

where $C_P = C_V + R$ is the **heat capacity at constant pressure** for 1 mole of an ideal gas.

Now go along BC, the temperature being T_2. The pressure and volume must be related by $PV = RT_2$, so along BC the pressure must be $P = RT_2/V$. When the volume changes from V to $V = V + \mathrm{d}V$ the work done on the gas will be $w = -P\mathrm{d}V = -(RT_2/V)\mathrm{d}V$. The total work done on going from B to C will thus be

$$-RT_2 \int_{V_B}^{V_C} (\mathrm{d}V/V) = -RT_2[\log V]_{V_B}^{V_C}$$

and, when we put in the limits $V_B = RT_2/P_1$ and $V_C = RT_2/P_2$, this gives (check it!)

$$(\Sigma w)_{\mathrm{BC}} = RT_2 \log(P_2/P_1)$$

In every infinitesimal step the heat intake is simply $q = -w$, since U depends only on temperature ($T = T_2$ along BC) and so $\mathrm{d}U = w + q = 0$. Thus,

$$(\Sigma q)_{\mathrm{BC}} = -(\Sigma w)_{\mathrm{BC}} = -RT_2 \log(P_2/P_1).$$

Finally, we want to evaluate the sum of all the q/T. Again there are two steps, A→B and B→C. Along AB the temperature changes in every infinitesimal step (see Fig.19) and the sum $\Sigma q/T$ becomes an integral:

$$(\Sigma(q/T))_{\mathrm{AB}} = \sum_{\mathrm{AB}} C_P(\mathrm{d}T/T) \rightarrow \int_{T_1}^{T_2} C_P(\mathrm{d}T/T) = C_P[\log T]_{T_1}^{T_2},$$

where we've used the standard integral (3.28) in Book 3. This gives, for the third quantity in (**??**),

$$(\Sigma(w/T)_{\mathrm{AB}} = C_P \log(T_2/T_1).$$

Along BC, instead, the temperature is constant and we only need divide $(\Sigma q)_{\mathrm{BC}}$ by T_2, getting

$$(\Sigma(q/T))_{\mathrm{BC}} = -R \log(P_2/P_1).$$

Path ADC

Now we have to do the other path, ADC! But first take a look at the results, so you can see where it's all going. The values that come out are all collected in Table 2, first for path ABC and then for path ADC.

Path ADC is really no harder than ABC. You change the pressure first, keeping the temperature constant, until you reach D; and *then* hold the pressure constant, increasing the temperature as you go from D to C. The total intakes of work (w), heat (q), and the quantity q/T, can be obtained in exactly the same way as before. But they don't have to give you the same results, as you can see from the Table

(Do this for yourself, putting in the right values of T and P along the new path, and check your results against those in the Table below.)

When you're through, you'll have discovered something very important:

First, on getting to C, both the total work done and the total heat intake will depend on which way you got there: but their sum, which is $\Delta U = \sum w + \sum q$, will *not* – the **internal energy** U is a *function of state* and depends only on the variables (T, P) that specify the state.

	Path ABC
$(\Sigma w)_{\text{ABC}}$	$-R(T_2 - T_1) + RT_2 \log(P_2/P_1)$
$(\Sigma q)_{\text{ABC}}$	$C_P(T_2 - T_1) - RT_2 \log(P_2/P_1)$
$(\Sigma w/T)_{\text{ABC}}$	$C_P \log T_2/T_1) - R \log(P_2/P_1)$
	Path ADC
$(\Sigma w)_{\text{ADC}}$	$RT_1 \log(P_2/P_1) - R(T_2 - T_1)$
$(\Sigma q)_{\text{ADC}}$	$-RT_1 \log(P_2/P_1) + C_P(T_2 - T_1)$
$(\Sigma w/T)_{\text{ADC}}$	$-R \log(P_2/P_1) + C_P \log T_2/T_1)$

Table 1 Path integrals of w, q, and q/T along ABC and ADC

Second, there is another function of state, the **entropy** S, which changes by $\Delta S = \sum(q/T)$ in going from A to C; and again it doesn't matter which way you go as long as you get there!

Another way of putting this is to say that if, instead of going along the two separate paths ABC and ADC, you keep going at C and then go on to D and finally A (so you do ADC *in reverse*, then the path-independent quantities ΔU and ΔS will both be zero! You're back at A and any state function must have its original value. The closed path ABCDA is called a **cycle**: *in any closed reversible cycle,* $\Sigma w + \Sigma q$ *and* $\Sigma(q/T)$ *are both zero.*

So far we've only been concerned with *changes* ΔU, ΔS in the functions U and S i.e. the *differences* in their values between the end points of any path leading from an 'initial state' to a 'final state'. Like the potential energy in Physics (Book 4) U and S are "arbitrary to within an additive constant", which means we can agree on some **standard state** in which they can be given zero values. If we're using T and P to label the states we can then reckon, for example.

$$S = S(T, P) = S(T^\dagger, P^\dagger) + \Delta S(T^\dagger \to T, P^\dagger \to P),$$

where the 'dagger' superscript labels a standard state quantity and the ΔS indicates the change leading from the standard state to the given state. As in Section 5.2, it doesn't matter what path you take: just as in the first step (AB) along Path ABC, where pressure has the constant value $P = P^\dagger$,

$$S(P^\dagger, T) = S(P^\dagger, T^\dagger) + \int_{T^\dagger}^{T} C_P \frac{\mathrm{d}T}{T}, \tag{5.4}$$

where C_P is the heat capacity at constant pressure, which can be determined by experiment – for any system whatever, not just for an ideal gas. The integral must usually be evaluated numerically (see Book 3, Section 4.5). The change in entropy resulting from a change of *pressure* (T held constant) can be found in a similar way from the experimentally determined coefficient α in (**??**).

In summary, molar entropy values can be obtained for many kinds of system by the methods of this Section: the entropy is a 'known' function of state, given in Tables in many textbooks of Chemistry. Now we want to know more about it – what properties it has, how it can be used, and what it means.

5.3 Some properties of the entropy

In the last Section we talked only about *reversibe* changes, where the system considered was always in equilibrium. This allowed us to *define* the entropy. But the changes that take place in a chemical process, such as a reaction, are *not* in general reversible. What can the entropy tell us about such changes?

The answer is very simple: in any process that takes place spontaneously (i.e. by itself, without any 'push' from outside the system) the entropy can only increase.

$$\mathrm{d}S \geq 0. \tag{5.5}$$

The = sign holds only for a reversible process – and that never happens naturally. For all natural processes inside an isolated system, the entropy must increase, $\mathrm{d}S > 0$. This beautifully simple statement expresses the real content of the Second Law of Thermodynamics – so called because (small as it is) it seems to hold good throughout the Universe! Since the equality in (**??**) holds only in very special cases, the equation is also often said to express the *Principle of Entropy Increase*. Let's look at two applications.

First think of two systems put into thermal contact, but isolated from the rest of the world, so that no heat or work can go in from outside. Before they come into thermal equilibrium they may have different temperatures, System 1 being at temperature T_1 and System 2 at temperature T_2. In Fig.20 the two systems are shown in a box (thick black lines), which prevents heat or work going in from outside.

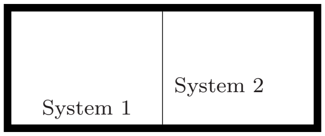


Figure 20

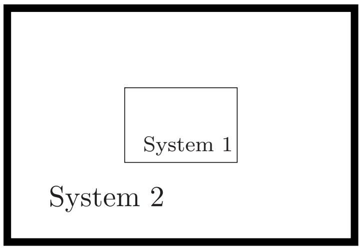


Figure 21

The total entropy of the two-part system will be $S = S_1 + S_2$ (Why? – think about it, using (**??**) and the two parts, free to exchange heat, may absorb amounts q_1 and q_2, so long as $q_1 + q_2 = 0$ (the whole system being isolated). According to (**??**), which can be called the *Principle of Entropy Increase*, we must have

$$\mathrm{d}S_1 + \mathrm{d}S_2 = \frac{q_1}{T_1} + \frac{-q_1}{T_2} = q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0$$

This means that the body at temperature T_1 will absorb heat (q_1 positive) from the body at temperature T_2 *only when* $T_2 > T_1$. In other words, in any natural process, heat will only flow 'downhill' from the hotter of the two bodies to the colder. **Heat never flows 'uphill'!**

Next think of System 2 as a large 'heat bath, in which System 1 (the 'system of interest') is placed – as in Fig.21, where System 2 totally encloses System 1 and both are isolated from the rest of the world (as indicated by the thick black lines). System 1 rapidly comes into equilibrium with its surroundings, at which point $T_1 = T_2 = T$ – their common temperature. (Remember Section 5.1, thinking of our System 1 as the thermometer.)

Now things may be happening inside System 1, which we don't know about: perhaps, for example, its heat content is increasing because some kind of chemical reaction is going on – something we considered in Section 5.3. All we do know is that the heat bath can supply or absorb :any amount of heat and that it does so at the common temperature T So how can we use (5.5), the Principle of Entropy Increase?

The entropy change of System 1 plus System 2 (which together may be the whole world!), in any tiny step, will be $\mathrm{d}S = \mathrm{d}S_1 + \mathrm{d}S_2$; and when the systems exchange thermal energy $q_1 + q_2 = 0$, so thinking always in terms of our 'system of interest' we can say $\mathrm{d}S_2 = -q_1/T$. So (**??**) tells us that

$$\mathrm{d}S_1 + \mathrm{d}S_2 = \mathrm{d}S_1 + \frac{-q_1}{T} \geq 0$$

in any natural process, where the only quantities left refer to System 1. From now on, then, we'll drop the label "1" and write this key result as

$$\mathrm{d}S + \frac{-q}{T} \geq 0. \tag{5.6}$$

We'll come back to this in the next Section, showing how it can be combined with the First Law () to tell us whether a given chemical reaction will happen or not – or whether the reactants will simply stay there quietly in equilibrium. But first – just a few words of history. The idea of entropy didn't come first from Mathematics, or Physics, or Chemistry, but from Engineering – from the study of steam engines! (You can skip the next part, in small type, if you want to keep moving, but it will help you to understand what you've learnt so far.)

Heat engines

At the end of the last Section we noted that the idea of entropy would be important in talking about "heat engines". Now we can see why. The cycle of changes indicated in Fig.19 describes any device that takes in heat at temperature T_1 and lets heat go out at temperature T_2. If $T_1 > T_2$ it is called a "heat engine". But if $T_1 < T_2$ it is a "refrigerator". In both cases you have to do work – you never get anything for nothing!

Table 1 shows how much heat goes into the system along each part of the cycle, starting at A in Fig.19 and continuing through B,C,D, and back to A, always in the anticlockwise direction. We assume all changes are reversible.

From the Table:

Heat input along AB $=(\Sigma q)_{\text{AB}} = C_P(T_2 - T_1)$

Heat input along BC $=(\Sigma q)_{\text{BC}} = -RT_2 \log(P_2/P_1) = Q_2$

Heat input along CD $=(\Sigma q)_{\text{BC}} = -C_P(T_2 - T_1)$

Heat input along DA $=(\Sigma q)_{\text{DA}} = RT_1 \log(P_2/P_1) = Q_1$

Work input along AB $=(\Sigma w)_{\text{AB}} = -R(T_2 - T_1)$

Work input along BC $=(\Sigma w)_{\text{BC}} = RT_2 \log(P_2/P_1)$

Work input along CD $=(\Sigma w)_{\text{CD}} = R(T_2 - T_1)$

Work input along DA $=(\Sigma q)_{\text{DA}} = -RT_1 \log(P_2/P_1)$

Total work done in cycle $= R(T_2 - T_1) \log(P_2/P_1)$

To summarize, for the case $T_1 > T_2$:

Heat taken in at the higher temperature $T_1 = RT_1 \log(P_2/P_1) = Q_1$

Work done on the gas, in a whole cycle, $= R(T_2 - T_1) \log(P_2/P_1) = -W$

When the work done *on* the system comes out *negative*, as in this case (where W is a positive quantity), the *system is doing work* W on the outside world. It is acting as an engine, taking in heat energy Q_1 and turning out useful work W. The ratio (work produced)/ (heat absorbed) is called the *efficiency* of the engine. For this particular kind of cycle (called a **Carnot cycle**), where every step is taken in a *reversible* way, the efficiency is the maximum possible:

$$\text{Efficiency of Carnot engine} = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} \tag{5.7}$$

and this depends only on the temperatures of the heat source (T_1) and the heat 'sink' (T_2). Clearly the bigger the difference, the more efficient your engine will be; but to get 100% efficiency, turning all your heat into useful work, you'd have to have a sink at the absolute zero!

In practice, the theoretical maximum efficiency (**??**) can never be reached, because to make the cycle reversible every step would have to be taken infinitely slowly; it simply offers a target to aim for.

