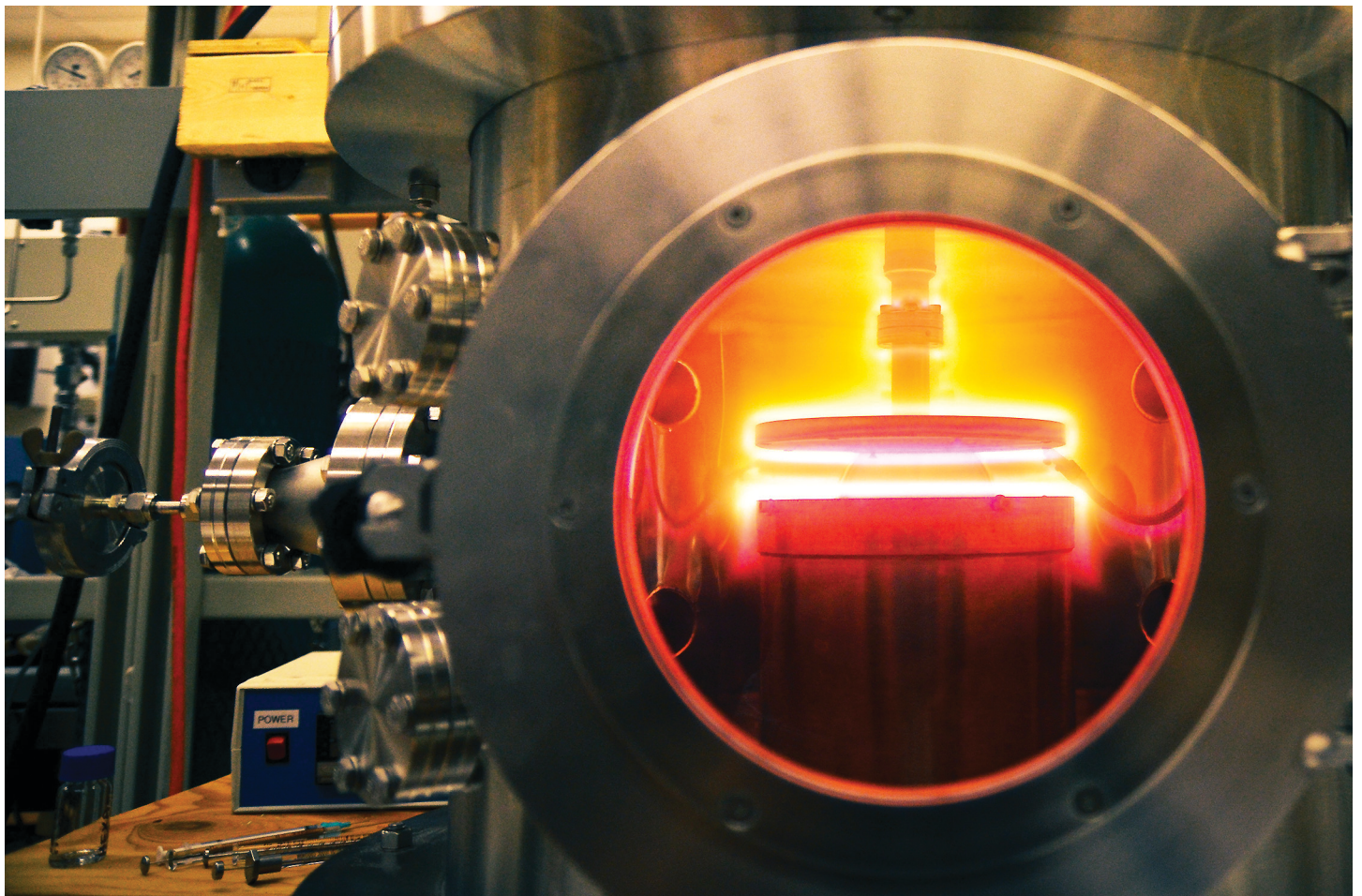


# Engineering: The challenge of temperature



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# Introduction

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In this course we examine one factor that very often seems to be found skulking around close to problems and solutions: temperature.

Almost whatever we do, wherever we are, temperature changes. Stay in the same spot and you'll find daytime and night-time temperatures can be markedly different. You may even find significant changes in temperature during the day. When moving you can encounter more rapid variations. For example, an aircraft might leave a tropical runway where the air temperature is thirty degrees Celsius and climb within minutes to a height where the outside temperature is minus fifty degrees.

It turns out that almost all the properties of a material change with temperature. So, anything you make will to some extent be sensitive to temperature. That sensitivity needs to be known about. 'What if the temperature changes?' is an excellent prompt for engineers.

There are advantages and disadvantages to thermal sensitivity and some of these are explored in here. On the one hand, we can do amazing things with thermal energy, such as moving matter around within a solid without risking melting or changing the basic shape of a component. On the other hand, it can be a real nuisance. It can make magnetic disks 'forget'. It can leave materials 'sapped' of their strength. Just a few degrees of temperature change can make some things unrecognisably different. Temperature really does present a universal challenge that must be faced – ignore it at your peril.

This OpenLearn course provides a sample of level 2 study in [Engineering](#).

# Learning Outcomes

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After studying this course, you should be able to:

- relate the temperature of a solid to the mean kinetic energy of its atoms
- use models for thermally induced effects that involve linear, exponential and step changes
- use exponentials, logarithms and graphical methods to interpret data from a thermally activated process in terms of Arrhenius's law
- identify the changes of phase taking place in a variety of critical phenomena
- provide examples of gradual, accelerating and sudden changes in the properties of materials that accompany changes in temperature.

# 1 Temperature – problem or solution?

'Have you taken the temperature effects into account?' ([Figure 1](#)) is nearly always a valid question in any discussion about a proposed engineering solution. Everything has a temperature, and everything behaves differently at different temperatures. It therefore deserves its own special place.

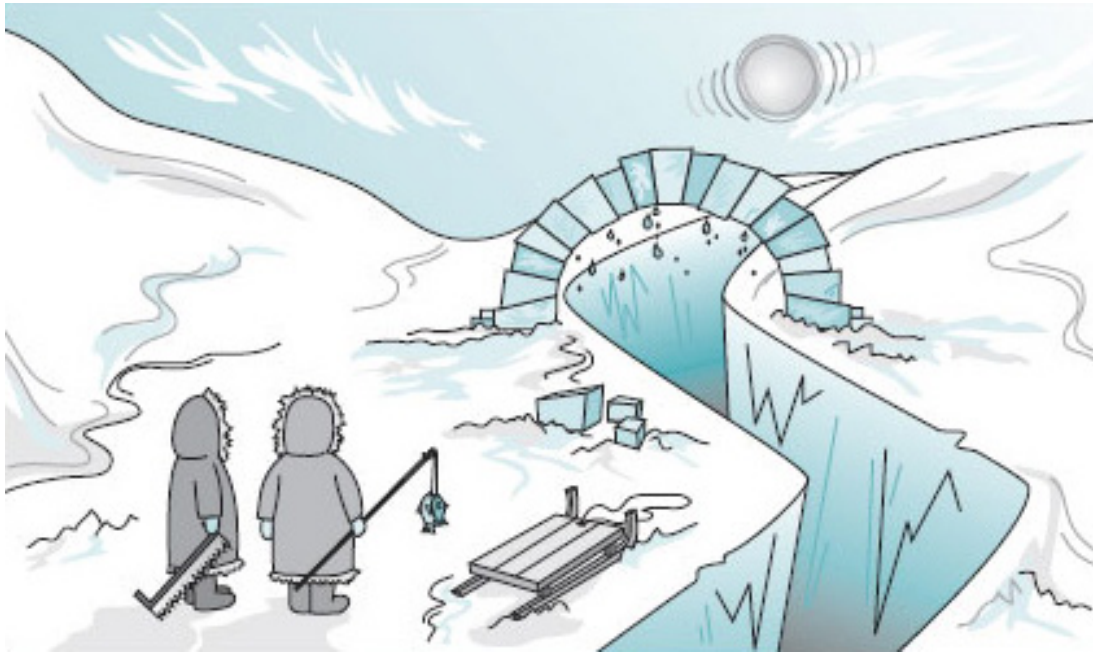


Figure 1 'Have you taken the temperature effects in to account?'

Almost whatever we do, wherever we are, the temperature changes. Stay in the same spot and you'll find the daytime temperature can be markedly different from that at night; you may even find a variation from hour to hour as weather systems move through, or heating systems fail. Moving around is not necessarily any better, and can expose us to even wider ranges of temperature. An airliner may leave the ground where the temperature is in the high twenties Celsius and climb within minutes to a height where the outside temperature is minus fifty.

It turns out that almost all materials properties change with temperature. So, anything you make will to some extent be sensitive to temperature and may well be acting (inadvertently) as some kind of thermometer.

There are advantages and disadvantages to thermal sensitivity. On the one hand we can do amazing things with thermal energy such as using it to fly without an engine (I'm thinking of gliders) or to move the matter within a solid without necessarily changing its shape or melting it. The latter is used to great effect in manipulating the properties of steels, glasses and semiconductors. On the other hand, thermal energy can be a real nuisance. It can make magnetic disks 'forget' recorded data, and it can cause joints to become loose or unstuck.

The relationships between various material properties and temperature do not all follow the same trends, and there are intriguing reasons for this that we will take this opportunity to examine. We shall also be looking at the practical implications of these different kinds of

relationship by working through a real-world engineering problem. This will exercise your mathematical abilities and, I hope, convince you of the usefulness of mathematical modelling.

## 2 Getting into hot water

### 2.1 Boiling water

Whether it's to wash clothes, make a cup of tea, or just make it safe to drink, water often has to be heated – sometimes to boiling point. There are many ways to do this, but a very common means is some form of electric water-boiler, such as a kettle or an urn. In all but the crudest ones, a device is fitted to ensure that heating does not continue once the boiling point of water is reached.

In deciding on the type and design of such a device, we can suppose that a company manufacturing electric water-boilers would have gone through a process similar to the solution-finding methods described in OpenLearn course T207\_1 *The engineer as problem-solver: the nature of problems*. Recalling from there the diagram of the decision-making route (which is attached below for ease of reference), the *need* is for electric water-boilers that have a device fitted to ensure that the water does not continue to be heated once it has reached boiling point.

Click on the 'view document' link below to view the diagram of a decision-making route  
[View document](#)

The next step is to think more deeply about the need and decide whether there is more to it than this. For example, it has been taken for granted that the need is for this device to work by itself. In other words, we would not be satisfied with a whistle that merely reports that the water is now boiling. So to make this part of the need explicit, the statement can be modified to say that the device must cut off the power automatically once the water has boiled ([Figure 2](#)).



Figure 2 Two common types of water-boiler with thermal cut-outs – an urn and a kettle

### Example 1

List five other aspects of the device that could be included to further define the need.

#### Answer

My list looks like this. It's already more than five items, and with a bit more thought it could be lengthened. You may have thought of some of these additional items.

- The device should work by cutting off the current.
- It should be triggered accurately near the boiling temperature.
- It should be re-settable once triggered (i.e. no irreversible changes).
- It should be reliable.
- It should be robust enough to work repeatedly over a long time without requiring maintenance, adjustment, or replacement of any parts.
- It should be cheap.
- It should be small enough not to add significantly to the size of the boiler.
- It should be easy to use.

Our responses to the preceding example begin to give a fairly detailed picture of the essential features of the solution being sought. Parts of the list can already be grouped together and called a *functional specification*. This includes such items as whether or not the device should be re-settable. If it *is* to be, this can be further defined by stating whether the re-setting is to be automatic or manual. If automatic, once the water has boiled, it would be allowed to cool by only a certain amount before the power is re-applied (i.e. a thermostat). If manual, it would let the water cool right down again (i.e. a cut-out). Such questions can only be answered by referring back to the final user, and are one reason for the existence of marketing departments.

The functional specification so far just itemises what the solution should do, but it says little about how *well* it should do it. To make the specification a true yardstick against which the solution can be measured, we need to quantify things.

With numbers against each quantifiable item on the functional list, it becomes a *performance specification*. It may state, for instance, that the device must operate when the water reaches a temperature within the range 97 °C to 100 °C. Much of this information again comes from the user, and it is surprising how flexible and arbitrary many of these numbers can be. For instance, thermometers for the control of domestic ovens could be specified with an accuracy of  $\pm 0.1$  °C of reading, and I daresay you'll find someone who'll install one and charge accordingly, but  $\pm 5$  °C is good enough. Specifications should be prepared and read very carefully, because it is not always easy to distinguish between the 'wish list' or 'guesstimate' numbers and those which really must not be exceeded. The example of the operating temperature of a water-boiler serves to illustrate the point: the 97 °C figure is more flexible than the 100 °C. If the lower limit were reduced to, say, 92 °C, the result would merely be water a little further below boiling point than otherwise. If, however, the upper limit were relaxed to 105 °C, the device may never be triggered as the water will boil away before it reaches that temperature, rendering it (and eventually the boiler itself) useless.