5.4 Some other useful state functions

The First Law in the form (**??**) tells us that, when work (w) is done on a system and thermal energy (q) is put into it, the internal energy U increases by

$$\mathrm{d}U = w + q \tag{5.8}$$

– written in a form where all quantities are considered small, so dU is a *differential.* This can now be combined with the Second Law (of entropy increase in any natural process) in the form (**??**) to give (remembering that the work done *on* the system is $w = -P\mathrm{d}V$, which is positive when the system is 'squeezed' – reducing V)

$$T\mathrm{d}S - q = T\mathrm{d}S - (\mathrm{d}U + P\mathrm{d}V) \geq 0,$$

or, on rearranging,

$$T\mathrm{d}S \geq \mathrm{d}U + P\mathrm{d}V. \tag{5.9}$$

This fundamental equation lets us write down the conditions for any system to stay in equilibrium, not changing in any way, when we are told which of the independent variables (T, P, V) are to be held constant.

At equilibrium, any small change in a function of state must be strictly reversible and the equality in (**??**) must apply: the function must be *stationary* against any small changes in the variables. We've already met two important examples, the internal energy U and the heat content $H = U + PV$. These functions are specially important in the study of systems which are *thermally insulated* from their surroundings, because then $q = 0$ – no heat can flow in or out – and $\mathrm{d}S = q/T = 0$. Under conditions of constant entropy (**??**) gives $\mathrm{d}U + P\mathrm{d}V \leq 0$. The two important cases are then

(i) At constant volume: dU must be either zero or negative. If zero, the internal energy is not changing and the system is in equilibrium. If dU is negative then the value of U can only go down, until equilibrium is reached.

(ii) At constant pressure (the usual case): $\mathrm{d}H = \mathrm{d}U + P\mathrm{d}V$ must be either zero or negative. If zero, the heat content is not changing and the system is in equilibrium. If dH is negative then the value of H can only go down, until equilibrium is reached.

In summary, a system completely isolated from its surroundings, prevented from exchanging thermal energy *and* from changing its volume, will be in equilibrium only when *U is a minimum.* But a system thermally insulated from its surroundings, but free to change its volume (only the *pressure* being constant), will be in equilibrium only when *H is a minimum.*

When a system is *not* insulated from its surroundings (the more usual case) we need to take account of any *entropy* changes that may occur. We do so by defining two more functions of state, both being called "free energies": the first is $F = U - TS$ and is the **Helmholz free energy**, while the second is $G = H - TS$ and is the **Gibbs free energy** (both, as usual, being named after the people who first used them). The way these functions behave shows the importance of the entropy in determining the direction of change.

Again, think of how the functions depend on small changes of the variables used in defining them. First look at $F = U - TS$, remembering that now heat flow is allowed, so $\mathrm{d}S$ will no longer be zero: to first order in the differentials, the Helmholz free energy will change by

$$\begin{aligned} \mathrm{d}F &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\ &= (\mathrm{d}U - T\mathrm{d}S + P\mathrm{d}V) - P\mathrm{d}V - S\mathrm{d}T, \end{aligned}$$

where the term in parentheses (...) is something we've come across already in (**??**) – where we found it must always be either zero or negative. The last equation can therefore be written as a very general condition:

$$\mathrm{d}F \leq -P\mathrm{d}V - S\mathrm{d}T. \tag{5.10}$$

The differential change in the Gibbs free energy, $G = H - TS$, can be handled in a similar way (do it for yourself!) and leads to a parallel result:

$$\mathrm{d}G \leq V\mathrm{d}P - S\mathrm{d}T. \tag{5.11}$$

These two inequalities simply tell us how the conditions (i) and (ii), above, must be extended when a system is free to exchange heat with its surroundings. In words, they become (iii) At constant volume and temperature: $\mathrm{d}F$ must be either zero or negative. If zero, the free energy F is not changing and the system is in equilibrium. If $\mathrm{d}F$ is negative then the value of F can only go down, until equilibrium is reached.

(iv) At constant pressure and temperature: $\mathrm{d}G$ must be either zero or negative. If zero, the free energy G is not changing and the system is in equilibrium. If $\mathrm{d}G$ is negative then the value of G can only go down, until equilibrium is reached.

All this may seem a long way from 'real chemistry', where you mix liquids and solids in flasks or test tubes and wait to see what happens – whether a gas is given off, or there's an explosion. But you've taken giant strides towards understanding what *can* happen and what can't possibly happen because it's against the laws of Nature!

Before you can do real chemistry there's just one more step to take: in chemical reactions the *composition* of the system is changing. In Chapter 3 we talked about a moles of A reacting with b moles of B and producing, perhaps, c moles of C and d moles of D. So we're going to need other variables, besides T, P, V, namely the *quantities* of different substances. We'll think about that in another Chapter, but first let's take a break and look at some quite new ideas that will help us to *understand* what the laws of thermodynamics mean in terms of the atoms and molecules in the 'system' we're talking about.

Exercises – to follow

Chapter 6

Statistical interpretation of the Second Law

6.1 Order and disorder – spontaneous change

Perhaps someone has printed out for you the first ten pages of the last chapter and you have them in a nice neat pile on the table, Page 1 at the top, Page 2 underneath it, going down to Page 10 at the bottom. We say the 'system' is 'perfectly ordered' with every part in its proper place.

But then somebody opens the door and the wind blows in, scattering the pages all over the room. The wind spoils the perfect order: when you pick up the pages and put them back on the table the pages will be 'disordered' – the last page you picked up (which will go on top of the pile) might be 5, and the one before it could be 2, and so on, down to perhaps 1 (at the bottom, because it was the title-page and you picked it up first). How many disordered states of the system, the heap of pages, is it possible to find? In fact it is $N! = 1 \times 2 \times 3 \times 4 \ ... \ \times 10$, called **factorial N**, as you discovered near the beginning of Book 1. And this comes out to be *over three and a half million*! So it will take you some time to put them back into the single state of perfect order. Without the page numbers to help you it would take you much longer.

When a system is 'disturbed' in some way it usually ends in a state where the 'order' is reduced – or the 'disorder' is increased. After the wind has scattered the pages it's no good opening the door again and expecting the wind to put them back in the right order! This suggests that the degree of disorder in the state of a system might be *measured* numerically by the *number of ways* of getting it into that condition. In the present chapter we try to develop this idea and apply it to a *thermodynamic* system; and to do so we start by recalling what we know about probabilities.

Suppose you're talking about the **probability** of something happening and that you want to measure it by giving it a *number*, e.g. 0.5 or 1/2. We used this idea in Sect 4.1, when we were talking about throwing dice or throwing darts and noting the results. In general, we are making an 'experiment' or an *observation* of something (an 'event') that might happen. For example, the die may fall with the 3 uppermost, or the dart may land at a distance between 4 and 5 cms from the vertical line you're aiming at.

If we give a number to each possible event and find that in a long series of observations (N, say) a particular one of them (Event 'i', say) is found n_i times, then we say it has a *probability* $p_i = n_i/N$ of happening. The histogram in Fig 16, where the dartboard was marked out in 1 cm wide strips gives us a **probability distribution** in which we've counted the numbers of 'hits' in each strip and written in the fractions $p_1 = n_1/N,\ p_2 = n_2/N,\ ...$ for all the strips.

The probability distribution gives a *summary* of the results of N repeated observations of what happens when you do the same experiment a large number of times. Once the probabilities have been established, they can be used to predict what will happen in *future* experiments, as long as the conditions of the experiment are not changed (e.g. you don't bring in a champion dart thrower! - or change your distance from the dartboard). If you go on repeating the same experiment, you'll expect to find a fraction p_i of them, in the long run, falling in the ith strip.

The 'system' considered in this example, involves three things – the dartboard, the dart, and the thrower. But instead of doing the same experiment N times on this one system you could imagine the experiment being performed on N **identical copies** of the system (identical dartboard, identical dart, and equally skilled thrower). This imaginary set of identical copies of the single system is called an **ensemble** (a French word for an assembly of players e.g. musicians). The ensemble gives a simple and direct interpretation of a probability distribution: instead of talking about one system whose condition is uncertain, we think of a large number of copies, in which a fraction p_i of them are in the certain condition corresponding to the index 'i'. It's a clever idea and later in this chapter we'll see how useful it can be; but really it's just an alternative way of interpreting the numbers $p_1, p_2, p_3,\ ...$, which come out of repeated experiments on the one real system, in terms of simultaneous experiments on *imaginary copies*.

What we're going to do now is show how the whole of thermodynamics can be built up from the *statistical* ideas introduced so far: this leads into the subject of **statistical thermodynamics**.

Spontaneous change in an isolated system

In earlier Chapters we established the concepts of heat, temperature, pressure, and so on, for a system of 'everyday' size, big enough to be seen and experimented on in the laboratory. Such systems are said to be of "macroscopic" dimensions. But we know they are built up from vast numbers of atoms and molcules, much too small to be seen, which are of "microscopic" (in fact *sub*-microscopic) dimensions. The aim of this Chapter is to show how the properties of 'macro-systems' can be understood in terms of those of their constituent atoms and molecules. Since a macrosystem is nothing more than an enormous collection of microsystems it seems this will require only a knowledge of the 'laws of motion' for the individual particles – which we know about from Book 4. But the Physics in Book 4 includes only **Classical Mechanics**, which does not apply to systems of 'atomic' dimensions.

One of the two greatest discoveries of the last century, alongside Relativity Theory (Chapter 7 of Book 4), was Quantum Theory, the system of equations we need in discussing atoms and molecules. The laws of Classical Mechanics pass over smoothly into those of **Quantum Mechanics** when the particles involved are as small as electrons. But the equations of quantum mechanics are difficult and not yet within our reach, so what do we do? Fortunately, all we need in this Chapter are two basic ideas, which can be stated simply in words: they are

> A) Any system of particles can be found only in
> certain distinct **quantum states**,
> which can be numbered $(1, 2, ...i, ...)$.
> Every state (i) has its own **energy** E_i
> and is described by a **wave function** Ψ_i.

You needn't worry about the independent variables in the function Ψ_i – typically they may be the coordinates in space of points where a particle is found. And the fact that such functions exist only for certain values E_i of the 'energy parameter' may remind you of Book 3, Section 8.3: in fact E_i and Ψ_i are **eigenvalues** and corresponding **eigenfunctions**, coming from a big differential equation.

The second basic idea is that

> B) There is generally a non-zero probability that
> a system in state i may make a **quantum jump**
> to state j, the energy changing from E_i to E_j
> by absorbing (or losing) energy $\Delta E = E_j - E_i$.

Again, you needn't worry about the details: the 'jump' usually arises from some kind of small 'disturbance' and ΔE may result from **absorbtion** (if positive) or **emission** (if negative) of a little bit (a 'quantum') of radiation energy (i.e. light). More of that in other books!

We're now ready to come to the central problem of this Section, considering first an isolated system, with a definite energy E, which we identify with the the internal energy denoted so far by U. For a macroscopic system there will generally be an enormous number of distinct states (g_E, say) with this energy,

$$E_1 = E_2 = \ ... \ = E_i \ = E_{g_E}, \tag{6.1}$$

and, since (from B), above) all transitions are consistent with energy conservation, there will be at any time some probability p_i of the system being found in any given state i.

Now let's put the following question:

> If the system starts in State i and is then left to itself, how will the probabilities of all other states j $(j \neq i)$ change as the system comes into internal equilibrium?

A completely satisfactory solution of this problem is exceedingly difficult to find but the answer itself seems obvious: if a number of states all conform equally well to imposed conditions (in the present case, that $E_1 = E_2 \dots = E_i \dots = E$), and transitions from one to another are free to occur, then after a sufficient time every state will turn up with the same frequency. This is usually taken as a postulate; the **postulate of equal *a priori* probabilities**. It is a natural consequence of 'A' and 'B' (above) and can be put as follows:

C) For a system isolated with energy E,
the equilibrium probabilities of all distinct
accessible states (i) of energy $E_i = E$
are equal.

Here "accessible" means reachable by quantum jumps, according to B). The whole of thermodynamics rests upon this one simple principle.

Suppose now the system starts off in one particular state, State 1, say. What will happen as it moves towards equilibrium, with all states equally likely? Boltzmann, long ago, studied this problem in the case where the 'system' was made up of gas molecules, each one with possible states of energy $\epsilon_1, \epsilon_2, \dots$. A collection of a large number (N) of such molecules forms a gas; and, if you think of this as an *ensemble* of identical copies of the one molecule with n_i copies having energy ϵ_i, then $p_i = n_i/N$ will be the probability of finding *any* molecule of the gas (no matter which) having that energy. Boltzmann concluded, after a long and difficult study of the effect of collisions, that – whatever the initial values of $p_1, p_2, \dots$ – taking all p_i equal, would *minimize* the function

$$H = p_1 \log p_1 + p_2 \log p_2 + \dots + p_i \log p_i + \dots = \sum_i p_i \log p_i. \tag{6.2}$$

This came to be known as Boltzmann's H-theorem.

Remember, however, that now we're talking about something very different: not just a single molecule, or even N molecules in a container, but rather any old chunk of matter, isolated from the rest of the world by putting it in an insulating box with rigid walls (so that no energy can flow in or out).

To be clear, let's take an imaginary system with only *two* states, with energies E_1 and E_2. If we look at them many times, in quick succession (so there's no time for any gradual, long-term changes to occur) we'll find the first state in a fraction $p_1 = n_1/N$ of the observations, and similarly for the second possible state. If we start the system off in State 1, then $p_1 = 1, p_2 = 0$ and $H = 0$. But if we come back after giving the system time to reach internal equilibrium, then the probabilities p_1, p_2 will just be fractions between 0 (impossibility) and 1 (certainty) and all we can say is that their *sum* must be unity: $p_1 + p_2 = 1$.

Taking p_2 (initially zero) as the independent variable, we can then substitute $p_1 = 1 - p_2$ and say that

At the start: $H = 1 \times \log 1 = 0$,
But in general: $H = -p_2 \log(1 - p_2) + p_2 \log p_2$,
a function of one variable, which we can easily minimize (Book 3) by differentiating and putting $\mathrm{d}H/\mathrm{d}p_2 = 0$. The result (check it for yourself) is that, as p_2 grows and p_1 goes down, H decreases until $p_1 = p_2 = \frac{1}{2}$ and H takes its least possible value.

6.2 Making contact with thermodynamics

The result just found is so important that we go at once to the general case of a system with any number of possible states. Will H, defined in (**??**), always reach its minimum value when the probabilities become equal?

The problem is to find the values of $p_1, p_2, \; ... \; p_i,$ for which

$$H = p_1 \log p_1 + p_2 \log p_2 + \; ... \; + p_i \log p_i + \; ... \; = \sum_i p_i \log p_i = \text{minimum value}, \quad (6.3)$$

subject to the condition (called an **auxiliary condition**)

$$p_1 + p_2 + \; ... \; + p_i + \; ... \; = \sum_i p_i \log p_i = 0, \quad (6.4)$$

which must of course be true because each p_i is just the fractional number of times you record State i. Adding them up for all states gives you $n_1/N + n_2/N + \; ..n_i/N + \; ... \; ... \; = (1/N)\sum_i n_i = N/N = 1$. But what was easy when there were only two states (and we could get rid of one of the two variables by using the auxiliary condition) is now much more difficult. The problem can't be simplified that way when there are many variables; and here we may have many millions of them!

So we'll look at this **stationary value problem** generally: but instead of H we'll consider first the arbitrary function $F(x, y)$ of just *two* variables x, y with the auxiliary condition $f(x, y) = 0$. We then have to satisfy the equations

$$F = F(x, y) = x \log x + y \log y = \text{minimum value} \quad (6.5)$$

subject to

$$f = f(x, y) = x + y - 1 = 0. \quad (6.6)$$

To find values of x and y that give a solution we consider small changes and write the last two conditions in differential form (introducing partial derivatives such as $\partial F/\partial x$):

$$\begin{aligned} \mathrm{d}F &= F_x \mathrm{d}x + F_y \mathrm{d}y = 0 \quad (F_x = \partial F/\partial x, \text{ etc.}) & (6.7) \\ \mathrm{d}f &= f_x \mathrm{d}x + f_y \mathrm{d}y = 0 \quad (f_x = \partial f/\partial x, \text{ etc.}). & (6.8) \end{aligned}$$

If we then multiply the second equation by any constant α and add it to the first we find

$$(F_x + \alpha f_x)\mathrm{d}x + (F_y + \alpha f_y)\mathrm{d}y = 0, \quad (6.9)$$

which must certainly be satisfied when the two separate equations are – and for *any* value of the constant α, which is called an **undetermined multiplier**.

Now dx and dy are not *independently* variable, for they must be related by (**??**). But for any value of the change in one of them (dx, say) we can make the second term in (**??**) vanish by chossing α so that the coefficient $(F_y + \alpha f_y)$ will be zero. In that case only the first term remains and, since dx is an arbitrary variation, it follows that $(F_x + \alpha f_x)$ must also be zero.

So where does this get us? It shows simply that, even when dx, dy are not independently variable, their coefficients in (**??**) can both be assumed to be zero is seeking a solution of the stationary value problem. The resultant equations,

$$(F_x + \alpha f_x) = 0, \qquad (F_y + \alpha f_y) = 0, \tag{6.10}$$

together with the auxiliary condition (**??**), are sufficient to determine the values of x and y for which F takes a stationary value.

Before going on, let's make sure that this new approach gives the same result as before: that, for a two-state system, $H(p_1, p_2)$ defined as in (**??**) reaches a stationary value when $p_1 = p_2 = \frac{1}{2}$. In this case, the partial derivatives are easily obtained. Putting $H(p_1, p_2) = F(x, y), \quad (x = p_1, y = p_2)$, it follows that

$$\frac{\partial F}{\partial x} = \frac{\partial}{\partial x}(x \log x) = \log x + x(1/x) = 1 + \log x, \quad \frac{\partial f}{\partial x} = 1$$

with similar results for the second variable, y. The conditions in (**??**) then become

$$(1 + \log x) + \alpha = (1 + \log y) + \alpha = 0.$$

The values of x and y that minimize F must therefore be equal. To find their common value we turn to the auxiliary equation, which now reads $x + y - 1 = 2x - 1 = 0$. The solution is thus $x = y = \frac{1}{2}$, in agreement with what we found, just before (**??**). Let's now turn to the general case, with as many variables as we like.

The general case

The procedure just used is **Lagrange's method of undetermined multipliers** and it can be used for functions of any number of variables, $x_1, x_2, x_3, \ldots x_n$. It applies even when there are several auxiliary conditions, $f(x_1, x_2, x_3, \ldots x_n) = 0, \quad g(x_1, x_2, x_3, \ldots x_n) = 0$ etc.: and it will be needed so often that we write it out in full for the case of n variables and two auxiliary conditions. The problem is thus

Required:	$F(x_1, x_2, x_3, \ldots x_n) =$ stationary value	(A)
subject to	$f(x_1, x_2, x_3, \ldots x_n) = 0$	(B$_1$)
	$g(x_1, x_2, x_3, \ldots x_n) = 0$	(B$_2$)

and the conditions for a solution can now be stated as follows

Condition: $F_i + \alpha f_i + \beta g_i \ = 0 \quad (\text{all } i)$ (C)

where $F_i = (\partial F/\partial x_i)\,,\ f_i = (\partial f/\partial x_i)\,,\ g_i = (\partial g/\partial x_i)\,.$

Now, at last, we can go back to (**??**) and (**??**), where the function F is Boltzmann's H and the variables (x_i) are probabilities (p_i), and solve our general problem.

The n equations (C) for stationary H, of which there may now be many millions, then involve the partial derivatives $(\partial H/\partial p_i)$ and $(\partial f/\partial p_i)$, for all i. And, since there is only one term depending on p_i in each of the two sums (**??**) and (ref6.2), these are easily found:

$$\frac{\partial H}{\partial p_i} = 1 + \log p_i, \qquad \frac{\partial f}{\partial p_i} = 1, \tag{6.11}$$

for all values of i.

The equations in (C) thus become

$$(1 + \log p_1 + \alpha) = (1 + \log p_2 + \alpha) = (1 + \log p_3 + \alpha) = \ \dots\ = 0 \tag{6.12}$$

and the probabilities which make H stationary must all be equal. Their common value p follows from the auxiliary condition: if there are g_E states $(n = g_E)$ and therefore $f(p_1, p_2,\ \dots\ p_n - 1) = g_E \times p - 1 = 0$. By differentiating H a second time, it is confirmed that $\partial^2 H/\partial p_i^2$ is positive and hence that the stationary value is a *minimum* for all p_i:

For an isolated system, with g_E
accessible quantum states of energy E,
the quantity $H = \sum p_i \log p_i$ reaches
a stationary minimum when all p_i are equal.

This important result is called the **Principle of equal a priori probabilities**: starting 'from the beginning', all possible states with the same isolation energy E will be found with the same frequency. In the previous Section we called it a "postulate" because it looked like a good guess – but now there is real evidence for believing it to be true. What's more, it gives us the key for understanding the Second Law of Thermodynamics. The fact that H can only *decrease* as an isolated system reaches internal equilbrium, with all states equally likely, reminds us of the spontaneous *increase* of the entropy S in any natural process. Could it be that $-H$, which will also increase as equilibrium is approached, is in some way a measure of the entropy?

Let's make a daring proposal – that S is *proportional* to H,

$$S = -kH = -k\sum_i p_i \log p_i. \tag{6.13}$$

k being a proportionality factor, which will depend only on our choice of units.

If this proposal is correct it will follow that the stationary value of S will result when all the terms of the sum in (**??**) have the same value, corresponding to equal probabilities

$$p_1 = p_2 = p_3 = \; ... \; = p_{g_E} = 1/g_E, \tag{6.14}$$

since g_E is the number of equal terms. The equibrium entropy (**??**) will thus be

$$S = -kg_E \times \frac{1}{g_E} \times \log\left(\frac{1}{g_E}\right) = -k(-\log g_E) = k \log g_E.$$

Thus, if (**??**) is correct, the entropy formula will reduce to

$$S = k \log g_E. \tag{6.15}$$

In other words

> The equilibrium entropy of an isolated system with g_E distinct quantum states of energy E is measured by the *logarithm* of g_E: $S = k \log g_E$.

Put more simply, this means the entropy of the system is determined by 'the number of ways in which its internal energy can be divided out among its component parts'.

Of course, we don't yet *know* that (**??**) is correct: H^2, for example, would also have the property of incrasing, like the entropy, as equilibrium was approached. But the end result (**??**) does have the property of ensuring that the entropy of two *independent* systems (A and B) will be the *sum* of their separate entropies (as follows from the thermal definition (Section xxx). To show this, we only need note that for two independent systems the number of possible states will be $g_E^{AB} = g_E^A \times g_E^B$, since any of the g_E^A states of A may be combined with any of the g_E^B states of B. The entropy formula (**??**) then gives for the two-part system

$$S^{AB} = k \log(g_E^A \times g_E^B) = k(\log(g_E^A + \log g_E^B) = S^A + S^B.$$

The logarithmic relationship (**??**) is in fact *unique* in leading to the additivity property of the entropy so defined; and this strongly suggets that (**??**) is indeed correct. To make really sure, we should prove also that it leads to the other properties of the thermally defined entropy. We'll do that in the next Section.

6.3 But how does the *temperature* come in?

So far, in looking for a statistical interpretation of thermodynamics, we've only been thinking about the internal equilibrium of an isolated system with fixed energy. But that doesn't allow us to *heat* the system by putting thermal energy into it: to do that we must take away the insulation, so that the system can exchange energy with its surroundings – and only then can we begin to talk about temperature! What does temperature *mean* in terms of the probabilities of the various energy states?

In Chapter 2 the idea of temperature was introduced by thinking about the equibrium between two systems, when energy could flow between them: the second system could be a large 'heat bath', able to supply energy to the first system without any noticeable change in itself, and when the two systems came into equilibrium they were said to be "at the same temperature" – that of the heat bath. So let's do the same, but thinking of the 'entropy', as defined by (**??**), and asking how the system will come into equilibrium with the heat bath when the two are free to exchange energy.

Call the first system 'A' (the one we're interested in) and the second system 'B' (the heat bath or 'thermostat'), whose job is simply to supply heat energy to A if it's cooling down, or absorb energy from A if it's getting too hot. In this way, still using our ideas about 'hotness' as an indicator of 'temperature', we can say the thermostat "maintains the temperature" of System A. The internal energy of A will no longer have a precise value E, but will fluctuate ('wobble') around a certain *mean* value $\bar{E}$; and *this* is the quantity we are trying to keep constant. Let's identify it with the thermodynamic internal energy, U:

$$U = \bar{E} = p_1E_1 + p_2E_2 + \ \dots\ = \sum_i p_iE_i, \tag{6.16}$$

which corresponds to the system being found in State i, with energy E_i, in a fraction p_i of the observations we make on it, and so represents a true average value.

Going back to the beginning of this Section, where we looked for a stationary value of H defined in (**??**), subject to the condition (**??**), we can now repeat everything with *one extra condition* – that U stays constant with a certain 'equilibrium value'. In summary we'll require

$$\begin{aligned} H &= p_1\log p_1 + p_2\log p_2 + \ \dots\ = \text{stationary value}, &(6.17)\\ 1 &= p_1 + p_2 + \ \dots\ = \sum_i p_i \quad = \text{constant}, &(6.18)\\ U &= p_1E_1 + p_2E_2 + \ \dots\ = \sum_i p_iE_i \quad = \text{constant}. &(6.19)\end{aligned}$$

For any small variations $\mathrm{d}p_1, \mathrm{d}p_2,\ \dots$ of the probabilities, we must now insist that

$$\begin{aligned} \mathrm{d}H &= \frac{\partial H}{\partial p_1}\mathrm{d}p_1 + \frac{\partial H}{\partial p_2}\mathrm{d}p_2 + \ \dots\ = 0,\\ & \quad \mathrm{d}p_1 + \mathrm{d}p_2 + \ \dots\ = 0,\\ \mathrm{d}U &= \mathrm{d}p_1E_1 + \mathrm{d}p_2E_2 + \ \dots\ = 0. \end{aligned}$$

On multiplying the last two equations by undetermined multipliers, α and β respectively, and adding the results to the equation for $\mathrm{d}H$, it follows that

$$\left(\frac{\partial H}{\partial p_1} + \alpha + \beta E_1\right)\mathrm{d}p_1 + \left(\frac{\partial H}{\partial p_2} + \alpha + \beta E_2\right)\mathrm{d}p_2 + \ \dots\ = 0.$$

But the partial derivatives of H have already been used in (**??**), $\partial H/\partial p_i = 1 + \log p_i$ for all i, and on setting the coefficient of $\mathrm{d}p_i$ to zero in the last equation we get $(1 + \log p_i) + \alpha + \beta E_i = 0$ for all i values. Thus, for a stationary value of H,

$$\log p_i = -(1 + \alpha + \beta E_i), \quad p_i = \exp -(1 + \alpha) \exp -\beta E_i.$$

This looks simpler if we write $\exp -(1+\alpha) = A$ (it's just another constant after all). And the final result, giving the equilibrium probabilities of all states in terms of their energies, is then

$$p_i = Ae^{-\beta E_i}, \tag{6.20}$$

– reminding us at once of Maxwell's famous law in Section 4.2 for the probability of finding any molecule of an ideal gas in a state with energy ϵ_i. But there are very important differences.