Armed with this quantitative data, the time has come to generate some ideas. But wait! The engineers can't do this without having in their heads a store of knowledge and understanding of how things work. A mark of a really good engineer is an interest in a wide range of technologies and sciences. This enables them to draw analogies, to

transfer ideas from one context to another, and to make rapid but accurate predictions of what will and won't work. It is this kind of holistic approach that enables the innovations by context covered in OpenLearn course T207\_1 *The engineer as problem-solver: the nature of problems* to come about. For the water-boiler device, what is essential is knowledge of how temperature affects different materials and material properties. From this we can begin to propose effects to be exploited in a thermal cut-out.

I want to rule out the use of the approach of using a *routine solution* at this stage. Of course one could just find a catalogue or website that lists thermal switches that are already on the market. Instead, I am encouraging an *innovative* approach – and that calls for a deeper knowledge of the effects of temperature.

In Sections 3, 4 and 5, we'll look at temperature effects in detail. Afterwards you will find yourself equipped not only to produce more ideas when you return to the water-boiler, but also to take the next step of evaluating these ideas in terms of their appropriateness for this application.

## 2.2 Thermal effects in outline

Temperature is, of course, the measure of 'thermal' conditions. Nowadays it is measured by thermometers and expressed as a number on an agreed scale. Some features of thermometers and of their use are discussed in **Thermometers and process control**

The *theoretical construct* of temperature relates it to the kinetic energies of atoms. This gives clear insights into the way temperature affects the behaviour of materials. Energy is given to things to make them hot and taken from things to make them cold. Within solid matter, thermal energy is stored primarily in the kinetic energy of atoms. So, when we say that a particular object or substance has a certain temperature, we are in fact quantifying the amount of kinetic energy possessed by the atoms of that object or substance – see Box 1 Temperature and energy. To say that temperature is 'that which is measured by a thermometer' does not provide a definition which helps an understanding at the atomic scale.

### Box 1 Thermometers and process control

Measuring temperature is not quite like measuring length with a ruler, where the length to be determined is compared with the length of the ruler. Thermometers convert the condition of temperature into other physical things, such as a resistance, voltage or pressure; we say they are temperature *transducers*. The temperature 'reading' is really a graduated indication of one of those other physical quantities. It is not very useful until the instrument has been calibrated against a defined numerical scale of temperature.

Here are some effects by which temperature is sensed and given number:

- expansion of a liquid in a tube, often mercury in glass
- resistance of a metal wire, platinum in good instruments
- voltage output from a thermocouple, that is, the junction between wires of two different metals
- pressure of a constant mass of gas kept at constant volume
- brightness or colour of radiation emitted by a glowing furnace.

Industrial processes may require a steady or changing temperature. Changes may be spatial or temporal. Temperature may be tightly controlled by using a thermometer as the sensor in a feedback loop. On the other hand, if it is simply necessary to know whether the temperature is high enough for a process to work, or low enough for safety, the thermometer may merely monitor conditions or be coupled to an alarm to indicate when a threshold has been crossed. With such a diversity of uses, accuracy may not be the paramount virtue of a thermometer. Any of the following features may be of particular relevance for certain applications:

- **Accuracy:** A thermometer will agree with the International Temperature Scale to a specified precision and will have been calibrated between some standard temperatures.
- **Range:** The instrument must be able to give readings at the process temperature. For example, below  $-38\text{ }^{\circ}\text{C}$  and above  $360\text{ }^{\circ}\text{C}$  a mercury-in-glass thermometer is useless. Radiation pyrometers are used to measure high temperatures.
- **Sensitivity:** A process may need close control of temperature or need to be tolerant of some deviation. Close control needs a sensitive thermometer, that is one giving noticeable response to a small change in temperature.
- **Response time:** A long response time means that short, sharp fluctuations of temperature are averaged out.
- **Repeatability:** Actual values may be less important than that successive batches of a process get the same treatment.
- **Reliability:** A malfunctioning instrument might close down the plant.
- **Corrosion-proofing:** Furnace atmospheres can be very reactive chemically; the thermometer sensor may have to be protected by a ceramic sheath, which will slow its response.
- **Output:** Telemetry of signals to a central control point favours thermometers with electrical output.
- **Compatibility:** May need to be compatible with other instrumentation.
- **Cost:** Cost per unit, or total cost of manufacturing, is almost always a consideration.

### Exercise 1

In a mercury-in-glass thermometer, the length of a narrow column of mercury is measured. Explain how this is related to the local air temperature.

#### Answer

The mercury in a mercury-in-glass thermometer is presumed to be at the same temperature as the air that surrounds it. Changes in temperature lead to expansion of the mercury within the tube that encloses it – the tube is thick-walled, but the mercury can expand or contract along the length of the tube.

## Box 2 Temperature and energys

How much thermal energy is associated with a given temperature? At this stage I just want to show you how to translate the *absolute temperature* of a substance,  $T$  in kelvin into the

average energy, in joules, associated with the random motions of one of its particles. The link between energy and temperature will be discussed further in [Section 4](#).

The conversion factor that links joules to kelvin is one of the basic physical constants that was established in the nineteenth century. Named in honour of one of the pioneers of the field, Boltzmann's constant has the symbol  $k$  and the value of  $1.38 \times 10^{-23} \text{ J K}^{-1}$ .

Boltzmann's constant multiplied by absolute temperature ( $kT$ ) gives the average kinetic energy of a particle in a substance that is at temperature  $T$ .

Consider room temperature, say 300 K. The average energy of particles in a substance at 300 K is:

$$kT = 1.38 \times 10^{-23} \times 300 \text{ J} = 4.14 \times 10^{-21} \text{ J}$$

That's an inconveniently small number, and there are two ways to get something more useful from it.

The first is to consider a large number of particles, say a mole, instead of just one. In that case a mole of particles at room temperature consists of  $6.023 \times 10^{23}$  particles with an average energy of  $4.14 \times 10^{-21} \text{ J}$ .

A mole is a special quantity of a substance, measured in terms of the number of constituent particles (atoms or molecules), namely  $6.023 \times 10^{23}$  particles. One gram of hydrogen contains this number of atoms.

That means that at room temperature we can expect thermal energy to amount to

$$6.023 \times 10^{23} \times 4.14 \times 10^{-21} = 2.5 \text{ kJ per mole of particles}$$

For comparison, you can put 2.5 kJ of energy into a small rechargeable battery, so I feel comfortable with that measure.

The other way to get a more meaningful description of thermal energy is to convert from joules to a unit more in tune with the energy of bonds between atoms. Such a unit is the electron volt (or eV) and you get it by dividing the value in joules by the electronic charge,  $e$ , another fundamental physical constant.

In terms of electron volts, 300 K works out as:

$$\frac{kT}{e} = \frac{1.38 \times 10^{-23} \times 300}{1.6 \times 10^{-19}} = 0.026 \text{ eV per particle}$$

or about one-fortieth of an electron volt. Electron volts are convenient for measuring the energy binding individual atoms together – typically a few eV per pair of atoms – so at room temperature an atom in a solid with the average energy does not have enough energy to break free of its bonds.

You can build your confidence with this kind of conversion by doing the next exercise.

## Exercise 2

Complete the following table that connects temperature with thermal energy in eV particle<sup>-1</sup> and kJ mole<sup>-1</sup>.

**Table 1**

T/K	Average energy / eV particle <sup>-1</sup>	Average energy / kJ mole <sup>-1</sup>
300	0.026	2.5
1000	1	
		300

**Answer****Table 2**

T/K	Average energy / eV particle <sup>-1</sup>	Average energy / kJ mole <sup>-1</sup>
300	0.026	2.5
1000	$kT/e = 0.086$	$6.023 \times 10^{23} \times kT = 8.31$
11600	1	$6.023 \times 10^{23} \times kT = 96.4$
36100	$kT/e = 3.11$	300

**SAQ 1**

Calculate the temperature of a solid in which the atoms have an average energy of 0.13 eV.

**Answer**

Since 300 K corresponds with an average energy per atom of 0.026 eV, an average energy of 0.13 eV, some 5 times higher, will correspond with an absolute temperature that is also 5 times higher, namely 1500 K.

Alternatively, working from first principles,

$$\frac{kT}{e} = \text{energy in eV}$$

$$\frac{1.38 \times 10^{-23} \times T}{1.6 \times 10^{-19}} = 0.13 \text{ eV}$$

Rearranging,

$$T = \frac{1.6 \times 10^{-19} \times 0.13}{1.38 \times 10^{-23}} = 1507 \text{ K}$$

## 2.3 How things change with temperature

The temperature-dependent effects used in most thermometers have a fairly steady change over a good range of temperature ([Figure 3a](#)). By contrast, phase changes, of which melting and boiling are the common examples, happen at sharply critical temperatures ([Figure 3c](#)): at +1 °C your dahlias will survive, at -1 °C they are dead of frostbite.

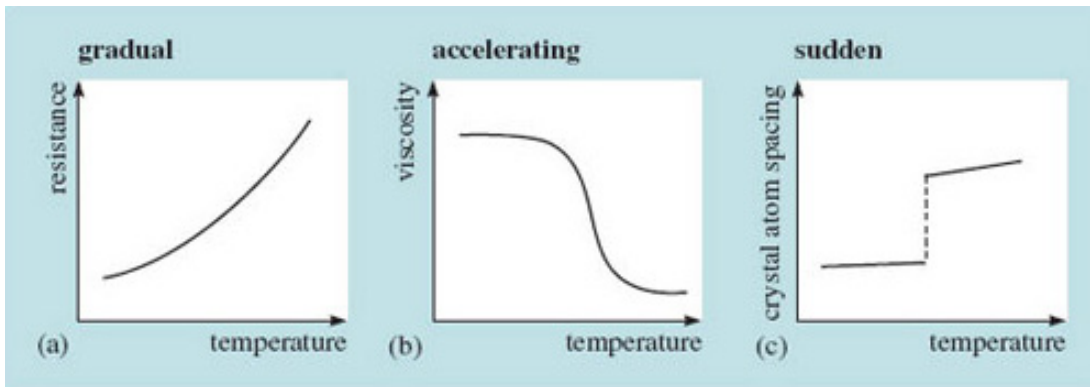


Figure 3 Changes with temperature: (a) gradual, (b) accelerating, (c) sudden

Between these extremes of gradual and sudden change are temperature-sensitive phenomena which accelerate from insignificance to drama over a narrow but finite temperature range. Examples are the rates of many chemical reactions, and the electrical conductivity of semiconductors. [Figure 3\(b\)](#) illustrates one of these and, although it will not always be obvious whether to regard a particular change as 'gradual', 'accelerating' or 'sudden', we shall find the theoretical models for each category to be sharply distinct.

Notice that the horizontal axis in [Figure 3](#) is temperature, not time. These graphs show how a material property depends on its temperature. There is nothing here about how quickly the temperature is changing. For instance, you could thaw ice by bringing the temperature up very slowly, and it would still all turn to water at 0 °C, and this would still be classed as a 'sudden' change, because it is how the property changes as you move along the temperature axis that is being described.

- *Gradual* changes are modelled in terms of the *average* thermal energy of the particles of the system. During a *gradual* change (of a property with temperature) doubling the change of temperature, say up ten degrees rather than up five degrees, will change the property by a factor of two or so (twice as big a change or half as small a change).
- *Accelerating* changes are modelled in terms of the *fraction* of the particles that have much higher than average thermal energy. During an *accelerating* change (of a property with temperature) the rate of change of the property varies with temperature.
- *Sudden* changes are modelled in terms of the *balance* between disorder generated by the vibration of atoms and order induced by inter-particle forces. During a *sudden* change (of a property with temperature) exceeding some critical temperature,  $T_{crit}$ , is what triggers the change.

Because the models differ, our ideas about influencing and exploiting each sort of behaviour differ. We need to understand these behaviours because, within each category, there are 'opportunities' and 'challenges', from both the service and process points of view.

Before moving on to Section 3, have a go at Exercise 3 in the next section to reinforce your ideas on gradual, accelerating and sudden temperature changes.

## 2.4 Summary of Section 2

- Thermometers sense temperature. They are transducers providing observable and quantifiable signals in variables other than temperature. Thermometers are calibrated to give numbers in accord with an internationally agreed scale. Various attributes influence the selection of an instrument for a task.
- Temperature can determine the rate at which certain physical and chemical changes proceed, and whether some changes can occur at all.
- Distinct modelling patterns characterise gradual, accelerating or sudden property variation with temperature.