First, let's remember we're not talking about a single molecule in a gas, but about what we called "any old chunk of matter" in a thermostat: we don't even need to know what it's made of! The exponential dependence of finding it in a given state, of energy E_i, is indeed a very general law.

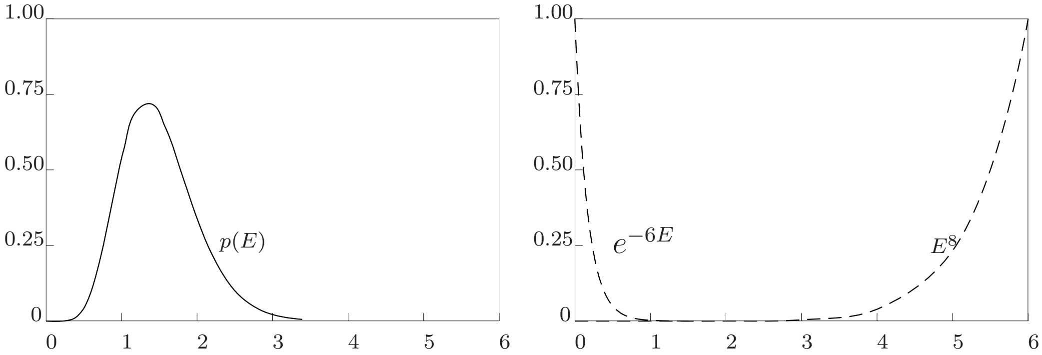
A second difference is that Maxwell's law for molecules shows a *peak* in the probability distribution – a *most probable* value of the kinetic energy – whereas here, in (**??**), the probability of finding the system with energy E_i just seems to fall off continuously as the energy gets larger: it would seem that the most probable state is the one with zero energy! But we know from studying the ideal gas that internal energy has to do with molecular motion and that as a system gets hotter the energy rises; so how can it be that any system is always most likely to be found in the lowest possible energy state? Something must be wrong.

In fact (**??**) refers to the probability of finding the system in a given *state* (i), with energy E_i – not the probability of finding it with a given *energy*, E say – which is what really interests us. If the probability of finding a particular state, of energy E, is given by the law (**??**) as $Ae^{-\beta E}$ and there are g_E distinct states with the same energy E, then the probability of the system being found in *any* of the g_E states will be

$$p_E = g_E \times Ae^{-\beta E}. \tag{6.21}$$

This defines the **Boltzmann distribution** in its general form.

The difference between (**??**) and (**??**) should be carefully noted: when E is large, as it always is for a system of macroscopic size, the factor g_E rises extremely rapidly with increasing E, while the exponential factor *decreases* rapidly. The probability (**??**) is plotted in Fig.22a (after normalizing), for trial values $g_E = E^8$ and $\beta = 6$. The separate factors are plotted in Fig.22b: which shows clearly how the peak in Fig.22a arises from the competition between the 'going down' and 'going up' factors – just as in Fig.18, for Maxwell's law. Note however that the curve of E^8 is plotted on a different scale to make it fit in the Figure: at $E = 6$, the actual value of E^8 is 1,679,616 (!!). Both factors are close to zero in the region of the peak, but the normalizing factor A multiplies their product to produce the peak shown in Fig.22a. The area under the curve is unity and as the peak becomes narrow it must become higher and higher. Try to imagine how sharp it will be if you take $g_E \approx 10^{20}$: this is the kind of situation that arises for a macroscopic system!



(a) $p(E) = AE^8 \exp(-6E)$ (b) The factors $\exp(-6E)$ and E^8

Figure 22. Origin of the Boltzmann distribution

Note that if the constant β is given a smaller value the peak will move to a higher energy – the system will get hotter: β may be taken as an *inverse* measure of the **temperature** by putting

$$\beta = \frac{1}{kT}, \tag{6.22}$$

where the same constant k is used here as in the entropy definition. (Doing this just relates the size of the degree to the unit of entropy.)

In the next Section we confirm that T introduced in this way has all the properties of temperature (as introduced in Section 6.2). And this will give us a new route to thermodynamics, based on the Boltzmann distribution instead of the entropy equation (**??**).

6.4 The partition function; another route to thermodynamics

Equation (**??**) contains two undetermined constants: the second (β) will be used as a measure of temperature, while the first is easy to get rid of by noting that the sum of probabilities, over all states, must be unity. Thus

$$\sum_i p_i = A \sum_i e^{-\beta E_i} = 1,$$

and substituting in (**??**) leads to

$$p_i = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}. \tag{6.23}$$

The denominator in this expression is called the "partition function" (or "sum-over-states") of the system and is often denoted by Z:

$$Z = \sum_i e^{-\beta E_i}. \tag{6.24}$$

Note that here the states are all counted separately, even if many of them have the same energy; but if there are g_E states with the same energy E the last equation may be written in the alternative form

$$Z = \sum_E g_E e^{-\beta E}, \tag{6.25}$$

in which the sum is over distinct values of E. (Take care not to get confused between the two forms! – they're just different ways of counting, one-at-a-time or in groups.)

The second parameter in (**??**), namely β, as we have already guessed, is too important to get rid of; it brings in the temperature concept. For *two* systems, A and B, in 'weak interaction' so that their total energy is just the sum of their separate energies, the energy states of the two together will be $E^{AB} = E^A + E^B$. And if A has g_{E^A} of energy E^A, while B has g_{E^B} of energy E^B, then the two together can have energy E^{AB} in $g_{E^{AB}} = g_{E^A} \times g_{E^B}$ different ways. The energy distribution law for the combined system, in equilibrium with the same thermostat, will therefore be, from (**??**),

$$p_{E^{AB}} = g_{E^{AB}} \exp(-\beta E^{AB}) = g_{E^A} g_{E^B} \times \exp(-\beta E^A - \beta E^B).$$

But the exponential of the sum of two terms is the *product* of their separate exponentials; so this expression factorizes, giving

$$p_{E^{AB}} = g_{E^A} \exp(-\beta E^A) \times g_{E^B} \exp(-\beta E^B) = p_{E^A} \times p_{E^B} \tag{6.26}$$

– each part of the combined system A + B has a Boltzmann law of its own, with the same value of the parameter β, as long as they stay in the same thermostat. Think of A and B as two thermometers: they will have a common value of β until you take one of them out – in which case its β-value will change until it comes into equilibrium with its new environment, which may even be another thermostat. The amazing thing is that these results, which describe the properties of **temperature**, don't depend on what the thermometers are made of (liquid in a glass tube, or gas in a flask): a temperature measured by the value of beta is 'absolute' in the sense that it doesn't depend on what particular experiments we do to establish it. Presently, we'll find that it agrees exactly with the temperature measured on an ideal gas thermometer.

One other important result that follows from (**??**) is that the partition function Z^{AB} for a system AB composed of two weakly interacting parts, A and B, is simply the product of those for the separate systems: for if we sum over all energy levels of systen AB and use (**??**) we get

$$\begin{aligned}
Z^{AB} &= \sum_{E}^{AB} g_E^{AB} \exp(-\beta E^{AB}) \\
&= \sum_{E}^{A} \sum_{E}^{B} g_{E^A} g_{E^B} \exp(-\beta E^A - \beta E^B) \\
&= \sum_{E}^{A} g_{E^A} \exp(-\beta E^A) \times \sum_{E}^{B} g_{E^B} \exp(-\beta E^B),
\end{aligned}$$

which is the product of the separate partition functions. Thus, as long as the interaction energy is a negligible fraction of the total energy, so $E^{AB} = E^A + E^B$ for all energy levels,

$$Z^{AB} = Z^A \times Z^B. \tag{6.27}$$

This result can clearly be extended to systems composed of *many* interacting parts: if the total energy is a *sum* of the energies of its parts, then the partition function (PF) for the whole system will be a *product* of PFs for its separate parts. In the next Chapter we'll see what this means for the macroscopic systems we meet in Physics and Chemistry. First, however, we'll see how calculating PFs can lead us directly to the functions of state which are needed in understanding chemical reactions.

6.5 Thermodynamic functions: the second route

In Section 6.2, the entropy of a system was related to 'the number of ways g_E of dividing out its energy E among its constituent parts' – which doesn't help very much if we have no idea how to get g_E in the formula $S = k \log g_E$, first proposed in (**??**). This also applies to an *isolated system*, when in reality we always deal with systems *in their surroundings*, perhaps in a thermostat which holds the temperature T constant, or perhaps in a container of fixed volume V, or perhaps kept under given pressure P but allowed to expand. The formula (**??**) doesn't even allow for the existence of these thermodynamic variables!

On the other hand, the Boltzmann law (**??**) contains both the temperature T and the quantity g_E, which appears in the entropy formula and also depends on E (even if we don't yet know how to get it!). What we do know is that a system in thermal equilibrium at temperature T has an almost constant energy (let's call it E^*), set by the temperature, around which only tiny fluctuations occur: this value $E = E^*$ is the *most probable energy*, at which the Boltzmann distribution has its extremely sharp peak, and has already been identified as the thermodynamic internal energy U. If the system were to be isolated with that energy its entropy would be

$$S = k \log g_{E^*}. \tag{6.28}$$

And now we can bring in the Boltzmann distribution (**??**) by putting $E = E^*$ at the peak and remembering (**??**). The logarithm of the factor $g_E \exp(-\beta E)$, evaluated at its peak where $E = E^*$, can then be re-written as

$$\log\left[g_{E^*}\exp\left(\frac{-E^*}{kT}\right)\right] = \log g_{E^*} + \frac{-E^*}{kT}$$

and the entropy formula (**??**) thus becomes (substituting for $\log g_{E^*}$)

$$S = k\log g_{E^*} = k\log\left[g_{E^*}\exp\left(\frac{-E^*}{kT}\right)\right] + \frac{E^*}{T}. \tag{6.29}$$

There's nothing mysterious here: we've only played around with the mathematics. But now we're going to use the extreme sharpness of the peak in the Boltzmann factor by saying that, in good approximation

$$k\log\left[g_{E^*}\exp\left(\frac{-E^*}{kT}\right)\right] \approx k\log\sum_E g_E\exp\left(\frac{-E}{kT}\right),$$

where the left-hand side contains just one term, the one where the energy has its most probable value E^*, while the right-hand side is a sum of millions of terms, extending over *all* energy levels. How can that be? At first sight it seems impossible. But suppose for a moment it is true: if it is, then we can use the *sum* over all energy levels in (**??**) – instead of the single term with $E = E^*$. The result is then an alternative expression for the entropy:

$$S = k\log\sum_E g_E\exp\left(\frac{-E}{kT}\right) + \frac{U}{T}, \tag{6.30}$$

where the most probable energy E^* has been written as U in the last term. But the sum over all energies is evidently just the partition function Z, as defined in (**??**), and the last result thus reads $S = k\log Z + (U/T)$. On multiplying throughout by T it follows that the function $F = U - TS$, which we met in Section 6.4 and called the **Helmholz Free Energy**, can be expressed very directly, for any system whatever, in terms of the partition function:

$$F = -kT\log Z. \tag{6.31}$$

This quantity will appear as a function of variables like T and V, which determine the thermodynamic state of the system, and other properties may be obtained from it: for example,

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \quad U = F - T\left(\frac{\partial F}{\partial T}\right)_V, \quad P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{6.32}$$

The partition function therefore provides the key for understanding the behaviour of macroscopic systems in terms of their constituent atoms and molecules. We come down to the details in Chapter 7.

First, however, we have to be sure the approximation leading to (**??**) is satisfactory. To do so, we must look closely at the peak in Fig.22; for what we are saying is that all the terms in the sum $\sum_E g_E\exp\left(\frac{-E}{kT}\right)$, on either side of the single biggest term with $E = E^*$ can be thrown away when we evaluate the logarithm of the sum – which is hard to swallow!

The reason it works is simple. Suppose we are throwing away five million terms on either side of the largest, all of them being almost as big: what difference does it make?

We have two expressions for the entropy: they are (**??**), obtained for the system in isolation with $E = E^*$; and (**??**), obtained allowing for fluctuations around E^*. If we approximate the second expression by including in the sum only the ten million terms with roughly the same peak energy E^*, it becomes (since the logarithm of a product is the *sum* of the logarithms of the two factors)

$$S \approx k \log(10^7) + k \log \left[g_{E^*} \exp\left(\frac{-E^*}{kT} \right) \right].$$

This differs from the isolation entropy (**??**) by only $(7 \times 2.303)k \approx 16k$.

To get some 'feeling' for what this means, remember that the energy of one molecule of an ideal gas at temperature T (see Section 4.4) was found to be about $\frac{3}{2}kT$. So if we add n molecules to an ideal gas at temperature T the entropy will increase by about $n(\frac{3}{2}kT)/T = \frac{3}{2}nk$. In other words the difference just found between the two approximations is roughly the entropy of 30 molecules! Any *macroscopic* system of the kind considered in thermodynamics (e.g. one mole of gas) will contain a number of the order of 10^{23} molecules: for a system of macroscopic dimensions the entropy formulas (**??**) and (**??**) are in essentially perfect agreement. Of course, this has not been *proved*; but the proof is only a piece of mathematics, confirming the conclusion we've already reached. If you really want to be sure about all this you can turn to Exercise xxx and try to show just how sharp the peak must be!

Exercises – to follow

Chapter 7

Partition functions and properties

7.1 Getting started

'Real' chemistry still seems to be a long way off! What good is all that theory if it doesn't help us to do anything? We know that the partition function gives us (in theory!) a way of finding the thermodynamic functions we need in discussing chemical reactions; but how do we get them? That's the problem we now have to face.

The only systems for which the PFs can be obtained easily are those which consist of *independent particles*: this means that the total energy of N such particles is simply the *sum* of their separate enegies. Systems of this kind include, in good approximation, most gases, gas mixtures, and many types of crystal. If there are n_1 particles with energy ϵ_1, n_2 with energy ϵ_2, and so on, then we can take

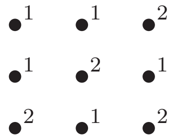
$$E = n_1\epsilon_1 + n_2\epsilon_2 + \ ... \ + n_i\epsilon_i + \ ... \ + \sum_i n_i\epsilon_i \tag{7.1}$$

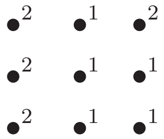
as our starting point. The next step is to use the fact that, for a system whose energy is the *sum* of the energies of its parts, the PF is simply a *product* of the PFs of the separate parts. But the counting of the number of *distinct states* g_E, for any given total energy E is not so easy. To continue, we'll study two important special cases: (i) the 'Einstein crystal', and (ii) the ideal gas.

(i) **The Einstein crystal**

In the simplest 'model' of a crystal, first used by Einstein, the particles are taken to be single atoms, each vibrating, with its own particular energy, around a point on a **crystal lattice**. If there are n_1 particles with energy ϵ_1, n_2 with energy ϵ_2, and so on, then we know E is given by (**??**); but we also need g_E, the number of different states of that energy.

Suppose we use $\bullet^1$, $\bullet^2$ to denote particles with energies ϵ_1, ϵ_2, respectively, and look at a bit of crystal with 5 atoms vibrating with energy ϵ_1 and 4 with energy ϵ_2. Then we must count





as two *different states*, even though they have the same vibrational energy $E = 5\epsilon_1 + 4\epsilon_2$. If instead there were N lattice points ($N \approx 10^{20}$ would give a bit of crystal big enough to see!) and the atoms at all of them had different energies, then g_E would have the value $N!$ – the number of ways you could rearrange their states without changing E. But if two states had the same energy, then swapping those two (wherever they may be) would make no difference and the $N!$ would be twice too big. Similarly, if 5 atoms had energy ϵ_1 as in the first picture above (all the rest still having different energies), the $N!$ would be 5! times too big and would have to be divided by that number to get the number of *distinct* states with the same total energy. You can guess the final result: the number of distinct states of total vibrational energy E (**??**) will be

$$g_E = \frac{N!}{n_1!n_2! \; ... \; n_i! \; ...}. \tag{7.2}$$

The partition function for an Einstein crystal can now be written down: it is

$$Z_{\text{cryst}} = \sum_E g_E e^{-\beta E} = \sum_{\substack{n_1, n_2, \; .... \\ (n_1 + n_2 + \; ... = N)}} \frac{N!}{n_1!n_2! \; ... \; n_i! \; ...} (e^{-\beta\epsilon_1})^{n_1} (e^{-\beta\epsilon_2})^{n_2} \; ... \; , \tag{7.3}$$

where the exponential of the sum is the product of exponentials for the separate terms. If only the first two energy levels for each vibrator need be considered (they become smaller as β increases), this complicated sum would be the binomial expansion (see Book 3, Exercise 4 on Chapter 5), namely

$$(x + y)^N = \sum_{\substack{n_1, n_2 \\ (n_1 + n_2 = N)}} \frac{N!}{n_1!n_2!} x^{n_1} y^{n_2},$$

with $x = e^{-\beta\epsilon_1}$, $y = e^{-\beta\epsilon_2}$. But an exactly similar result holds in the general case with any number of terms; it is called the **multinomial expansion** of the Nth power of the sum

$$e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3} + \; ... \; .$$

So (**??**) boils down to

$$Z_{\text{cryst}} = \sum_E g_E e^{-\beta E} = (e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3} \; ... \;)^N$$

The sum on the right is a sum over the vibrational energy levels of a *single* vibrating atom: it is a 'one-particle' partition function or 'pf' and is easy to evaluate – after all we've come down from a system of 10^{20} particles to just *one*! To summarize:

$$\boxed{\textbf{Einstein cystal:} \qquad Z_{\text{cryst}} = \textstyle\sum_E g_E e^{-\beta E} = z^N} \tag{7.4}$$

where the pf z is

$$z = (e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + \ \dots\ ) = \sum_i e^{-\beta\epsilon_i} \tag{7.5}$$

- just as if no other atoms were present.

You may be wondering why we used such a complicated way of getting a result we knew already; that for a system with independent parts the PF is a product of PFs for the separate parts. It was simply to bring out an important and fundamental difference between a crystal and a gas, the system we study next.

(ii) **The ideal gas**

The N atoms in an Einstein crystal, were all physically separate: each could be given a number and we could 'see' a difference between a state in which, on the one hand, Atom 2 had 1 unit of energy and Atom 5 had 3 units and, on the other hand, Atom 2 had 3 units of energy and Atom 5 had 1 unit. In that case the two states would be *distinct*, even when there were no other differences in the way the total vibrational energy was distributed. We went ahead and counted all the possible distinct ways of dividing out the total energy E among the atoms; and that gave us g_E.

In an ideal gas, however, all the moving atoms are in the same container, not in separate numbered 'boxes' on different lattice points; and there is only *one* state in which there are n_1 atoms (no matter which) with kinetic energy ϵ_1, n_2 atoms with kinetic energy ϵ_2, and so on. The atoms are said to be **indistinguishable particles**: we can't imagine any way of deciding which is which! And this makes an enormous difference to the calculation of a partition function. Instead of (**??**) we now have, putting $g_E = 1$ for each particular choice of $n_1, n_2, n_3,\ \dots$ that gives the total energy E in (**??**),

$$Z_{\text{gas}} = \sum_{\substack{n_1, n_2,\ \dots. \\ (n_1+n_2+\ \dots = N)}} (e^{-\beta\epsilon_1})^{n_1} (e^{-\beta\epsilon_2})^{n_2} \ \dots\ . \tag{7.6}$$

Although this looks much simpler than (**??**), there's no easy way of getting the sum!

So what do we do? In earlier sections it was possible to go all the way and find even the equation of state for an ideal gas; so there *must* be some way of getting the same results using the partition function approach – which, in principle, is much more general and powerful.

To evaluate the PF in the form (**??**) we must take account of another enormous difference between the ideal gas and the Einstein crystal: whereas the energy levels for a vibrating atom in a crystal are quite well separated, those for translational motion of an atom in a large container are exceedingly close. Let us denote the exponentials in (**??**) by

$$x_1 = e^{-\beta\epsilon_1},\ x_2 = e^{-\beta\epsilon_2},\ etc.,$$

so that the sum over all values of $n_1, n_2,\ \dots$ in (**??**), subject to $n_1+n_2+\ \dots\ = N$ becomes

$$Z = \sum_{\substack{n_1, n_2,\ \dots. \\ (n_1+n_2+\ \dots = N)}} x_1^{n_1} x_2^{n_2} \ \dots\ .$$

If we now define a one-particle partition function (pf), z, for a single atom moving alone in the container, as

$$z = x_1 + x_2 + x_3 + \ ...$$

then the multinomial expansion used in obtaining (**??**) tells us that

$$z^N = (x_1 + x_2 + x_3 + \ ... \ )^N = \sum_{\substack{n_1, n_2, \ .... \\ (n_1 + n_2 + \ ... = N)}} x_1^{n_1} x_2^{n_2} \ ... \ . \frac{N!}{n_1! n_2! \ ... \ n_i! \ ...} x_1^{n_1} \ x_2^{n_2} \ x_3^{n_3} \ ... \ . \tag{7.7}$$

This is simply a mathematical identity, but it suggests an approximation. If there are, for example, 10^{20} atoms in the gas; and the important range of energies comprises 10^{25} single-particle energy levels, then there will be only one atom for every 100,000 levels! A negligible number of the terms in the sum will have 2 or more particles in any level; nearly all of them will have n-values of 0 or 1. Remembering that (from Book 1) $0! = 1! = 1$, this means that the ugly coefficients in (**??**) will all reduce to $N!$. The end result of putting this result into (**??**) and using the original notation ($x_i = e^{-\beta\epsilon_i}$ etc.) is that (check it carefully for yourself!)

$$\boxed{\textbf{Ideal gas:} \qquad Z_{\text{gas}} = \textstyle\sum_E g_E e^{-\beta E} = z^N/N!} \tag{7.8}$$

where the one-particle pf is defined exactly as in (**??**). But now the energy levels refer to *translational* motion of a single particle in a container, instead of a vibrating atom held in a very small region around a point in the crystal lattice.

The equals sign has been used in (**??**) because in most cases the result is very nearly exact. But, before we can go ahead and apply the results we've got so far to actual gases and crystals, there's one more thing we need – and it comes from quantum theory. At the level of single atoms and molecules we can only get information about the energies ϵ_i, which come into all our partition functions, by using **quantum mechanics**. So far we've used only a few of the basic *concepts* of quantum theory, like the principles (A), (B), (C) in Section 6.1 , which apply generally to systems of any kind – big or small – and it was possible to present them in words. But now we need one or two formulas which give the energy levels ϵ_i available, according to the laws of quantum mechanics, to certain one-particle systems: typically a monatomic molecule moving in a container or 'box' and an atom attracted strongly towards a fixed point in space. These will be given in the next Section.

7.2 Getting the PFs: the last step

First let's think of one molecule of gas in a rectangular box, supposing it to be monatomic so it can be taken as a single mass point, of mass M, with no complications from internal motions. For simplicity, we'll take the box to be a cube with sides of length L but that's not important.

The ideal gas

According to quantum mechanics (which we'll come to much later in the Basic Books Series), the energy of translation ϵ can't take just *any* value we please: it must depend on three integers n_x, n_y, n_z, which are called **quantum numbers**. The 'allowed' energies, for a particle of mass M in a cubical box of side-length L, are given by a very simple formula:

$$\epsilon_{n_x,n_y,n_z} = \left(\frac{h^2}{8ML^2}\right)(n_x^2 + n_y^2 + n_z^2), \tag{7.9}$$

where h is a very small quantity called **Planck's constant**, with the value $h = 6.626 \times 10^{-34}$ J s. This constant has the dimensions of energy/frequency (energy×time) and is one of the most fundamental quantities in quantum mechanics; just as c, the speed of light, has a similar importance in relativity theory (Book 4, Chapter 8).

There is one quantum state for every set of three integer values of n_x, n_y, n_z, but there are no states for non-integral values. The one-particle pf (**??**) is a sum over all allowed states and can therefore be written. remembering from the last Section that $\beta = 1/(kT)$,

$$z_t = \sum_{n_x} \exp -n_x^2(h^2/8ML^2kT) \times (\text{similar terms in y and z}) \tag{7.10}$$

where the sums over all positive values of n_x, n_y, n_z are independent and can be made one at a time. Let's calculate the first one, calling it Σ and putting $n_x = n, \quad (h^2/8ML^2kT) = C$:

$$\Sigma = \sum_{n=0}^{\infty} \exp(-Cn^2) \approx \int_0^\infty \exp(-Cn^2)\mathrm{d}n.$$

How is it that the sum can be approximated in this way by an integral? It's basically because Planck's constant is so incredibly small that for any macroscopic sample of gas (perhaps 10^{20} molecules in a cube with $L = 1$ cm) n really seems like a *continuous* variable and a 'unit step' ($\Delta n = 1$) can be treated as 'infinitesimal'. (Look at Exercise xxx at the end of this chapter.) The integral above is in fact a well-known definite integral, whose value is $\int_0^\infty \exp(-Cn^2)\mathrm{d}n = \frac{1}{2}\sqrt{\pi/C}$. On using this result and inserting the value of C, the product of the three factors in (**??**) gives the final result:

$$z_t = \left(\frac{2\pi MkT}{h^2}\right)^{\frac{3}{2}} V, \tag{7.11}$$

where $V = L^3$ is the volume of the container.