### Exercise 3

Here is a list of 12 items to fit into [Table 3](#) as the opportunities or challenges labelled A to L. The list probably contains some terminology and many ideas that are unfamiliar. I don't expect that you will be able to recognise and match them all, so try to place at least one in each of the categories – gradual, accelerating and sudden.

1. Creep deformation (slow change in shape of a material under stress)
2. Homogenisation of castings (reduction of non-uniformity of composition)
3. Glass shattering under thermal shock
4. Convection in a domestic water system
5. Quenching (sudden cooling from high temperature) and tempering (re-heating to a moderate temperature to allow regrowth of crystals and thereby improve ductility) of steel
6. The temperature dependence of resistivity demands highly uniform cross-section of a lamp filament
7. p–n junctions (regions in a semiconductor where differently doped regions meet) are stable against homogenisation (don't intermix) at room temperature
8. Fuses in electrical circuits
9. Superconducting transitions are all at inconveniently low temperatures (so far!)
10. Provision of surface compressive stress enables 'safety glass' for car windows
11. Onset of unwanted reactions in chemical processes
12. Silicon melts at 1414 °C, so diffusion of dopants to control semiconducting properties cannot be done at arbitrarily high temperatures.

### Answer

1. Creep deformation – it is thermally activated, so it's an accelerating change that is a challenge in service: **E**.
2. Homogenisation of castings – a processing opportunity that is thermally activated (accelerating): **H**.
3. Glass shattering under thermal shock – a thermal expansion challenge (gradual) during service: **D**.
4. Convection in a domestic water system – this is related to thermal expansion (gradual) in service and it represents an opportunity: **A**.

5. Quenching and tempering of steel – a sudden change that offers a processing opportunity: **I**.
6. The temperature dependence of resistivity demands highly uniform cross-section of lamp filament – a processing challenge relating to a gradually changing property: **J**.
7. p–n junctions are stable against homogenisation at room temperature – the interdiffusion of dopants is thermally activated (accelerating), so semiconductors once doped are stable in service at or near room temperature processors: **B**.
8. Fuses in electrical circuits – sudden melting of a fuse wire in service is used to advantage: **C**.
9. Superconducting transitions are all at inconveniently low temperatures – this is a service challenge for a critical phenomenon: **F**.
10. Provision of surface compressive stress enables 'safety glass' for car windows – this opportunity for processing is based on gradual thermal expansion: **G**.
11. Onset of unwanted reactions in chemical processes – here a process challenge is thermally accelerated: **K**.
12. Silicon melts at 1414 °C, so diffusion of dopants to control semiconducting properties cannot be done at arbitrarily high temperatures –this is a process challenge for semiconductor processors, this time (cf. 7) associated with a (sudden) phase change: **L**.

**Table 3 Examples of gradual, accelerating and sudden changes**

		Gradual	Accelerating	Sudden
<b>Service</b>	Opportunity	Electrical resistance thermometer	Heat-curable glues	Onset of ferro-electric properties
		Bimetal switches	Enhanced performance of detergents in hotter water	Can leave cooking to simmer
	Challenge	<b>A</b>	<b>B</b>	<b>C</b>
		Crazed glaze on crockery	High-temperature limit on semiconductor performance	Some permanent magnet materials demagnetise at modest temperatures
<b>Process</b>	Opportunity	Need to compensate timer in clocks and watches	Excessive corrosion of high-temperature components	Water pipes burst through freezing
		<b>D</b>	<b>E</b>	<b>F</b>
	Challenge	Density variation provides convective mixing in castings	Temperature control of workability of glass	Chemical reaction selection by use of critical temperature
		Metal tyres and bearing sleeves can be shrink-fitted to wheels/shafts	Sintering of powders to continuous solid (a route to near net shape forming)	Melting allows casting processes

Challenge	<b>G</b> Continuous welded railway lines may buckle in extreme heat or crack in extreme cold	<b>H</b> Over-ageing of precipitation-hardened alloys  Continued diffusion of previously implanted dopants in subsequent processing of microcircuit chips	<b>I</b> Upset metallurgy in the heat-affected zones of welds  Cracks in porcelain due to crystal transition in quartz
	<b>J</b>	<b>K</b>	<b>L</b>

## 3 Gradual temperature effects

### 3.1 Modelling properties

This section provides a model for properties interpreted in terms of the average thermal energy of all the constituent atoms of a material. Since absolute temperature  $T$  is a measure of average atomic kinetic energy, we shall expect to be looking at properties that change gradually with  $T$ , roughly proportionally, over a wide range. In terms of the classification introduced in [Figure 3](#), we shall be looking at changes like [Figure 3\(a\)](#). The experimental descriptions of such changes usually use power series, setting the property  $X$ , for example the length of a specimen, as a function of a change in temperature,  $\Delta T$  (here the Greek capital letter delta,  $\Delta$ , is used to express a change in the quantity that follows it):

$$X = X_0 (1 + \alpha \Delta T + \beta (\Delta T)^2 + \dots)$$

Often the constant  $\beta$  is small enough that  $\Delta X$  is almost proportional to  $\Delta T$ . Then  $\alpha$  is called the *linear temperature coefficient* of the property (expansion, resistance or whatever) and we can express the change in  $X$  as:

$$\Delta X = X - X_0 = X_0 \alpha \Delta T$$

In particular, I want to discuss details of the thermal expansion of solids, but the temperature dependence of the electrical resistance of metals, the thermal conductivity of solids and the Young's modulus of many materials also vary in a gradual way.

#### Exercise 4

The length of a steel rod is precisely measured to be 1.000000 m at 300 K. When heated to 350 K it is measured again and found to be 1.000550 m. Assuming the change to be linear, calculate the coefficient  $\alpha$ .

#### Answer

$$X = X_0 (1 + \alpha \Delta T)$$

The change in length of the steel rod is

$$X - X_0 = 1.000550 - 1.000000 \text{ m} = 0.000550 \text{ m}$$

The change in temperature is

$$\Delta T = 350 - 300 \text{ K} = 50 \text{ K}$$

$$\alpha = \left( \frac{X - X_0}{X_0} \right) \frac{1}{\Delta T} = \frac{0.000550}{1.000000} \times \frac{1}{50} = 0.000011 \text{ K}^{-1}$$

## 3.2 Room to rattle: modelling thermal expansion

In general, as the temperature of a piece of solid is raised the volume it occupies increases. I say 'in general' because as we shall see it is not always the case, and we ought to investigate whether we can exert any control over the phenomenon – which could be useful. Evidently, if a solid expands, the average spacing between its constituent parts must have increased. Since matter is made up of atoms, the issue is really about the volume occupied by the arrangements of atoms that make up any particular solid.

First, it's a good idea to remember that in a solid, atoms are held together by a network of bonds. The nature of these bonds can be classified into three distinct, strong types (ionic, covalent and metallic), though often in practice the bonding within a material may contain characteristics of more than one type. In addition, there are often weaker, secondary bonds between atoms. For the present it is enough to say that atoms are bonded together in a way that holds any pair of atoms at a particular separation, measured from the centre of one atom to the centre of another. Figure 4 illustrates this for a simple plane of identical atoms – fully three-dimensional networks are more realistic but less easy to draw.

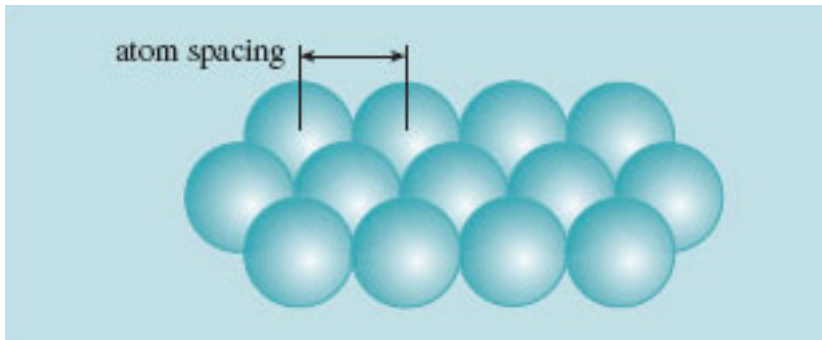


Figure 4 Atoms in a solid can be represented as spheres, arranged in planes as a component of some three-dimensional configuration

What happens if we try to force the atoms closer together, say by compressing the solid, squeezing it uniformly from all sides? Well, apparently there are strong forces that oppose this, almost as if the atoms were hard spheres; most solids are pretty incompressible. What happens if we try to pull the atoms apart then? Once again, the bonds resist, attempting to maintain the spacing as if the atoms were 'glued' one to another.

So where does temperature come into the story? The equilibrium spacing, that is the distance between atom centres, is in fact determined by the way electrons around each atom interact with those of neighbouring atoms. The model of solids I am describing is not quite one with hard spheres glued together – it's a bit more subtle. For a start, the atoms are not stationary but vibrating around their mean position. The vibration is a consequence of their thermal energy. So the thermal energy of the atoms interacts with the binding energy of the electrons that hold the atoms with a particular spacing. A more sophisticated picture is therefore one of an assembly of atoms that rattle around mean positions in the network.

The model needs to link 'more atomic kinetic energy (temperature)' with 'bigger spacing'. The way we can do this is to associate the amplitude of vibration with thermal energy and thence to temperature. In effect, as thermal energy is added to a solid, the atoms tend to occupy a bigger volume. It turns out that it's much harder to squeeze the atoms closer together than it is to pull them slightly further apart, so larger-amplitude vibrations will tend to push atoms further apart to create the space in which to rattle about.

Thermal expansion is a property that is reasonably well described by this model. The length of a line of atoms in a plane of atoms at any instant of time is now the sum of many different atom spacings, owing to those vibrations. The average spacing will be greater if the amplitude of vibration increases. Thus thermal expansion fits into the model.

That's the model. How does it work in practice? It works best for denser materials like metals with their close-packed atom structures. In the relatively open crystals and glasses formed from inorganic compounds, distortions of the crystal structure can accommodate some of the increase in average spacing. Consequently these materials show rather lower expansion coefficients  $\alpha$  – compare soda glass, porcelain and silica with the metals in [Table 4](#). And there are ways of otherwise coping with thermal expansion. See [Box 3 Invariant metals](#).

### Example 2

Using data from [Table 4](#) below, calculate the following changes in dimension that result from uniform temperature changes:

- (a) the changes in length, width and thickness of an alumina tile that measures 30 mm × 10 mm × 0.5 mm after it has been heated uniformly by 200 °C;
- (b) the change in volume and density of the same alumina tile.

### Answer

(a) The linear model of thermal expansion suggests that the change in dimension is:

$$\Delta X = X - X_0 = X_0 \alpha \Delta T$$

and we need to apply this separately to the three dimensions,  $L$ ,  $H$ ,  $W$ , noting that a change of 1 °C is the same as a change of 1 K:

$$\begin{aligned}\Delta L &= 30 \times \alpha \Delta T = 30 \times 8 \times 10^{-6} \times 200 = 0.048 \text{ mm} \\ \Delta H &= 10 \times \alpha \Delta T = 10 \times 8 \times 10^{-6} \times 200 = 0.016 \text{ mm} \\ \Delta W &= 0.5 \times \alpha \Delta T = 0.5 \times 8 \times 10^{-6} \times 200 = 0.0008 \text{ mm}\end{aligned}$$

Each dimension is 0.16% larger ( $\alpha \Delta T = 1.6 \times 10^{-3}$ ).

(b) The original volume was  $30 \times 10 \times 0.5 = 150 \text{ mm}^3$

The new volume is  $30.048 \times 10.016 \times 0.5008 = 150.721 \text{ mm}^3$ . The volume of the hot tile is thus  $0.721 \text{ mm}^3$  larger, which is an increase of  $(0.721/150) \times 100 = 0.48\%$ . Notice that each dimension contributes 0.16% to the net volume change, which is effectively  $3 \times 0.16\%$ . The mass is unchanged, so the density must have decreased by 0.48%.

### SAQ 2

Using data from [Table 4](#), determine the following:

- (a) the change in circumference of a thin hoop of steel having a diameter of 1.200 m after it has been uniformly heated by 300 K;
- (b) an estimate of the change in length of a rod of soda glass that is originally 10 mm long after one end has been heated by 400 K (assume that the temperature of the rod varies linearly from the cool end to the hot end, and work with the average temperature change of the rod).