From (**??**) it follows immediately that the free energy F of a monatomic gas is given by

$$F_{gas} = -kT \log Z = -kT[N \log z_t - \log N!].$$

One small problem: if you look for $\log N!$ in a book of mathematical Tables you won't find it, because even 10! is over four million – and here we're dealing with N of the order 10^{23}, so its factorial is going to be something you can't imagine! In Exercise xxx, however, you'll find how to get a simple and extremely accurate approximation to it, namely

$$\log(N!) \approx N \log N - N \tag{7.12}$$

which is called **Stirling's approximation**. Using this value, along with (**??**), the final expression for F_{gas} becomes (check it!)

$$F_{gas} = -NkT(\log z - \log N + 1) = -NkT\left[1 + \log\left(\frac{(2\pi MkT)^{\frac{3}{2}}V}{Nh^3}\right)\right]. \tag{7.13}$$

This result is going to give us all the properties of an ideal gas! First, however, we'll get a corresponding result for the Einstein cystal.

The Einstein crystal

The allowed energy levels for a particle of mass M, moving along the x-axis and attracted towards the origin by a force $F = -k|x|$, are given by

$$\epsilon_n = (n + \tfrac{1}{2})h\nu, \tag{7.14}$$

where the quantum number n is again a positive integer. The quantity ν is the **frequency** with which the particle would vibrate according to classical mechanics (see Book 4) and depends on the **force constant** k: the bigger k, the more strongly is the particle bound to its lattice point. The classical frequency is

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{M}} \tag{7.15}$$

and the corresponding pf, for this type of vibration, is thus

$$z_v = e^{-\frac{1}{2}h\nu/kT}\sum_{n=0}^{\infty} e^{-nh\nu/kT} = \frac{e^{-\frac{1}{2}h\nu/kT}}{1 - e^{-h\nu/kT}}$$

where we've used the sum of the geometric series found in Book 1 (Section 5.1).

For an atom in a crystal lattice, there are *three* independent modes of vibration, along the x-, y- and z-axes; and for an **isotropic crystal** each gives an identical factor in the 3-dimensional pf. The vibrational PF thus becomes , from (**??**),

$$Z_{cryst} = (z_v^3)^N = e^{-\frac{3}{2}Nh\nu/kT} \times \left(\frac{e^{-\frac{1}{2}h\nu/kT}}{1 - e^{-h\nu/kT}}\right)^{3N} \tag{7.16}$$

The free energy thus comes out as

$$F_{cryst} = \tfrac{3}{2}Nh\nu + 3NkT\log(1 - e^{-h\nu/kT})^{3N}. \tag{7.17}$$

The two free energy expressions (**??**) and (**??**) allow us to predict a large range of physical and chemical properties for systems composed of gases and crystals.

7.3 Properties of gases and crystals

First let's remember what we know about the thermodynamic functions, U, H, F and G, defined in Section 5.4, using T, V or T, P as the independent variables which determine the thermodynamic *state* of the system. The *properties* of a system tell us how it responds to *changes* in the independent variables; and usually we'll be thinking of *reversible* changes (as we were in Section xxx), so small and slow that the equilibrium of the system is not disturbed. Such changes are often called "quasi-static" ('almost stationary') – meaning that the system changes 'smoothly', without jumping about all over the place. And in this case the properties of interest will usually be defined as derivatives (or partial derivatives).

For example, in a container of fixed volume, may be heated by changing the temperature T. The internal energy U then increases in proportion to the change $\mathrm{d}T$ and we write $\mathrm{d}U = (\partial U/\partial T)_V \mathrm{d}T$, the rate of increase of U with T at constant volume. The coefficient of $\mathrm{d}T$ is called the system's **heat capacity at constant volume**, written as C_V.

If, however, the system is free to expand (at pressure P say) it will do an amount of work $w = P\mathrm{d}V$, so the *heat* intake will be reduced by that amount, becoming $\mathrm{d}U - P\mathrm{d}V$: but that is the change, when P is constant, of the heat content $H = U + PV$. The rate of increase of heat content at constant pressure will also be proportional to $\mathrm{d}T$ and defines another property, the **heat capacity at constant pressure**, written as C_P. The two important heat capacities of any system (which we already came across in Section 5.4) are thus

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \qquad C_P = \left(\frac{\partial H}{\partial T}\right)_P. \tag{7.18}$$

The state functions U and H, along with the 'free energies' F and G, were seen to be important (Section 5.4) as a means of stating **equilibrium conditions** for chemical reactions. Reactions proceed until one or other of the state functions reaches a minimum value; and this is always a consequence of the fundamental property of entropy increase equation (5.5). In particular, we found that under conditions of constant volume and temperature it was F, the Helmholz free energy ($F = U - TS$) that reached a minimum; but under constant pressure and temperature if was G, the Gibbs free energy ($G = H - TS$). Both these functions involve the *entropy* and in earlier Sections of the present Chapter we've found ways of getting them (in principle!) from what we know about molecular motion. In Section 7.2 we found it was enough to know the **partition function** of the system, however complicated it may be; but the PF itself didn't lead directly to the entropy, but rather to the Helmholz free energy (F). So before going into detail we want to be sure that F can in fact give us everything!

And that follows straight from the definition $F = U - TS$. For if U, T and S change, respectively, by $\mathrm{d}U, \mathrm{d}T, \mathrm{d}S$, the corresponding change in F will be

$$\begin{aligned}
\mathrm{d}F &= \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T \\
&= \mathrm{d}U + P\mathrm{d}V - P\mathrm{d}V - T\mathrm{d}S - S\mathrm{d}T \\
&= -(T\mathrm{d}S - \mathrm{d}U - P\mathrm{d}V) - P\mathrm{d}V - S\mathrm{d}T
\end{aligned}$$

and according to (**??**) the quantity in parentheses (...) is zero in any reversible change.

For the infinitesimal quasi-static changes considered here, $\mathrm{d}F = -P\mathrm{d}V - S\mathrm{d}T$; and if V is held constant the ratio of the differentials $\mathrm{d}F$ and $\mathrm{d}T$ gives

$$S = -\left(\frac{\partial F}{\partial T}\right)_V . \tag{7.19}$$

So, to summarize: if we need the entropy itself we can always get it from the partition function, which gives the free energy F as a function of the state variables V and T. It follows that *all* the important functions of state are determined, once we know F. For example, as noted in (**??**),

$$U = F - T(\partial F)(\partial T)_V .$$

The first properties to consider in detail involve the equation of state, which – for an ideal gas – is not new to us!

The equation of state for an ideal gas

From (7.13), which gives F as a function of V and T, the pressure exerted by the gas on its container follows as the partial derivative

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{NkT}{V}\right).$$

(Note that log(const $\times V^{-1}$ is the only term in (**??** depending on volume.) The gas law follows at once as

$$PV = NkT = RT, \tag{7.20}$$

where R is the 'gas constant' and T the temperature 'on the ideal gas scale'. We have been considering N particles and the arbitrary constant k, which we put in at the beginning, is now identified as the gas constant per particle, $k = R/N$. At the same time, the equation of state (**??**) allows us to change the independent variables (T, V) to temperature and pressure (T, P), which are often more convenient.

Next, we can find an expression for the entropy S by evaluating (**??**), noting that the log-term also depends on T. The result (check it – even if it takes a bit of time!) is

$$S_{gas} = Nk\left[\frac{5}{2} + \log\left(\frac{(2\pi MkT)^{\frac{3}{2}}V}{Nh^3}\right)\right], \tag{7.21}$$

and is usually called the "Sakur-Tetrode formula". Its derivation was one of the early triumphs of the statistical approach to thermodynamics. Why was it so important? – because it showed for the first time how the entropy depended on 'non-thermal' quantities like the mass of individual molecules. It also suggested that the entropy obtained using statistical mechanics has an *absolute* value, which can be obtained even at the absolute zero of temperature by letting $T \to 0$. In general, as T approaches zero, $F \to -kT\log(g_0e^{-E_0/kT})$ (the first term in the PF) with the limiting value $-kT\log g_0 + E_0$. By comparing this with $E_0 - TS$ (E_0 being the limiting value of U it appears that

$$S \to -k\log g_0 \quad \text{for } T \to 0. \tag{7.22}$$

Here g_0 is the **degeneracy** of the lowest energy state of the whole system, so $S \to 0$ as $T \to 0$ if the lowest state is **non-degenerate**, with $g_0 = 1$. This is often described as the **Third Law of Thermodynamics**. It is important if you want to talk about processes (e.g. chemical reactions) at extremely low temperature; but, since it is the *change* ΔS that matters most, the Third Law is usually stated in the form (due to Planck)

$$\Delta S \to 0 \quad \text{for any process at } T \to 0. \tag{7.23}$$

The heat capacities, C_V and C_P, of an ideal gas

From the definitions in (**??**), both C_V and C_P can be expressed as derivatives of the entropy, which we know. Thus, from the fact that $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$, it follows that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

and, since $\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P$, it also follows that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P.$$

The formula (**??**) takes the form

$$S = Nk(\text{constant} + (3/2)\log T + \log V)$$

and the partial derivative $(\partial S/\partial T)_V$, in the expression for C_V becomes

$$(\partial S/\partial T)_V = Nk(3/2)T^{-1}$$

. which gives $C_V = (3/2)Nk = (3/2)R$ for 1 mole of gas.

To get C_P, however, we need to change the independent variables from T, V to T, P, since P is the one to be kept fixed in doing the partial differentiation. That's easy because the equation of state (**??**) tells us that $V = NkT/P$; and on substituting this value of V the entropy formula (**??** becomes

$$S = Nk(\text{constant} + (5/2)\log T - \log P).$$

Keeping the pressure fixed and differentiating with respect to T, we now find

$$(\partial S/\partial T)_P = Nk(5/2)T^{-1}$$

and this gives $C_P = (5/2)Nk = (5/2)R$ for 1 mole of gas.

The two molar heat capacities for an ideal gas are therefore quite different:

$$C_P - C_V = R. \tag{7.24}$$

This difference is important in changes that occur too rapidly to allow much heat flow to take place. This is the case when sound travels through the air, by a series of rapid compressions and expansions. Such processes are **adiabatic**, while the equation of state PV = constant applies only when T is kept constant by permitting heat flow. Under adiabatic conditions, on the other hand, the equation of state becomes PV^γ = constant, where $\gamma = C_P/C_V$. The end of the story is that the difference between the heat capacities determines the speed of sound!

Some properties of the Einstein crystal

An expression for the free energy F of a crystal containing N monatomic molecules, using Einstein's model, was given in (**??**). In the derivation it was supposed that each atom had only *vibrational* energy and that only the corresponding pf need be evaluated. But what holds the atom in place at its lattice point? Surely, in addition to the kinetic energy of vibration, there must be a *potential* energy due to its interaction with the rest of the crystal. If we call this term $-\chi$ (it must be negative because energy will have to be *added* to pull the atom out of the crystal) then the energy of the single vibrating atom will be

$$\epsilon_{n_1,n_2,n_3} = -\chi + (n_1 + n_2 + n_3 + \tfrac{3}{2})h\nu, \tag{7.25}$$

instead of (**??**). The one-particle pf, including the potential energy, will follow as before, each additive term in ϵ leading to its own multiplicative factor in the exponential. So the previous pf will be multiplied by $\exp \chi/kT$ and Z_{cryst} in (**??**) will be multiplied by $\exp N\chi/kT$, giving

$$Z_{cryst} = e^{N\chi/kT} \times e^{-\frac{3}{2}Nh\nu/kT} \times \left(\frac{e^{-\frac{1}{2}h\nu/kT}}{1 - e^{-h\nu/kT}} \right)^{3N}. \tag{7.26}$$

The corrected free energy expression will then be $F = -kT \log Z$:

$$F_{cryst} = -N\chi + \tfrac{3}{2}Nh\nu + 3NkT \log(1 - e^{-h\nu/kT})^{3N}, \tag{7.27}$$

instead of (**??**). You needn't do all that work every time! Whenever you add a term x to the one-particle energy, you need only add a term Nx to the free energy F of the whole N-particle system.

As an example of using (**??**) let's just calculate a heat capacity, C_V. This is interesting because, long ago, Dulong and Petit noticed that the molar heat capacities of many crystalline solids had constant values of about $3R$ over a wide range of temperatures, but then fell rapidly to zero at low temperature: we want to know why.

From the free energy F we can get $U = F - T(\partial F/\partial T)_V$. If you do this you should find

$$U_{cryst} = -N\chi + \tfrac{3}{2}Nh\nu + 3Nh\nu/(e^{h\nu/kT} - 1).$$

On defining $\Theta_v = h\nu/k$, which has the physical dimensions of temperature and is called a '**characteristic temperature**' for the vibrational motion, this expression takes the form

$$U_{cryst} = -N\chi + \tfrac{3}{2}Nk\Theta_v + 3Nk\Theta_v/(e^{\Theta_v/T} - 1) \tag{7.28}$$

and the heat capacity follows easily by differentiating:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3Nk(\Theta_v/T)^2 e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2} \tag{7.29}$$

– which gives you a good exercise in calculus! (And the next bit is a good exercise on limits – see Book 3 for both)

At temperatures well above the characteristic temperature $\Theta_v/T << 1$ and if you expand everything in powers of Θ_v/T you should find

$$C_V = 3Nk[1 + \text{terms of order } (\Theta_v/T)^2 \approx 3R \quad for\ \Theta_v/T << 1. \tag{7.30}$$

On the other hand, for low temperatures (Θ_v/T large), C_V rapidly falls to zero as you can show (do it!) from (**??**).