**Table 4 Temperature linear coefficient of expansion (thermal expansivity) around room temperature for a selection of materials**

Material	$\alpha/10^{-6} \text{ K}^{-1}$ *	Material	$\alpha/10^{-6} \text{ K}^{-1}$ *
Invar	0.1	nickel	14
fused silica	0.5	stainless steel	16
porcelain	2	copper	17
brick	7	tin	18
alumina	8	brass	21
soda glass	9	aluminium	24
steel	11	lead	30
concrete	12	nylon	100

\*The heading ' $\alpha/10^{-6} \text{ K}^{-1}$ ' can be read as 'alpha, in units of 10 to the minus 6 per kelvin'. The numbers in this column must be multiplied by the unit in the heading to get the full numerical value. Thus the expansion coefficient for porcelain is  $2 \times 10^{-6} \text{ K}^{-1}$ .

#### Answer

- (a) The length of the circumference of the cool hoop is  $\pi d$ , whereas the hot hoop circumference will be  $(1 + \alpha \Delta T)$  times longer, making it  $\pi d(1 + \alpha \Delta T)$  – that is, an increase of  $d\alpha \Delta T$ . It is as if the diameter had linearly expanded on heating; take care though, as we have been able to neglect the change in thickness of the thin strip from which the hoop is made. Thus, the circumference expands by an amount

$$\pi d \alpha \Delta T = 3.14 \times 1.2 \times 10^{-6} \times 300 = 1.2 \times 10^{-2} \text{ m} = 12 \text{ mm}$$

- (b) Since only linear changes are involved we can determine an average expansion of the whole rod, as if it were all at the temperature at the midpoint, i.e. 200 K hotter than the initial condition. So, using  $\alpha = 9 \times 10^{-6}$  and  $\Delta T = 200 \text{ K}$ , the rod will be longer by  $\alpha \Delta T \times 10 \text{ mm} = 1.8 \times 10^{-2} \text{ mm}$ .

### Box 3 Invariant metals

Invar®, an alloy containing 64% iron and 36% nickel, has a minute coefficient of expansion at room temperature of  $0.1 \times 10^{-6} \text{ K}^{-1}$ , which is less than 8% of the coefficient of either of its constituents. It is described as being (almost) *invariant*. What could be compensating for the thermal effect? The answer is in the temperature dependence of a magnetic interaction of the atoms; iron and nickel are both magnetic materials. For this particular alloy the rate at which the magnetic coupling slackens with temperature and allows the chemical bonding to pull the atoms closer just balances the normal thermal expansion effect. The alloy was discovered by Charles-Edouard Guillaume in 1899 and immediately replaced an awkward bimetal method of expansion compensation in clock pendulums ([Figure 5](#)).

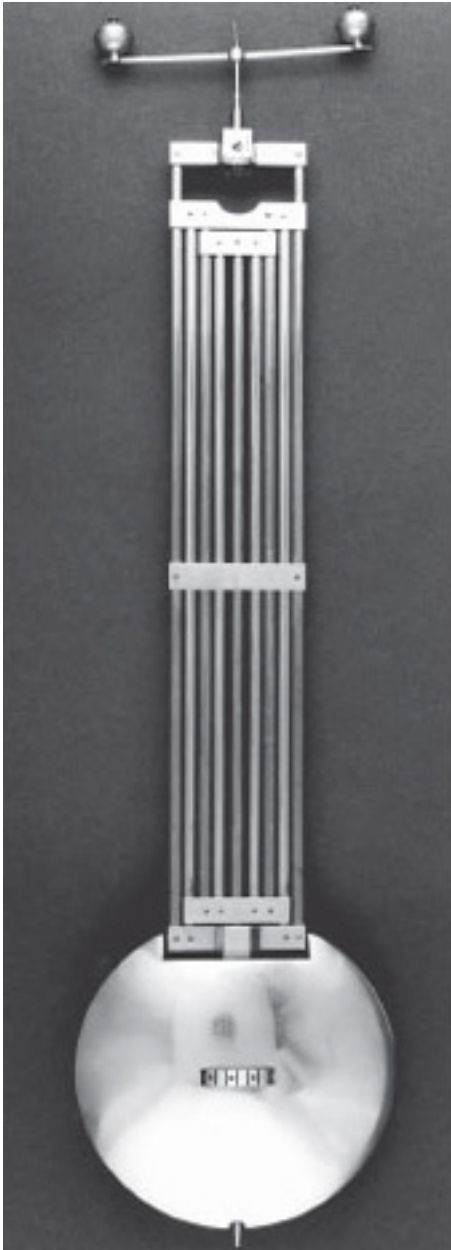


Figure 5 A clock with bimetallic pendulum compensation

Guillaume went on to discover Elinvar in 1912. This alloy, 35% Ni, 10% Cr, 55% Fe, has **zero** temperature coefficient of Young's modulus. Elinvar – elastic *invariant* – solved the worst problem of inconstancy of spring-driven balance wheels in watches, which was that the elasticity of the spring decreased with rising temperature and slowed the watch. A combination of a berylliumbronze wheel and an Elinvar spring allows a simple structure whose oscillation is temperature independent, with expansion and elastic effects compensating one another. If the new alloys had been more expensive they might not have been favoured. It would be nice to think that the principle described led to the discovery, but the explanation came after the discovery.

Guillaume's alloys found application in clocks, watches and other precision instruments, and led to the award of the Nobel Prize for Physics in 1920.

### 3.3 Thermal stresses

When the temperature of an object increases (say, by  $\Delta T$ ) it expands. According to the linear model of thermal expansion the length increase is described by

$$L = L_0 (1 + \alpha \Delta T)$$

What if there is a temperature change, but some constraint prevents the proper thermal size changes? The constraint has to exert a force to prevent the change of size, so a thermal stress will be induced. There are many situations where thermal stress is made use of (for example, thermostat switches, toughened glass) or has to be worried about (cracked welds, bent rails, gas-tight seals).

Every case is in itself a problem of stress analysis, but there are essentially three kinds of situation – look at each, keeping in mind our interest in effects that might be used to make a thermal switch:

- A homogeneous body (i.e. all the same stuff) subject to external constraint (fixed in some way) suffers a uniform change of temperature (it all gets hot together). This situation can cause buckling of railway lines and cracking of welds – see [Box 4 Homogeneous body, uniform  \$\Delta T\$ , external constraint](#).
- A composite body (i.e. made of at least two different materials) whose constituents have different properties generates internal constraint (each material interferes locally with the other) when  $T$  changes. Glass-to-metal seals needed in vacuum technology have to overcome this problem, as do pottery glazes – see [Box 5 Composite body, uniform  \$\Delta T\$ , internal constraint](#).
- A homogeneous body again, but with non-uniform temperature change (i.e. different bits at different temperatures). When the temperature change is rapid the body is said to suffer thermal shock. This is what cracks glass bottles when you try to sterilise them by pouring in boiling water. How does your ceramic hob get on when you pour cold water on it? – see [Box 6 Homogeneous body, non-uniform  \$\Delta T\$](#) .

There are more complex cases as well – see [Box 7 What about welding?](#) for example.

### 3.4 Summary of Section 3

- The temperature of an object is intimately linked to the average kinetic energy of the atoms from which it is made. As a result, some materials properties such as electrical resistance and mean atom spacings change gradually with temperature. These properties can be modelled with a simple linear equation like the following one that describes thermal expansion:

$$L = L_0 (1 + \alpha \Delta T)$$

where  $\alpha$  is the temperature coefficient of expansion.

- If the thermal expansion of solids is constrained, stresses are induced within them. When not managed properly, thermal stresses can lead to distortions and cracks. However, useful engineering components and devices can be constructed that take advantage of 'gradual' thermal sensitivity.

### Box 4 Homogeneous body, uniform $\Delta T$ , external constraints

The classic example of the buckled railway line ([Figure 6a](#)) is an easy geometry to calculate.

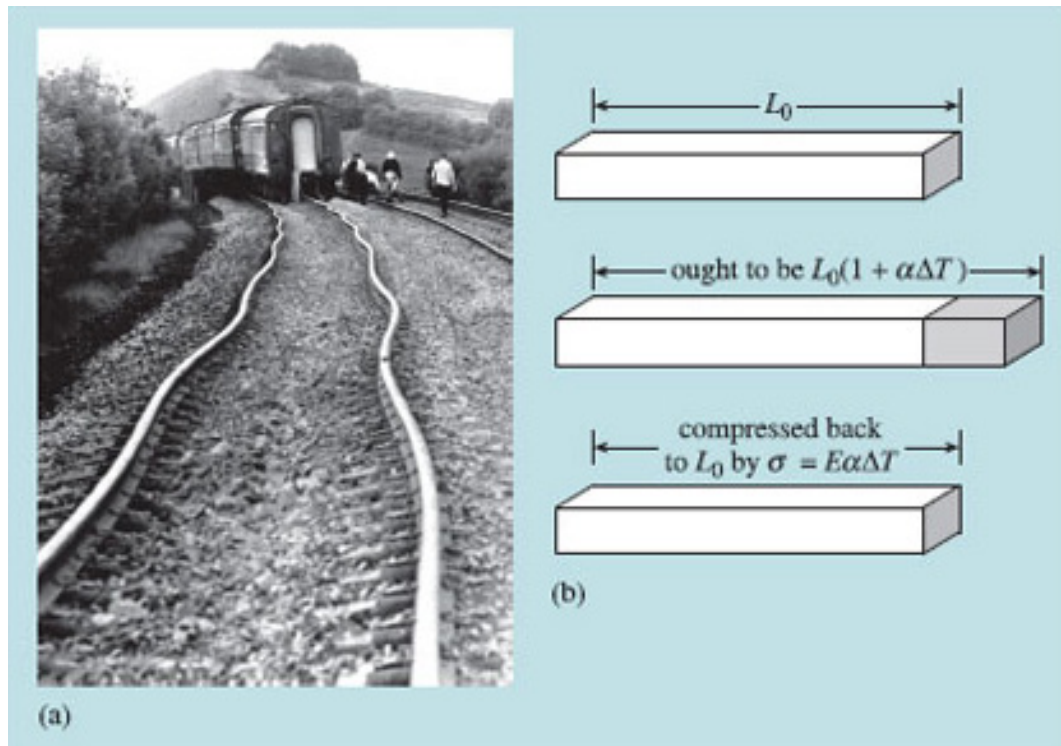


Figure 6 (a) buckled rails, (b) calculating the strain

Suppose the length of a rail is  $L_0$  when its ends just touch adjacent rails and then the temperature goes up by  $\Delta T$  ([Figure 6b](#)). The length ought to become  $L_0(1 + \alpha\Delta T)$  but is constrained to remain  $L_0$ . It is therefore as if the rail had expanded and then suffered a compressive strain  $\alpha\Delta T$  which would have needed an (elastic) stress  $E\alpha\Delta T$ . This could cause the rail to buckle; some of the wiggle in [Figure 6\(a\)](#) was probably caused by the passage of the train – but it needn't be as bad as this picture suggests before it's serious enough to cause a derailment. One way out of the problem is to make provision for expansion and so remove the constraint: for example, rail gaps and bridge roller bearings. However, modern high-speed trains require smooth tracks with continuous welded rails, so another solution is called for here. One answer is to clamp and weld up the rails either in hot weather or else when mechanically stretched, so that stresses in the rails in service are always tensile – buckling is associated with compressive stresses.

### Box 5 Composite body, uniform $\Delta T$ , internal constraints

#### Pretty pots

A relatively simple example to model is the glaze on a pot. In [Figure 7\(a\)](#) a thin glassy sheet (of thickness  $x_1$ ), the glaze, is stuck onto a thicker slab ( $x_2$ ). A look back at data in [Table 4](#) suggests that a glass will have a higher expansion coefficient than porcelain, so  $\alpha_1 > \alpha_2$ . So, the glaze will be inclined to expand on heating (and contract on cooling) *more* than the pot to which it is bonded. There will have to be some kind of compromise.

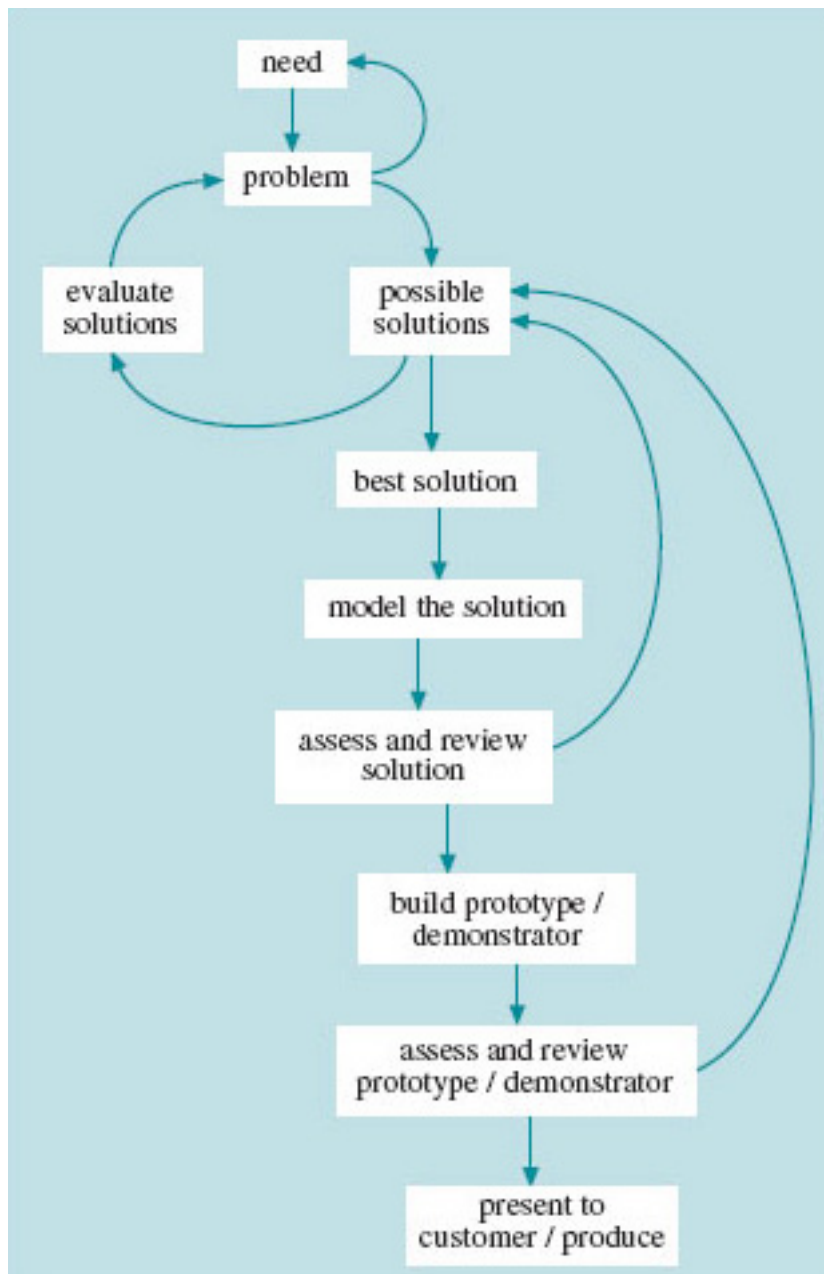


Figure 7 (a) thin glaze on a thick ceramic pot, (b) Chinese pot

In fact, the problem begins at the stage where the glaze is fired onto the pot and initially both glaze and pot contract on cooling. As the pot cools from its firing, the glaze begins to harden and it can no longer accommodate to the body. A thermal stress develops. The glaze should contract more than the pot, but both must move together. So the glaze is in tension because it is prevented from contracting as much as it would if free of the pot, as if the pot is 'pulling' it somewhat – that's tension. The pot is in compression because the glaze is tending to induce more contraction of the surface, 'pushing' atoms closer, than would occur if the pot were unglazed – that's compression. To calculate the size of the thermal stresses you would have to convert the resulting tensile and compressive strains into stresses using the Young's modulus for each material. We don't need to do that to predict what might happen. Because there's much more pot than glaze, the thermal stress is likely to pull the glaze so strongly that it cracks, which might produce a pretty pot (Figure 7b) but it is not the way to make a *strong* one.

### Bimetal strips

We can use the same ideas to anticipate what happens when two thin strips of metals with markedly different expansivities are bonded together to form a flat composite body. When such a *bimetal strip* is heated one layer will be trying to expand more than the other – it will be held back a little, effectively compressed slightly by the second layer. In turn, the second layer will be in tension as it is expanded beyond the thermal strain owing to the presence of the first layer. If neither metal yields, the result is that the strip must bend.

Bimetal strips are used as a cheap, robust way of indicating a temperature. Central heating pumps are often triggered to switch on and off as relays are tripped by the bending of a strip in response to changes in room temperature.

Simple, non-digital instruments in motor vehicles are based on the deflection of an indicator needle in response to the heating of a bimetal strip. Such instruments sense the strength of an electric current. A higher current causes more heating of the strip and that in turn causes the bimetal strip to bend more; the needle movement is driven by this bending ([Figure 8](#)).

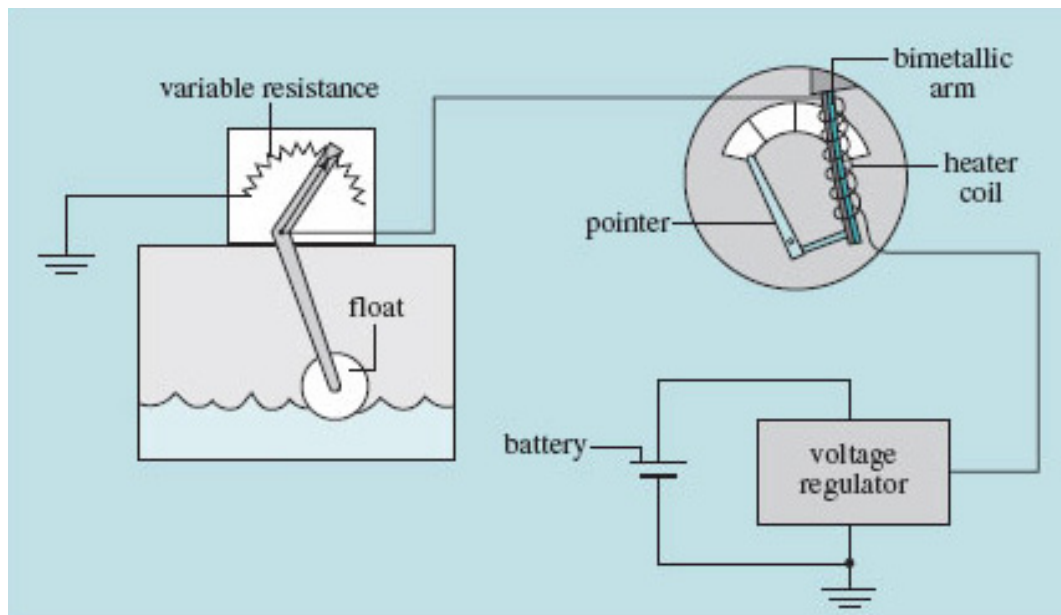


Figure 8 A bimetallic instrument gauge

### SAQ 3

Propose two materials from which to construct the most responsive bimetallic strip, based only on the materials and data in [Table 4](#), giving reasons for the choice made.

### Answer

The most responsive strip will have the greatest mismatch between the thermal expansion coefficients of the two materials, provided neither metal yields. You should therefore choose from the extremes, though the yield criterion probably means that lead should be excluded. So, Invar and aluminium ought to work well, with Invar and brass a close second.

### Box 6 Homogeneous body, non-uniform $\Delta T$

Thermal shock arises because heat flow is not instantaneous. Suppose the surfaces of a plate are suddenly cooled, energy being extracted at some rate (measured in watts per square metre). The temperature inside cannot be uniform and will vary with time, somewhat in the manner shown in [Figure 9](#).

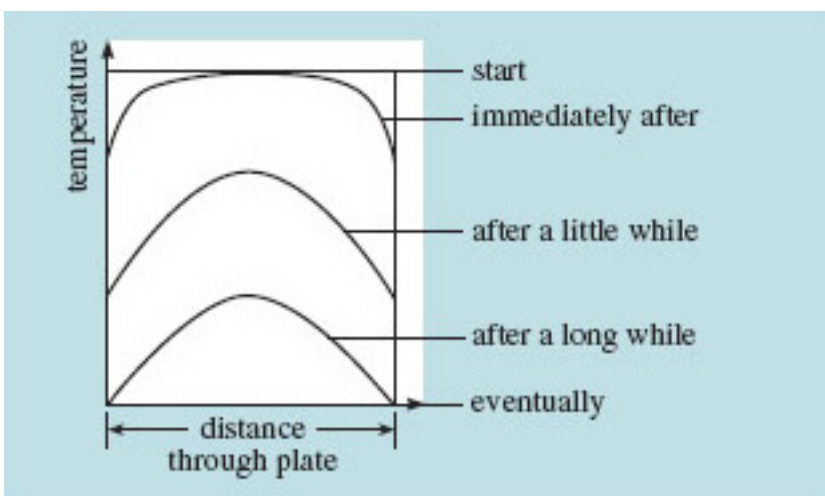


Figure 9 Variation of temperature with time within body subject to rapid cooling from two opposite surfaces

At time  $t = 0$ , when cooling begins, and after an infinite time, there are no internal stresses. At all other times every slice of the object should be a slightly different size from its adjacent slice, but is constrained by its neighbour. Complex non-uniform stresses are the result.

We can, however, see what factors influence the magnitude of these stresses. Clearly, very steep temperature gradients make for high stress, and the gradient depends on how much energy has to flow from the inside to the surface and how quickly it can do so. The cooling of a thick, hot slab made of a material which has poor thermal conductivity, high heat capacity per unit volume, and high expansion coefficient, will induce intense stresses. If, additionally, the material efficiently converts the 'effective strain to high stress via a high Young's modulus, and if it is crack-sensitive, you've got a problem on hand. Consider the chances of a ceramic turbine component when the engine is shut down; or a more homely example, how a ceramic hob survives having cold water spilt on it. The trick in that case is rather neat, as we shall see.

#### Ceramic hob materials

The photograph of a domestic ceramic hob ([Figure 10](#)) suggests a puzzling suite of properties.

The hot spots for cooking must be localised, so the material should not be a good thermal conductor or that will spread the heat sideways. If the hob is a bad conductor it must be thin

to allow sufficient power transfer for its function. So how can it be strong enough to survive the following?

- thermal shock if cold water is poured onto a hot ring
- thermal stress due to steep temperature gradients at the edges of the hot spots
- having a full saucepan dropped on it from one metre height – this is used as a standard acceptance test.



Figure 10 Ceramic hob

What is your recommendation for thermal expansion coefficient?

It must be as small as possible; thermal shock resistance can be achieved by keeping thermal strain low and by reducing temperature gradients (by having good conduction). The latter characteristic is denied us, so low expansion is imperative.

Fused silica glass has a very low expansion coefficient and a low enough thermal conductivity. What is unacceptable about a glass for this purpose?

Glasses are very brittle. As glaziers well know, once a piece of glass is scratched, cracks easily spread through it and it will break. Glass objects are bound to be scratched in service.

One solution is a ceramic based on lithium aluminium silicate, LAS, which crystallises in hexagonal planes of atoms leading to a curious response to heat. Its expansion coefficient depends on direction within the crystal:  $+6.5 \times 10^{-6} \text{ K}^{-1}$  in the plane of the hexagon and  $-2.0 \times 10^{-6} \text{ K}^{-1}$  perpendicular to the hexagon. Yes – a negative coefficient of expansion. As the atoms spread sideways the layers can pack down into their hollows a bit more. This unusual behaviour confers near-zero coefficient upon specimens of LAS that are made up of a large number of randomly oriented crystals.

To make a ceramic hob in the required dimensions would be impossible by ordinary ceramic techniques, but plate glass is easily made. So the material is first prepared as a glass and sheets are made by hot rolling (it is very viscous). Then a heat treatment encourages crystallisation with the hexagon axes randomly oriented. If the individual crystals are very small they can accommodate anisotropic shape changes without inducing large thermal stresses between differently oriented crystals. Also, small crystal size confers strength on the ceramic body by limiting the size of intrinsic flaws which could act as cracks.

#### SAQ 4

In cold climates, the temperature on the outward-facing side of a window pane is often many degrees cooler than that on the side facing inwards. Explain the nature of thermal stresses arising in the glass of a pane that is tightly constrained.

#### Answer

The warmer side will be trying to expand more than the cooler side. Both sides are assumed to be constrained and cannot change their dimensions (in fact, a metal or plastic frame may add additional stress to the glass). The result may be tensile stresses in the cooler side – it is stretched back from its would-be contracted state – and compressive stresses in the warmer side – it is squashed back from its would-be expanded state. Either or both would apply, depending on the temperature at which the installation was done, establishing the constraint.

### Box 7 What about welding?

Welding is a classic example of where internal stresses generated by temperature effects can lead to eventual failure. A welding process may involve several passes of molten metal being laid down, with each pass having its own heating and cooling cycle. There is likely to be constraint associated with the parts being welded. There will be a temperature gradient from the weld into the cooler base material.

So whenever welding is carried out, it leaves the joint with a legacy of built-in stresses. As the fusion zone – the weld metal and melted metal of the component – cools after solidifying, it contracts more than the adjacent metal which has not been subjected to the same high temperature. This may in itself cause cracks to form, and if it doesn't there still must be a matching of strains between the weld metal and its surroundings. The extra thermal contraction of the weld leads to stresses because of constraint effects of material away from the weld. The stresses cannot normally exceed the yield stress, but below about 500 K the yield stress of most steels is high enough for appreciable stresses to build up. We call these *residual stresses*.