Nobody could even begin to understand such things before the middle of the last century. There's much more to do, but before ending Book 5 we'll turn back briefly to chemical reactions – which, after all, form a large part of the vast subject of Chemistry.

Exercises – to follow.

Chapter 8

Finally – back to Chemical Reactions

8.1 Defining the system and its variables

Most of chemistry is about systems containing homogeneous parts called **phases**. Each phase is usually solid, liquid, or gas; and every bit of any phase (in equilibrium) has the same properties as any other (e.g. temperature, pressure) – which is what is meant by "homogeneous". Properties of this kind, and the variables which describe them, are said to be **intensive**

The *composition* or **content** of each phase is determined by stating the *amounts* of each different chemical substance or **species** it contains: these are the **components** of the phase. For example, a container holding water (liquid), ice (solid), and water vapour (gas) is a three-phase system (not counting the container itself!), though it contains only one component, every phase being built up from water molecules alone.

In chemical reactions, where the composition of each phase may be changing, other variables will be important; especially the *amounts* of the different species in each given phase. And in this last chapter we'll begin to get a bit closer to the things that actually go on in a chemical laboratory: what makes a reaction go? – and will it continue until all all the molecules present have been used up in forming new molecules? – or will it stop long before that when lots of the reactants are still left over?

The condition of any chemical system depends on the thermodynamic variables, typically temperature (T) and pressure(P, or volume and temperature(V, T), under which every phase is kept. As we know already, these variables are not all *independent*; they may be related by an **equation of state** and it is usually enough to specify just two of them, (P, T) or (T, V), as the *independent* variables. Things are going to get more and more complicated it seems and we must go ahead step by step!

For most of the time we'll be thinking of a system with only one phase, the simplest being a gas – which we know most about. The gas need not have a fixed content; it may be a mixture in which there are a moles of substance A and b moles of a second species B, which we'll call the **reactants**, and these may be completely used up in producing the

products e.g. x moles of X and y moles of Y. In that case, as in Section 3.1, we write

$$a\mathrm{A} + b\mathrm{B} \rightarrow x\mathrm{X} + y\mathrm{Y}$$

and say the equation describes **one unit of reaction**.

Remember what this *chemical* equation means: a, b, x, y are simply numbers and the equation says that when a molecules of substance A combine with b molecules of B the result will be x molecules of X and y molecules of Y. So if these numbers are all multiplied by L (which is the number of molecules per mole) the same equation will tell you that a *moles* of A and b moles of B can react to give x and y moles of X and Y, respectively.

In Section 5.4 we introduced the thermodynamic functions H, F, G alongside the internal energy U and the entropy S. By considering how these 'state' functions change in any natural process ($\mathrm{d}S \geq 0$) it was possible to set up conditions for a system to be in equilibrium under given conditions. Thus, under constant temperature and pressure, the Gibbs free energy G would depend on variations of T and P according to $\mathrm{d}G \leq V\mathrm{d}P - S\mathrm{d}T$ and would therefore always decrease until it reached a *minimum value*.

What we have to do now is extend these ideas to systems in which a chemical reaction can take place; and to keep things as simple as possible we'll take a single-phase system, a **gas mixture**. Suppose the amounts of reactants and products, at any stage in the reaction are, respectively, $n_\mathrm{A}, n_\mathrm{B}$, ... and $n_\mathrm{X}, n_\mathrm{Y}$, ...: these numbers *have nothing to do with the a, b, x, y in the chemical equation* – they are the amounts of the various species present at the instant we're thinking of and will be changing as the reaction goes on. The *content* of the phase will be changing and we shall need to know how the thermodynamic functions depend on $n_\mathrm{A}, n_\mathrm{B}$, ... $n_\mathrm{X}, n_\mathrm{Y}$, ... How can we find this dependence?

Let's start from the internal energy U and imagine how it will grow as the system is built up from nothing by slowly adding molecules – so slowly that the system is always in equilibrium. If we put in only small amounts of heat ($q = T\mathrm{d}S$) and work ($w = -P\mathrm{d}V$) (see p.xxxx) U will increase by $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$, but now we're also adding molecules and every molecule will bring its own bit of internal energy! So in this imaginary building up process U will be constantly increasing, with

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu_\mathrm{A}\mathrm{d}n_\mathrm{A} + \mu_\mathrm{B}\mathrm{d}n_\mathrm{B} + \ ... \ + \mu_\mathrm{X}\mathrm{d}n_\mathrm{X} + \ ... \ + \mu_\mathrm{Y}\mathrm{d}n_\mathrm{Y} + \ ... \ , \qquad (8.1)$$

where the coefficients $\mu_\mathrm{A}, \mu_\mathrm{B}$, etc. (we don't yet know what they are!) will be called **chemical potentials** of the various components. All we can say is that $\mathrm{d}n_\mathrm{A}$, for example, will be doubled if we add twice as many molecules of A; so n_A will be an extensive variable. On the other hand, the coefficients μ_A etc., like T and P, will be intensive variables not depending on the *number* of A-molecules present; in general, however, they will depend on the *ratios* between the quantities (n_A, n_B, etc.), which determine the *composition* of the phase.

Now suppose that, in each tiny step, $n_\mathrm{A}, n_\mathrm{B}$, etc. are all increased in proportion to the amounts already present: so $\mathrm{d}n_\mathrm{A} = \xi n_\mathrm{A}$ etc., where ξ (the Greek letter "xi") is an infinitesimal number. The variable ξ goes from 0, at the start of the 'building-up' process, to 1 at the end. The extensive variables will all increase in a similar way, so the increases in U, S, V will be

$$\mathrm{d}U = \xi U, \quad \mathrm{d}S = \xi S, \quad \mathrm{d}V = \xi V.$$

But the intensive variables $\mu_{\mathrm{A}}, \mu_{\mathrm{B}}$, etc. will not change at all, being independent of the amounts of material, and therefore () may be re-written as

$$\xi U = T\xi S - P\xi V + \sum \mu_{\mathrm{A}} \xi n_{\mathrm{A}}.$$

All we have to do now is divide all terms by ξ and remember that $U - TS + PV = G$, the Gibbs free energy of the system. The result is then, written in full,

$$G = \mu_{\mathrm{A}} n_{\mathrm{A}} + \mu_{\mathrm{B}} n_{\mathrm{B}} + \ \dots\ + \mu_{\mathrm{X}} n_{\mathrm{X}} + \ \dots\ + \mu_{\mathrm{Y}} n_{\mathrm{Y}} + \ \dots\ . \tag{8.2}$$

–which is quite general, being true for whatever amounts, $n_{\mathrm{A}}, n_{\mathrm{B}}, \ \dots$ of the substances A,B, etc. are present. This equation shows that the chemical potential, μ_{A} say, can be looked at as the Gibbs free energy per mole of substance A: multiply it by the number of moles of A and you get the contribution of A to the total free energy G.

Equations (**??**) and (**??**) allow us to give a calculus definition of the chemical potentials: for any species A,

$$\mu_{\mathrm{A}} = \left(\frac{\partial U}{\partial n_{\mathrm{A}}}\right)_{S,V,n_{\mathrm{B}}}, \qquad \mu_{\mathrm{A}} = \left(\frac{\partial G}{\partial n_{\mathrm{A}}}\right)_{T,P,n_{\mathrm{B}}}, \tag{8.3}$$

where the n_{B} are held fixed for all other components B≠A. The second form is more useful than the first, since it is easier to keep the independent variables T, P constant, rather than S, V.

The importance of equation (**??**) lies in the fact that the value of the free energy G depends on the amounts of all the components in every phase. These amounts may be changing in any process (e.g. evaporation, chemical reaction, etc.) and the process will continue until *equilibrium* is reached when G reaches a stationary minimum value. We want to know the composition of the system when equilibrium is reached.

The physical meaning of the potentials μ_{A} etc.in (**??**) soon becomes clear if we ask how any chemical component will divide itself between two different phases, such as the *liquid* in a closed container and the vapour (*gas*) in the space above it. Molecules pass between the two phases when the liquid evaporates. If $\mathrm{d}n_A$ moles of species A pass from the liquid to the vapour the liquid-phase part of th Gibbs free energy G will change by $-\mu_{\mathrm{A}}^{(l)} \mathrm{d}n_{\mathrm{A}}$, where a label 'l' has been put on the chemical potential to show that it is for component A *in the liquid phase.* But the same amount of A has now gone into the vapour, giving an increase $\mu_{\mathrm{A}}^{(g)} \mathrm{d}n_{\mathrm{A}}$ in the gas phase. The infinitesimal increase in G for the whole system, liquid + vapour, is thus

$$\mathrm{d}G = (-\mu_{\mathrm{A}}^{(l)} + \mu_{\mathrm{A}}^{(g)})\mathrm{d}n_{\mathrm{A}}$$

. This change must be zero when G reaches a minimum value, $\mathrm{d}G = 0$. Thus, in words,

> In any natural process, at given temperature and pressure, G will decrease until the chemical potential of any species reaches the same value in different phases.

This is an extremely important property of the chemical potential.

Everything done so far in this section applies only when no chemical reaction is actually taking place!. We now have to remove that restriction, but before doing so we must know how to get the thermodynamic functions for a **mixture**, and see how they depend on the the numbers of moles of all substances present.

8.2 Ideal gas mixtures

So far, in talking about gases, we've been thinking of N non-interacting particles (atoms or molecules, all of the same kind) in a container of volume V. By "non-interacting" we mean simply that the energy E of the whole system is (in good approximation) the sum of the energies ϵ of the separate particles. This has been our 'model' of an ideal gas.

When we come to study mixtures, using the same approximations, we'll start with N_A particles of type (or *species*) A, N_B of species B, and so on, all in the same container. Because the energies of different species are taken to be additive, their PFs will be multiplicative as we saw in Section 6.4. For the mixture this means $Z = Z_A \times Z_B \times \ ...$ with one factor for each component, and this means in turn that the thermodynamic functions for the mixture will be *sums* of those for the separate components. Thus, for the case of two components,

$$F = -kT \log Z = -kT \log Z_A Z_B = -kT \log Z_A - kT \log Z_B = F_A + F_B \qquad (8.4)$$

and, as we already know, it follows that all the state functions U, H, F, G will appear as similar sums.

On specializing to an ideal gas mixture, in which N_A molecules of A, N_B molecules of B, etc. occupy the same container of volume V, there will be one equation of type (7.20) for each component:

$$P_A V = N_A kT, \quad P_B V = N_B kT, \text{ etc.,} \qquad (8.5)$$

where for example P_A is the pressure exerted by molecules of species A on the walls of the container. The total pressure P is thus the sum of the **partial pressures**,

$$\begin{aligned} P &= -(\partial F/\partial V)_T = P_A + P_B + \ ... \\ &= N_A(kT/V) + N_B(kT/V) + \ ... \ = NkT/V, \end{aligned}$$

where $N = N_A + N_B + \ ...$ is simply the total number of molecules. This result is usually known as **Dalton's law**. The mixture thus has the same equation of state as a gas of one component alone with the same total number of particles.

Usually we express quantities in terms of the mole (Section 1.1), multiplying numbers of molecules by Avogadro's number L, so that the gas law appears in the form (**??**), namely

$$PV = RT, \text{ (1 mole,} \quad PV = nRT, \text{ (}n\text{moles).}$$

From now on we'll nearly always use moles in talking about the amounts of stuff we're dealing with.

8.3 Chemical reactions

To get a first idea of what can happpen as a system proceeds towards equilibrium – where everything stops – let's go back to simple reactions of the kind we talked about in Chapter 3, taking the case

$$a\mathrm{A} + b\mathrm{B} \rightarrow\ x\mathrm{X} + y\mathrm{Y}\ .$$

In words, a moles of a pure substance A react with b moles of B to give x moles of X and y moles of Y.

In going from reactants, on the left, to products on the right, we'll be interested in two kinds of change in the free energy G:

(i) ΔG_r, the change for one unit of reaction, in which the reactants are completely converted into the products with nothing else left over, calculated as the increase

$$\Delta G_r = xG_X + yG_Y - aG_A - bG_B$$

(final values minus initial); and

(ii) dG, the infinitesimal change of G when $n_A \rightarrow n_A + \mathrm{d}n_A$, etc. at any stage during the course of the reaction. Since the dns must always stay in the same ratio $a : b : x : y$ they can be written as

$$\mathrm{d}n_A = \xi a,\ \mathrm{d}n_B = \xi b,\ \mathrm{d}n_X = \xi x,\ \mathrm{d}n_Y = \xi y$$

and therefore, from (**??**),

$$\mathrm{d}G = \xi x G_X + \xi y G_Y - \xi a G_A - \xi b G_B = \xi \Delta G_r.$$

The variable ξ, first used in deriving (**??**), here measures "how far the reaction has gone": it is the **extent of the reaction**.