A simple way to visualise the formation of residual stresses is the 'three-bar model' of the welded joint. The fusion zone corresponds to a hot central bar which is flanked by two cold bars (see [Figure 11a](#)). The outer bars correspond to the material surrounding the weld. The bars (all initially of the same length,  $L_0$ ) are regarded as being fixed together by rigid end pieces – in other words, the bars must all remain the same length (because the fusion zone remains the same length as the adjoining material to which it is attached).

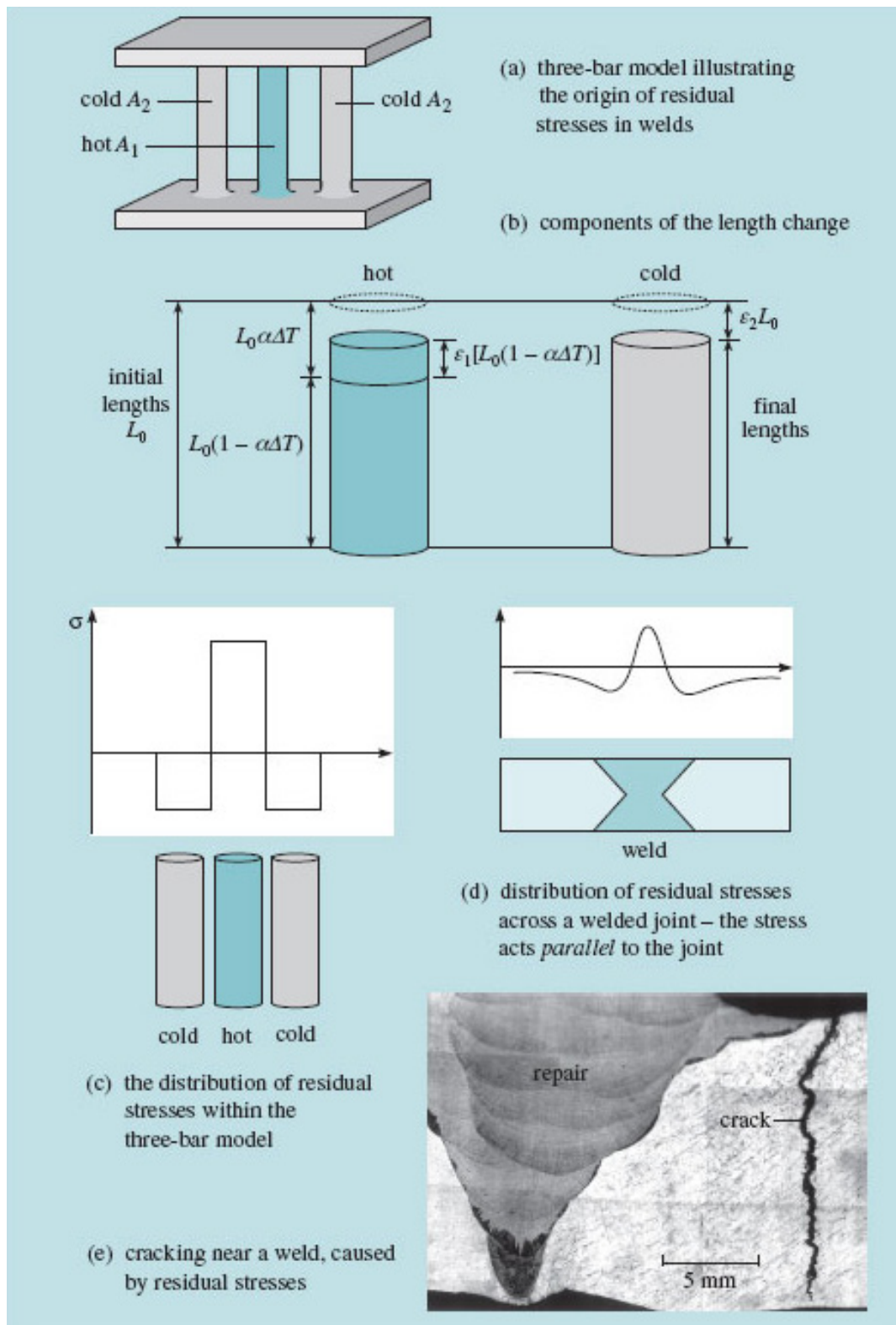


Figure 11 Three-bar model for analysing stresses in a weld

In this model of a weld the central bar is initially stress-free and hot; but stresses build up as the weld solidifies, cools and contracts. If the central bar has a coefficient of thermal expansion  $\alpha$  and cross-sectional area  $\Delta T$ , and cools through a temperature range  $\Delta T$ , if free it would undergo a thermal contraction of  $L_0\alpha\Delta T$ . However, it must be constrained to be the same length as the outer bars, and there will be an elastic strain of  $\epsilon_2$  needed to ensure this (Figure 11b). I'll assume that the two outer bars have identical cross-sectional area  $A_2$  and

undergo an elastic strain  $\epsilon_2$ . Now we can invoke two conditions. First, the *total* length change in the inner bar must equal that in the outer bars (the condition of compatibility):

$$\frac{L_0 \alpha \Delta T}{L_0} + \epsilon_1 = \epsilon_2$$

Using Hooke's Law,  $\sigma = E\epsilon$ , this expression can be written in terms of the Young's modulus  $E$  of the bars and the residual stresses ( $\sigma_1$ ,  $\sigma_2$ ) in the bars:

$$\alpha \Delta T + \frac{\sigma_1}{E} = \frac{\sigma_2}{E}$$

The second condition is that the force  $\sigma_1 A_1$  (*remember: force = stress  $\times$  area*) exerted by the inner bar on the outer bars must be equal and opposite to ( $2\sigma_2 A_2$  the force exerted by the outer bars on the central one (the condition for *equilibrium*):

$$\sigma_1 A_1 = -2\sigma_2 A_2$$

where  $\sigma_1$  and  $\sigma_2$  are the stresses in the inner and outer bars respectively. These equations can be solved for the residual stresses ( $\sigma_1$ ,  $\sigma_2$ ) in the bars.

### Exercise 5

Using the three-bar model just described, calculate the values of  $\sigma_1$  and  $\sigma_2$  for a steel weld where  $\Delta T = -200$  K (i.e. a drop in temperature),  $\alpha = 11 \times 10^{-6} \text{ K}^{-1}$ ; and  $E = 210 \text{ GN m}^{-2}$ . You will have to solve the two simultaneous equations containing  $\sigma_1$  and  $\sigma_2$ . Assume that  $A_1 = A_2$

### Answer

Starting off with

$$\alpha \Delta T + \frac{\sigma_1}{E} = \frac{\sigma_2}{E}$$

we can rearrange this to give:

$$E \alpha \Delta T = \sigma_2 - \sigma_1$$

Plugging in the numbers gives us:

$$(210 \times 10^9) \times (11 \times 10^{-6}) \times (-200) = \sigma_2 - \sigma_1$$

Then using  $\sigma_1 A_1 = -2\sigma_2 A_2$  with  $A_1 = A_2$ , we have that  $\sigma_1 = -2\sigma_2$ , which gives:  
 $\sigma_2 = -154 \text{ MPa}$  (negative sign implies compression)  
 and  $\sigma_1 = +308 \text{ MPa}$  (positive sign implies tension)

### Box 7 contd

The residual tensile stress of  $308 \text{ MN m}^{-2}$  in the central bar may be of the order of the room temperature yield strength for many steels – and it requires the weld to cool by only some 200 K more than the adjacent metal. (In practice the weld cools by much more than this, but the residual stress cannot rise too much above the yield strength because at such stresses the weld metal can strain extensively by plastic deformation.) In practice, of course, instead of the uniform residual stresses in the rods ([Figure 11c](#)) the residual stresses parallel to a welded joint will vary smoothly across the weld ([Figure 11d](#)).

Residual stresses can be reduced by heating the welded structure, because the yield strength falls with increasing temperature. The thermal stresses should not recur during cooling, because of the more uniform temperature distribution. This procedure is called *post-weld heat treatment* or *stress relieving*.

[Figure 11](#)(e) shows an example of where residual stresses led to cracking near a weld. In this example, a weld for a power plant pipe was found, after initial fabrication, to contain a crack – probably just from shrinkage effects, as described earlier. The cracked area was machined out, and the weld was repaired with a new layer of weld material, as shown. However, the repair process complicates the residual stress generation even further, and after a period of operation at high temperature a so-called 'reheat crack' formed in the material near to the repair.

## 4 Accelerating temperature effects

### 4.1 Characteristics of processes activated by thermal energy

This is a long section and needs to be studied carefully. Keep your eye on the overall goal of seeking useful thermal effects on which to base devices.

This section continues the discussion of heat at an atomic level. You will need this background to appreciate the characteristics of processes activated by thermal energy – for example, the softening of glass in a gas flame, the diffusion of atoms through solids, the electrical conductivity of ceramics, and many chemical reactions. Such processes relate not only to the manipulation of materials, but also to the way in which the properties of materials vary with temperature. The exponential function  $y = \exp(x)$  is an essential ingredient of the useful mathematical modelling that can be done in this case, so now is a good time to check you have the necessary background by reading [Box 8 Exponentials and logarithms](#).

#### Box 8 Exponentials and logarithms

Populations of rabbits are said to increase 'exponentially' if food is plentiful and predators are rare. Weed on a pond may appear to spread 'exponentially'. Money invested in a savings account appears to grow 'exponentially'. The mathematical function that can be fitted to all these scenarios is the exponential function  $y = \exp(x)$ ; it is plotted in [Figure 12](#) (a). The function  $\exp(x)$  is alternatively written as  $e^x$ .

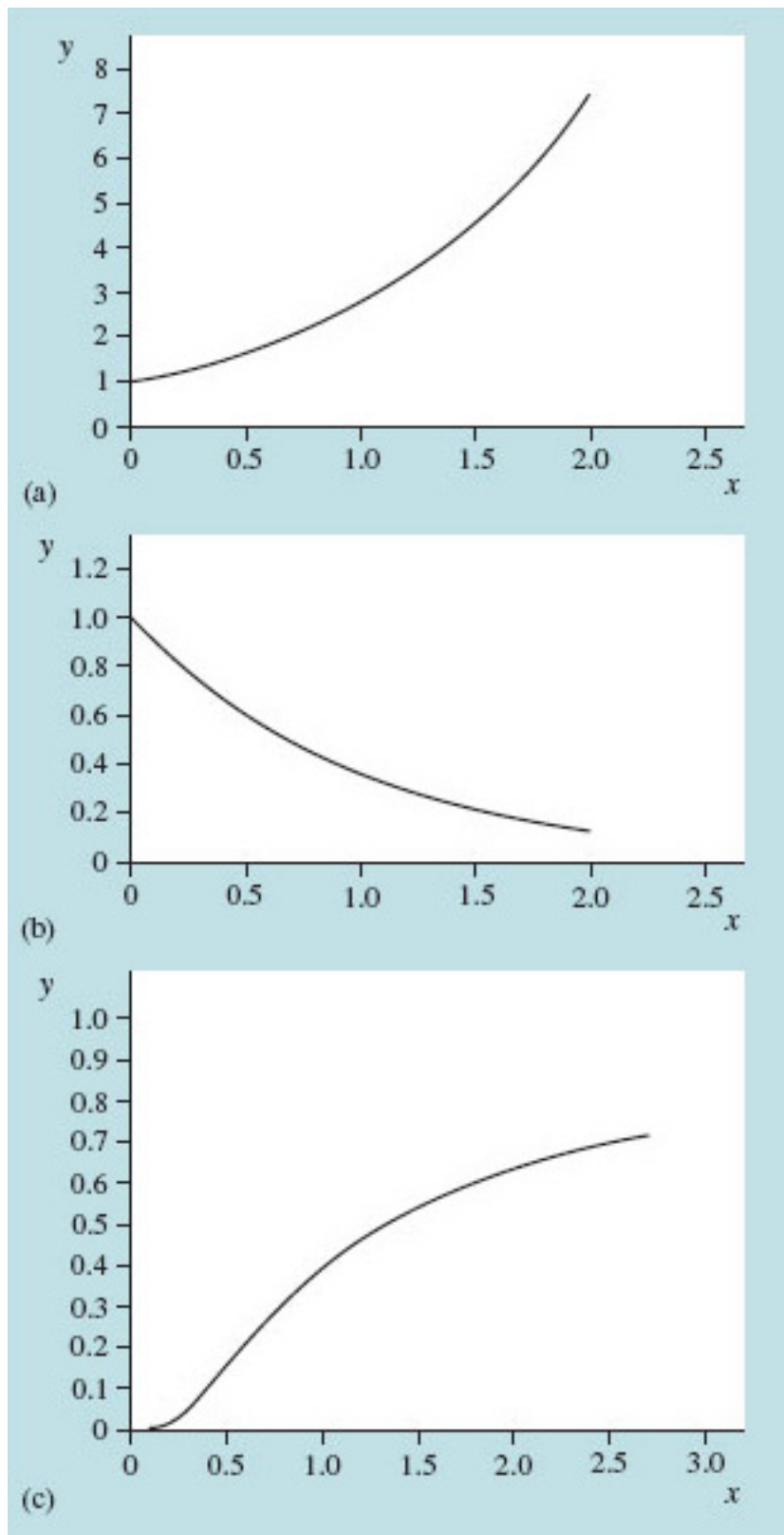


Figure 12 Exponential functions: (a)  $y = \exp(x)$ , (b)  $y = \exp(-x)$ , (c)  $y = \exp(-1/x)$

On calculators the button marked EXP is to do with powers of ten and is not the exponential function. To get  $\exp(x)$  the appropriate function key is usually the one labelled  $e^x$ .

The usefulness of the exponential function goes beyond rabbits, pond weed and banking. It arises in science in many different situations. Often its occurrence can be traced to a key

factor that changes in proportion to itself. Rabbits mature quickly and a large group reproduces in proportion to the number of rabbits. The potential of floating pond weed to capture energy from the sun and so grow in an almost empty pond is in proportion to the weed's existing surface area. The interest on a monthly savings account is earned in proportion to the amount in the account at the end of each month, so one month's interest adds to the initial sum as the basis for determining the next month's interest.

In these cases the model functions that relate the number of rabbits ( $N$ ), the area of weed ( $A$ ) and the balance of the savings account ( $B$ ) to time are as follows:

$$\begin{aligned} N &= N_0 \exp(t/\tau) \\ A &= A_0 \exp(t/\tau) \\ B &= B_0 \exp(t/\tau) \end{aligned}$$

in which the subscripts (zero) denote the values at time  $t = 0$ , and the symbol  $\tau$  (Greek letter tau) is a 'characteristic time'. The exponential function equals one (1.0) when the argument (here  $t/\tau$ ) is zero. At the time when  $t = \tau$ , the argument is 1.0 and the function equals the mathematical constant 'e', which has a value of 2.718 ... .

A similar exponential function describes the decay of a population that randomly dies out. For example, consider a large number of radioactive atoms that spontaneously undergo a decay, emitting one of the characteristic types of radiation (alpha, beta and gamma). Once any radioactive atom has 'emitted' its radioactivity it is, so to speak, spent. In any brief interval of time, the number of atoms that 'decay' depends simply on the number that remain. From this follows an exponential function that describes a slowing decline in activity of the original group with time (see [Figure 12b](#)):

$$N = N_0 \exp(-t/\tau)$$

Notice the negative argument ( $-t/\tau$ ) of the exponential function in this case. The decay of electrical charge in a leaking capacitor follows a similar trend, as does the temperature of a cup of tea relative to that of its surroundings. In each case the rate of loss of charge or heat is proportional to the amount that remains.

To 'undo' an exponential function we take natural logarithms ( $\ln$ ). So, to recover  $x$  from

$$y = \exp(x)$$

you must take the natural logarithm of both sides of the equation:

$$\ln(y) = \ln(\exp(x)) = x$$

That amounts to a definition of the natural logarithm function  $\ln(y)$ .

(On calculators natural logarithms are usually performed by means of the function key marked either 'ln' or 'log e'.)

Another occasion when the exponential function arises is in connection with the statistics of very large populations of identical particles. That means we may expect to see it when discussing several million million million atoms. In this context the argument of the exponential is usually some particular, fixed energy  $E$  divided by a thermal energy  $kT$ , and it is negative:

$$y = \exp(-E/kT)$$

This form of the exponential is very important in the context of thermally accelerating effects. [Figure 12\(c\)](#) shows how the exponential function looks when the variable is 'upside

down inside a negative exponential', as  $T$  is in this last equation. In this case the curve rises increasingly rapidly at first, but later flattens out.

## 4.2 Energy distribution

Atoms without much thermal energy will not be doing very much. Consider fifty million million ( $50 \times 10^{18}$ ) silicon atoms, bonded into a single massive network; I've chosen silicon, but any elemental solid would do. It will be a speck just large enough to be seen without a microscope. You know that if it is heated it will expand, at some stage it will melt and then eventually it will vaporise – that is because thermal energy effectively 'rattles it to bits'. Having thermal energy makes the atoms able to move. For them, the thermal energy is in part associated with energy of motion – kinetic energy. They may not be free to move far, however – not if the electrons have conspired to bond the atoms together. Within the constraints of being bound by the behaviour of the electrons, the atoms simply jiggle about, exchanging kinetic energy with each other.

### 4.2.1 Quantifying thermal energy

Thermal energy is associated with random motion – that is, in effect, a definition. Because it is random, it only makes sense to talk about it in connection with a large population of atoms. I began with fifty million million million silicon atoms – that should be enough. If whatever motion they have is random, some may have lots of it, others very little. With such a large population it is reasonable to try to think about an average motion or, better, to define an average energy of the particles. How do you go about this?

Suppose that [Figure 13\(a\)](#) represents data about the time spent by Open University students on their tutor-marked assignments (TMAs) in all courses last year. The horizontal axis is the time,  $t$ , in minutes and the vertical scale is the number of students,  $N(t)$ , taking a particular amount of time,  $t$ .

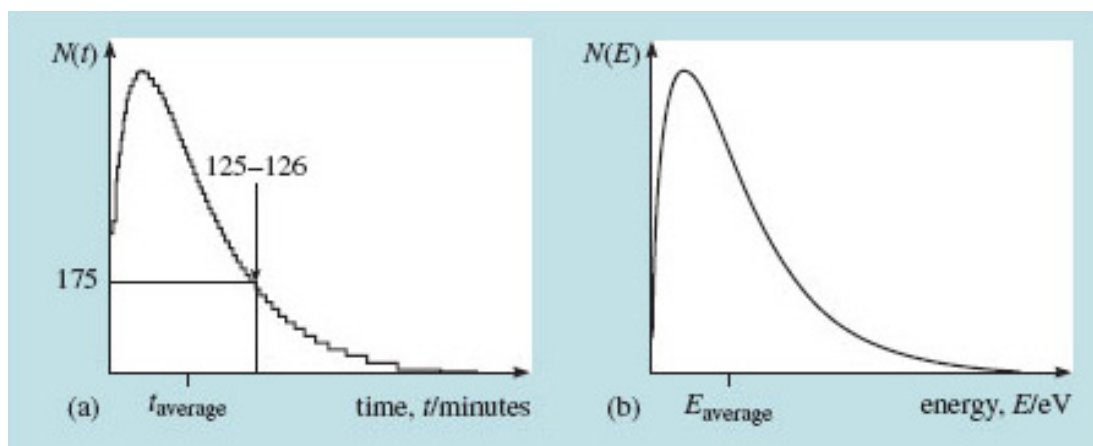


Figure 13 Distribution curves: (a) completion times for TMAs, and (b) energies of thermal particles

For any particular time on the horizontal axis you can use the curve to read off the number of students who took that long over their TMAs. Marked on the curve is the number of students who took between 125 and 126 minutes. To define the average time an Open University student spent on a TMA last year you must examine the statistics that the curve

represents, showing, as it does, how the population is distributed among various time intervals. Then you refer to a mathematics text to advise you how to calculate the average from a statistical distribution. You can probably see by eye that the average lies a little to the right of the maximum in the curve.

The same approach ought to work for the average kinetic energy of a group of atoms. So let's look at the statistics of particle energies in a thermal distribution. It turns out that the statistical distribution of thermal energies among a large population of atoms (millions and millions of them) looks exactly like the curve I proposed for the TMA scores. I've sketched it again in [Figure 13\(b\)](#), with axes appropriately labelled. Now the vertical axis represents the number of particles having energies in any narrow interval on the horizontal energy axis. As with the TMA times, the average energy will be a little to the right of the maximum. I shall come to the mathematics of such distributions shortly.

[Figure 13\(b\)](#) represents a distribution of energies, with energy  $E$  plotted along the horizontal axis and the number  $N(E)$  plotted on the vertical axis. This distribution has a precise mathematical form that can be derived from a few fundamental principles and assumptions. It turns out that in this context, temperature expressed in energy units ( $kT$ , refer back to [Box 2 Temperature and energy](#)) is just a measure of average energy. So, a higher temperature corresponds with a distribution that has a higher average energy, and this would certainly be the case for one that has a broader distribution peaking at higher energy. There is a lot of thermodynamics behind these assertions. You must take this and what follows on trust if you have not met the idea before.

## 4.2.2 The significance of the average energy

The average thermal energy of the atoms in a solid indicates how much they are 'rattling' or vibrating around their mean positions. Since the atoms are close together, virtually touching, and because atoms are almost incompressible, they cannot get much closer. But they can get further apart. So, since thermal energy is manifested in the vibrations of the atoms, bigger vibrations mean that the atoms must spend more time further apart. On average then, there is a tendency for a solid to expand when it is heated, as we have already discussed. It follows too that as thermal energy is removed, atoms on average vibrate less and spend more time closer together, and bulk material can then be expected to contract on cooling.

## 4.2.3 The significance of the distribution of energies

Near room temperature (300 K), the average bundle of thermal energy associated with a particle is 0.026 eV (look back at [Box 2 Temperature and energy](#)). This is not going to do much damage to something stuck together with bonds that have an energy of a few eV – just as the average wage earner can't participate in an auction of fine art. Look back at [Figure 13\(b\)](#), however, and notice that the distribution of energies extends further up the energy axis. Particles with much higher energy than the average may well be able to break free of their bonds and to initiate major changes in the bulk properties of the material of which they are a part. Though relatively few in number, in a population of millions you will always come across some particles with many times the average energy. It is important to know more about particles in the high-energy tail of the distribution of energies I sketched in [Figure 13\(b\)](#). In particular, how does their number change when the average energy increases?

[Figure 14](#) shows two schematic thermal distributions with different average values. I have put a real energy scale on the horizontal axis; the vertical axis shows the number of

particles,  $N(E)$ , with energies in a narrow band close to  $E$ . The total number of particles is represented by the area under the curve, and both curves represent the same number of particles.

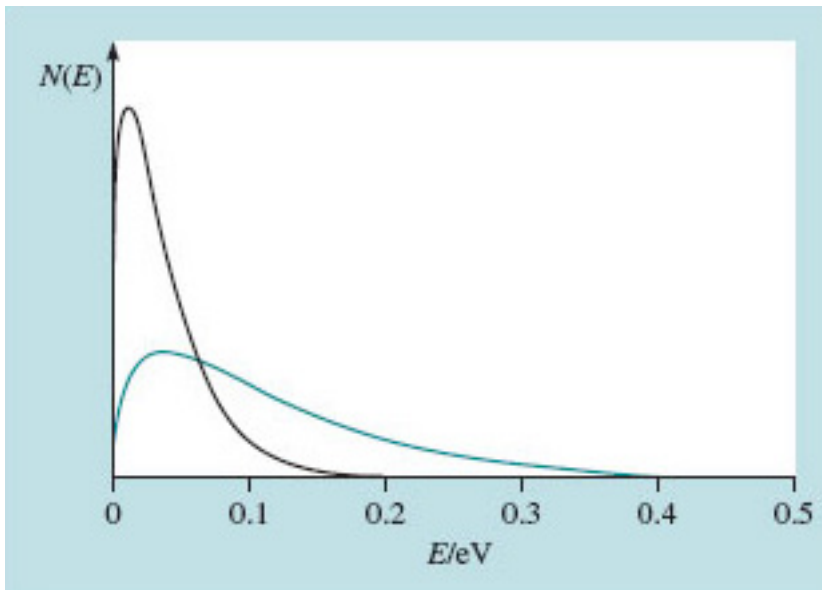


Figure 14 Thermal energy distributions at 300 K and 900 K

The taller, narrower of the distributions in [Figure 14](#) represents an energy distribution at a temperature of 300 K. The shorter, broader one represents a distribution at a temperature of 900 K. You can see that whereas at 300 K you cannot detect any particles having an energy above 0.2 eV, at 900 K – you might say three times hotter – several per cent of the particles have energies that exceed 0.2 eV. Extending this argument, it can be shown that at 2000 K, around one per cent of particles in such a distribution would exceed 1 eV. Although the full story of melting is more complicated, it is not too surprising that 2000 K is enough to shake many solids to bits.