What's the difference between the changes in (i) and (ii) – which look very similar? In (i) ΔG_r is the difference of G between the beginning and end of 1 unit of reaction, the reactants A and B (initially present in proportions $a : b$) being used up. But in (ii) we're talking about one tiny step during the reaction; and in any natural change the steps won't even be reversible – the next step may never happen, for that will depend on dG! In getting equation (**??**), we supposed the system was built up *reversibly* and the differential changes could be integrated to give the final composition of the system, when ξ has gone from 0 to 1. But in (ii) we're completely at sea, not knowing even the composition of the system at any given instant! All we do know is that the G-values for 1 mole of pure substance, at the given temperature and pressure, provide the *chemical potentials*. So dG in (ii) can be written as

$$\mathrm{d}G = \xi(x\mu_X + y\mu_Y - a\mu_A - b\mu_B) = \xi \Delta G_r. \qquad (8.6)$$

And this is all we need. If dG is negative, going 'downhill', the reaction will continue and the composition (indicated by n_A, n_B, n_X, n_Y) will go on changing; if it is zero then equilibrium has been reached and the reaction will stop; beyond that,the reaction will not go unless the conditions are changed.

There are three possible cases, which can be shown graphically by plotting G given in (**??**) – the whole free energy, not just the differential change dG – during the whole course of the reaction. These are indicated in Fig.23: in the first case (Fig.23a) G goes smoothly down from the inital state on the left, where "R" stands for reactants (*in whatever amounts they may be present*), to a 'final' state (labelled 'P' for products) on the right. Here the equilibrium state occurs when a whole unit of reaction has taken place, even if some of the pure substances remain.

In the second case (Fig.23b) G reaches a minimum *before* the reactants are fully used up, the position of the minimum depending only on the values of $n_{\rm A}, n_{\rm B}, n_{\rm X}, n_{\rm Y}$, even though ΔG_r for 1 unit of reaction is negative.

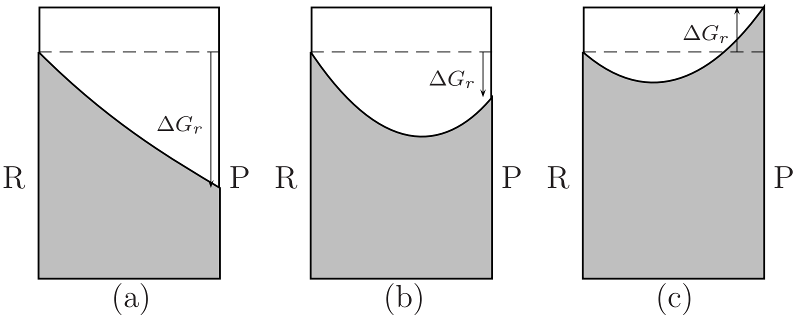


Figure 23. Variation of G in a reaction
Here "R" and "P" stand for Reactants and Products.
The reaction goes from R towards P.

In the third case (Fig.23c) G reaches a minimum soon after the start of the reaction; but this is remarkable because ΔG in this case is large and *positive* and at first sight the reaction looks as if it wouldn't go at all!

Evidently, then, a reaction will go even when complete conversion of reactants into products would suggest it was impossible – provided the quantities of reactants and the values of T and P are well chosen. What we must do now is find *how far* a reaction will go, depending on the conditions, before reaching equilibrium.

8.4 The equilibrium constant. Activities

In Section 3.2 it was found useful to define *standard state* quantities, such as $H^\circ_{\rm A}$ for the heat content of 1 mole of substance A under standard conditions (e.g. $T = 298K = T^\circ$, $P = 1$ atmosphere $= P^\circ$). Since thermodynamic functions are *functions of state* their values depend only on how the state is specified (Section 8.1) and not on how it was reached: they can be listed in Tables and used whenever they are needed. Thus heats of reaction, ΔH for a reaction $a{\rm A} + b{\rm B} \rightarrow\ x{\rm X} + y{\rm Y}$ could be found easily from Tables of *heats of formation*, ΔH_A etc., for the substances involved (formed under the same standard conditions).

The same is true for entropies and free energies and their changes in any given reaction. Thus, the entropy of 1 mole of substance A, under standard conditions can be denoted by

S°_A and calculated from Tables of similar quantities for its atomic constituents. Since we usually need values for given non-standard states, we must know how to get them: but that's not difficult. Suppose we have $G(T^\circ, P^\circ)$ for any substance, at standard temperature and pressure, and want to know the effect of changing the pressure at which a reaction $a\text{A} + b\text{B} \rightarrow\ x\text{X} + y\text{Y}$ is taking place. This means we need to know how G will change, for all the reactants and products, as the pressure changes from P° to the given pressure P. Now from (**??**) we know that for infinitesimal changes dT and dP (which, as usual, we imagine carried out reversibly) any G will change according to $\text{d}G = V\text{d}P - S\text{d}T$. So if we're working at constant temperature $T = T^\circ$ the only change to consider is $\text{d}G = V\text{d}P$. Any *finite* change $\Delta G = G(P_i) - G(P_f)$,from initial pressure P_i to final pressure P_f, can then be found as a definite integral (Chapter 4 of Book 3): thus,

$$\Delta G = G(P_f) - G(P_i) = \int_{P_i}^{P_f} V(P)\text{d}P, \tag{8.7}$$

where, for fixed temperature (and quantity of stuff!), V depends only on the pressure.

This is a very useful and general equation. For liquids and solids, for example, the volume usually changes hardly at all for any reasonable change of pressure: liquids and solids are almost incompressible. For a gas, however, the change may be large and to get it we need the **equation of state**. For 1 mole of an ideal gas, for example, this is given in (**??**): $PV = RT$ and on putting this in the last equation we find

$$G(P_f) - G(P_i) = RT \int_{P_i}^{P_f} (1/P)\text{d}P = RT \log(P_f - P_i),$$

where we've used the standard form (3.28) in Book 3, with upper and lower limits P_f and P_i in the definite integral. Finally, this result gives us what we need;

$$G(P_f) = G(P_i) + RT \log(P_f/P_i). \tag{8.8}$$

Now we can come back to the study of chemical equilibrium in an ideal gas reaction, remembering that the Gibbs free energy G_A for 1 mole of pure substance A is the *chemical potential* μ_A and that the pressure exerted by this component is its *partial* pressure P_A. Thus, writing $\mu_A = \mu^\circ_A + \log(P_A/P^\circ)$ for each component in equation (**??**), the condition for equilibrium $\text{d}G = 0$ becomes

$$\begin{aligned}\text{d}G = (x\mu_X + y\mu_Y - a\mu_A - b\mu_B)& \\ = \ & (x\mu^\circ_X + y\mu^\circ_Y - a\mu^\circ_A - b\mu^\circ_B) \\ & + RT(x\log(P_X/P^\circ_X) + y\log(P_Y/P^\circ_Y) - a\log(P_A/P^\circ_A) - b\log(P_B/P^\circ_B)) \\ = \ & 0.\end{aligned}$$

The first term in dG is just ΔG°_r, the free energy change for one unit of reaction under standard conditions. The remaining terms can be written more neatly as

$$RT \log \left[\frac{(P_X/P^\circ)^x (P_Y/P^\circ)^y}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \right]$$

–as you can verify if you use the rules for logarithms, which you learnt in Book 3. (Do it!)

In summary, then, on putting

$$K_p = \left[\frac{(P_X/P^\circ)^x (P_Y/P^\circ)^y}{(P_A/P^\circ)^a (P_B/P^\circ)^b} \right], \tag{8.9}$$

the equation which determines the partial pressures of all components, at any stage in the reaction, will become

$$RT \log K_p = -\Delta G_r^\circ. \tag{8.10}$$

The quantity K_p in (**??**) is called the (pressure-defined) **equilibrium constant** for an ideal gas reaction and applies for any number of gases, provided factors are added in the numerator and denominator, one for every species present. The last two equations are thus very general and – in one form or another – appear in all parts of chemistry. They have been derived for reactions of ideal gases; but they give us a 'framework' for dealing with real substances of all kinds. The changes to be made in going from ideal to real substances are often surprisingly small. To show *how* small we'll finish the chapter by mentioning **activities**, which provide the last generalization.

Activity

In getting the key equations (**??**) and (**??**), we used the chemical potentials for ideal gases, written in terms of partial pressures according to $\mu_A = \mu_A^\circ + RT \log(P_A/P^\circ)$ for each gas present. But there was no need to do so! Instead we could introduce a new quantity, related to μ by $\mu = RT \log \lambda$: the μs for *real* gases would then be related to those at standard external pressure P° by

$$\mu_A - \mu_A^\circ = RT \log \lambda_A - RT \log \lambda_A^\circ = RT \log(\lambda_A/\lambda_A^\circ$$

– which looks very similar to the previous equation and becomes exactly the same if we change the partial pressure ratio to an *activity* ratio. In fact, using the **absolute activity** λ_A for each substance is just a trick to make all our equations look like those for ideal gases, which we know so well! We can do without it, using only the chemical potentials, but it gives us a convenient way of describing the effect of *deviations* from ideal behaviour – even though we may need to use *experimental* data to find the numerical values of the activities. (Think about how you might do this, remembering that $G = H - TS$ and looking again at Section 3.2)

Looking back –

This has probably been the toughest book in the Series! Once again, you started without knowing anything much about the subject it presents – Chemistry. But with a good background in Mathematics and Physics (from Books 1-4) it's been possible to start from the very bottom of Chemistry, which is the part closest to Physics, and to build up to a general understanding of a very large part of the subject.

- We began, in Chapter 1, by reviewing the picture gradually put together over many hundreds of years in answering the question "What is everything made of?" It's now known that everything around us is built up from vast numbers of tiny **atoms**, of which there are over 90 different kinds all with their own masses and other properties, called the **chemical elements**. They appear in millions of different structures, called **molecules**, some containing only a few atoms, others (like some of the ones in our bodies) containing thousands.

  You learnt something about the structures studied in different parts of chemistry, from small molecules to giant crystals and metals, and about the **states of matter** – gases, liquids, and solids.

- Chapter 2 started with a simple 'model' of the simplest state – the **ideal gas**, in which N particles are bouncing about in a container and (as Physics tells us) produce a **pressure** on its walls. We were able to get an **equation of state**, pressure × volume = constant. Then we found that the value of the 'constant' depended on how 'hot' the system was: and this led us to the idea of **temperature** and temperature **scales**. Three variables now go into the equation of state, Pressure (P), Volume (V) and temperature (T); and they're all related – each depends on the other two. This connects you with Book 3, and you're away!

- In Chapter 3 we moved into the chemistry of **reactions** and studied the energy changes that take place when 'old' molecules (the **reactants**) come together to form new ones (the **products**). When **heat** is taken into account as a form of **energy** the principle of energy conservation (Book 4) becomes the **First Law of Thermodynamics**. This takes care of temperature changes, which could be left out in much of Physics, but are an essential part of Chemistry.

  You learnt how to work with **heats of reaction** and how important they are is studying the environment.

- You already know something about **probability**: Chapter 4 puts the idea on a mathematical basis, in the context of the ideal gas, asking about the probability of finding a gas molecule with velocity component v_x in the range v_x to $v_x + \mathrm{d}v_x$. The answer is given in terms of two important **distribution functions**, that of Gauss and that of Maxwell. We found both of them in a very simple way. They gave us the key to finding other properties of the ideal gas e.g. the average speed of a gas molecule and how it will depend on temperature.

- Chapters 5 and 6 are perhaps the most important in Book 5. In Chapter 5, various **processes** were studied e.g. gas in a container, undergoing a **cycle** of changes in which temperature and pressure are slowly varied until the system finally comes back to the starting point (T, P). The internal energy U, keeps is value for any cycle of changes. It is a **function of state**. The total intake of heat (Σq) and the work done on the gas (Σw) depend on the path taken, *not* only on the final values of T and P: they are *not* functions of state. But in the same cycle of changes $\Sigma(q/T)$ *is* path independent: it is a function of state, like the internal energy U and is called the **entropy**. We studied its properties and found that all natural processes (those that go 'by themselves') lead to **entropy increase**. And we found other functions, such as $G = U + PV - TS$ (the **Gibbs free energy**) which tell us how things will change in going towards **equilibrium** – where everything stops changing.

- Chapter 6 explains all these mysterious things in terms of what is happening *at the level of the molecules*! It leads into **statistical thermodynamics**, where things are seen to happen as they do because the **probability** of anything else happening is almost zero! We had to borrow a few new ideas, from quantum theory, but they could all be stated in words as simple principles. And you had to discover some new mathematical techniques to find what came out from those principles.

  The first thing to come out was a **formula for the entropy**: in words, S is the logarithm of the 'number of possible ways of dividing out the total energy E' of the system you have in mind. As an equation, $S = k \log g_E$ – which couldn't look simpler! But how do you *count* that number g_E ? It took a whole chapter and a lot of hard work to solve that problem and to find two ways of going from probabilities to thermodynamics, with all its ideas about temperature, functions of state, and so on. But we got there in the end.

- The second way of getting the entropy (in Chapter 6) involved another fundamental quantity, the **partition function**: this leads *directly* to all the thermodynamic functions you need. But it's quite hard to evaluate, even for idealized models of gases and crystals. Chapter 7 shows how it can be done in the simplest cases, leading to expressions for properties that can be measured in the laboratory.

- Chapter 8 came back to **chemical reactions**, where you may want to know exactly what can happen if you have n_A moles of a substance A and n_B moles of B and you let them react to give the products, X and Y say. Will all of A and B be used up? Or will **equilibrium** be reached before that happens? and how much of X and Y will be produced. Such questions are answered once you know the **equilibrium constant** for the reaction. This Chapter showed how to get constants of this kind from standard **Gibbs free energies** of the substances involved.

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