### 4.3 Thermally activated processes

*Thermally activated processes* are those that get going not because of average effects, but because the fraction of particles in the tail of the distribution increases with temperature. This is a basic property of the thermal distribution we have been discussing. For instance, what would take 30 000 years at room temperature may happen in under one second at 1000 K if it depends on how many particles have an energy in excess of 1 eV.

The next step in the study of energy distributions and temperature is therefore to see how the distributions in [Figures 13\(b\)](#) and [14](#) can be described by a mathematical expression from which meaningful numbers can be obtained.

The thermal energy distribution I have been using in [Figures 13\(b\)](#) and [14](#) is described mathematically by the following relationship:

$$N(E) = \frac{A}{\pi} \left( \frac{E}{kT} \right)^{1/2} \exp \left( -\frac{E}{kT} \right)$$

where  $A$  is a constant, and  $N(E)$  and  $E$  are as in [Figure 14](#). In this expression, since  $T$  is in units of kelvins,  $E/k$  must also be in kelvins.

That means that an energy in joules must be combined with Boltzmann's constant ( $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$ ). If the energy is in electron volts,  $k$  must be replaced by  $k/e$  which is  $86 \times 10^{-6} \text{ eV K}^{-1}$ .

What we need from the mathematical form of the distribution is a way of quantifying how the proportion of energetic particles changes with temperature.

Given the above mathematical form it is possible to show that the fraction of particles having energy greater than say  $E_1$  is approximately proportional to  $(E_1/kT)^{1/2} \exp(-E_1/kT)$ , provided  $E_1$  is much greater than  $kT$ . Under these circumstances the exponential part changes much more rapidly than the square root and therefore the fraction of particles having energies exceeding  $E_1$  predominantly varies exponentially, according to the function  $\exp(-E_1/kT)$ .

Rates of chemical reaction, some of the electrical properties of materials, the diffusivity of impurities in silicon and the 'softness' of glasses – all show this kind of dependence on the exponential of a characteristic energy compared with absolute temperature (Figure 15).

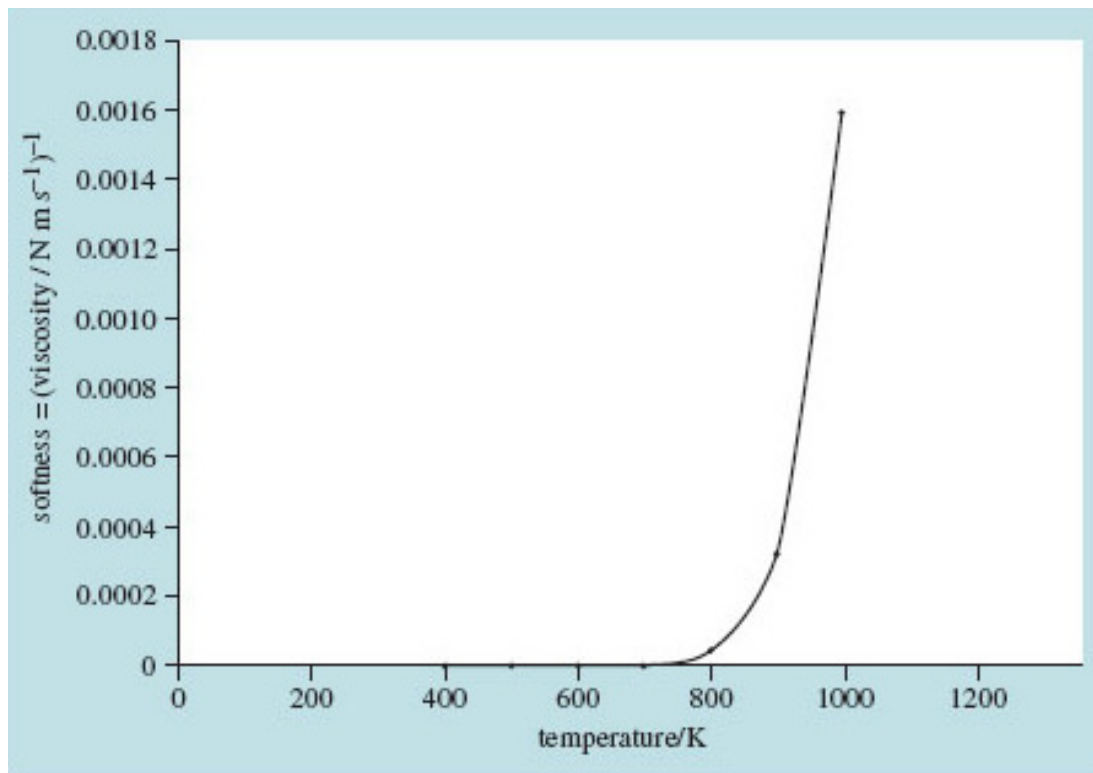


Figure 15 Softness of soda glass – softness is the reciprocal of viscosity, which has the units  $\text{N m s}^{-1}$

### 4.3.1 Arrhenius's law

In 1889 Arrhenius, a Swedish chemist, put forward a model to describe the way in which the rates of many chemical reactions could be accelerated by increasing temperature. His model is based on the idea that the rate at which such chemical reactions happen is proportional to the number of particles with enough thermal energy to overcome some sort of energy barrier. In other words, it relates the rate at which things happen to the fraction of particles having energies beyond some threshold energy. This threshold is characteristic of the process and is called an *activation energy*,  $E_a$ , for whatever process is involved. The rate,  $r$ , is therefore:

$$r = r_0 \exp(-E_a/kT)$$

In Arrhenius's model, the pre-exponential scaling factor,  $r_0$ , is a constant. Arrhenius's law has subsequently been found to apply in general to thermally activated processes such as diffusion (see [Box 9 Carburizing steel](#)) and the conductivity of ceramics (see [Box 10 Thermistors](#)).

### SAQ 5

Calculate how much faster a particular chemical reaction will proceed at 500 K compared with the rate at 300 K, if the activation energy of the reaction is 0.4 eV.

#### Answer

The rate at which the chemical reaction will proceed at 500 K is

$$r = r_0 \exp\left(\frac{-E_a}{kT}\right) = r_0 \exp\left(\frac{-0.4}{86 \times 10^{-6} \times 500}\right) = 9.1 \times 10^{-5} r_0$$

The rate at which the chemical reaction will proceed at 300 K is

$$r = r_0 \exp\left(\frac{-E_a}{kT}\right) = r_0 \exp\left(\frac{-0.4}{86 \times 10^{-6} \times 300}\right) = 1.8 \times 10^{-7} r_0$$

We don't need to know  $r_0$  to get the ratio of the rates, which is

$$\frac{9.1 \times 10^{-5}}{1.8 \times 10^{-7}} \approx 500$$

### 4.3.2 Competing processes

Let's look graphically at the way the rate of a thermally activated process changes with temperature. [Figure 16](#) shows two rates with different activation energies of 1.0 and 0.5 eV – which curve is which?

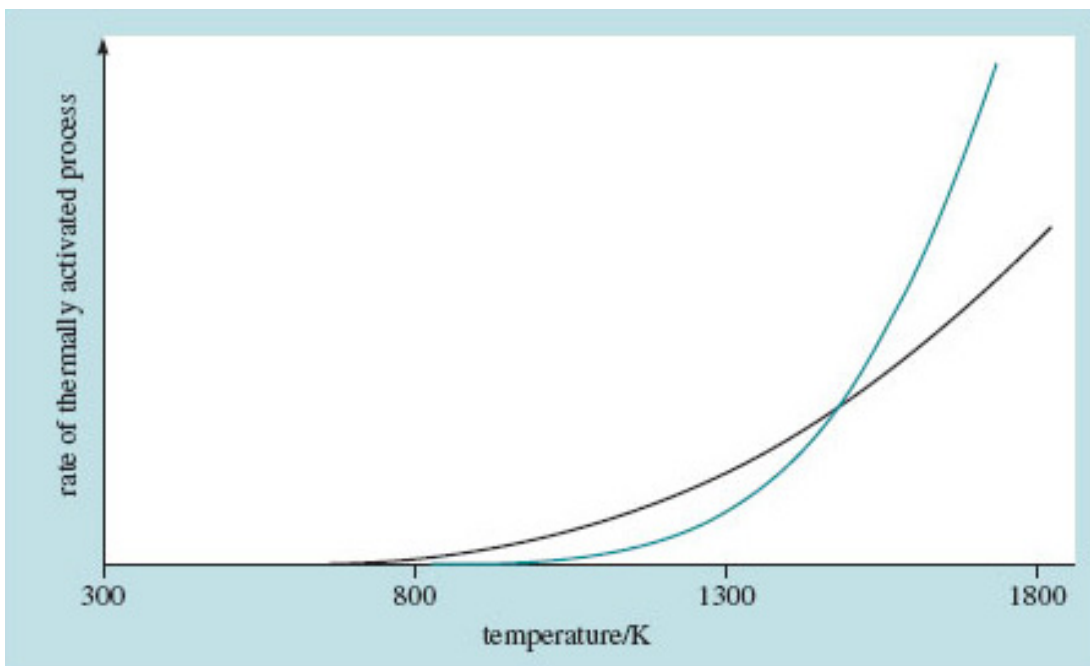


Figure 16 Reaction rates and temperature for activation energies of 0.5 and 1.0 eV

The process with the higher activation energy is the one that doesn't get going till the temperature gets up to around 1000 K, but once it has begun, it speeds up more quickly and, for the case illustrated, overtakes the process with the lower activation energy. It is sometimes like this with two thermally activated processes: at low temperature the lower activation process will predominate but above some temperature, the higher activation process may dominate proceedings.

This is worth remembering. If you are thinking of turning up the heat a little to hurry things along, take care not to unleash some other process with a higher activation energy of which you were previously unaware – I have in mind something like drying gunpowder with a blow torch!

### Box 9 Carburizing steel

Here's a conundrum. Steel with a high carbon content is hard-wearing, and that is just what is required for drive-shafts, bearings and gear teeth. But if we choose a recipe that makes steel hard for a service requirement, how can we get around the fact that its hardness will make it extremely difficult to shape in the first place?

One answer is to fashion the components from a steel of a more formable, low-carbon composition and then increase the carbon content of the surface. That solves the problem, provided we can meet the challenge of squeezing extra carbon into the surface after shaping the components. That's where diffusion comes in.

Diffusion is spontaneous movement of matter caused by the thermal motion of atoms; it happens easily in gases and liquids, but in solids diffusion is a slow process. Nevertheless, the management of diffusion, as a means of altering the local composition of a solid material, is vital in many fields of engineering. Carbon is diffused into the surfaces of steel components to harden them and dopants are manoeuvred in silicon using diffusion to control semiconducting properties.

In solids, the kinetic energy is in the form of vibration, so on the whole nothing moves anywhere – except 'occasionally' when an atom manages to jump all the way from one lattice site to another. This possibility is thermally activated, with an activation energy that keeps the process virtually inactive at room temperature; diffusion in solids starts to be significant at temperatures of several hundred kelvin. Even when atoms do jump, they jump in random directions, so the overall travel of mass is very small. For example, in carburizing steel at 850 °C (about 1100 K) for 90 minutes, a typical treatment ([Figure 17](#)), it is estimated that each carbon atom has travelled over 100 m by making random hops from one space between iron atoms to another.

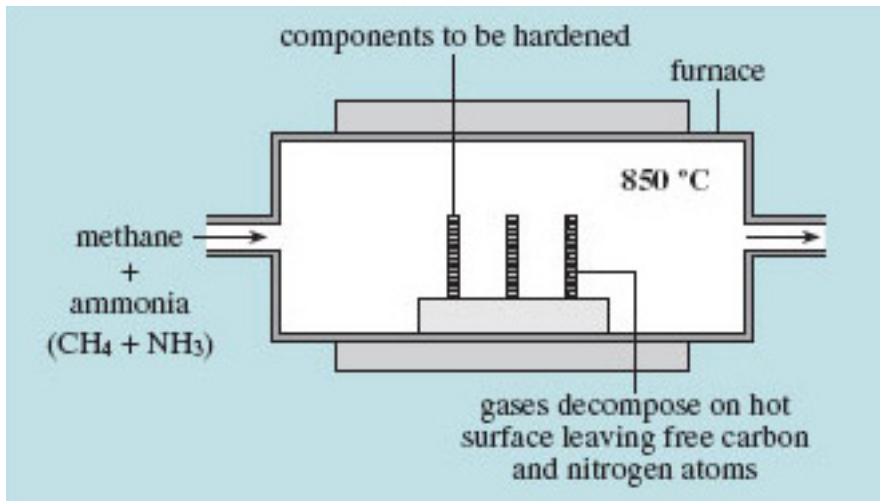


Figure 17 Carbonitriding steel in a furnace to create hardened surfaces

Yet, as shown in [Figure 18](#), the carbon has penetrated less than 1 mm; there are nearly as many steps back as forward.

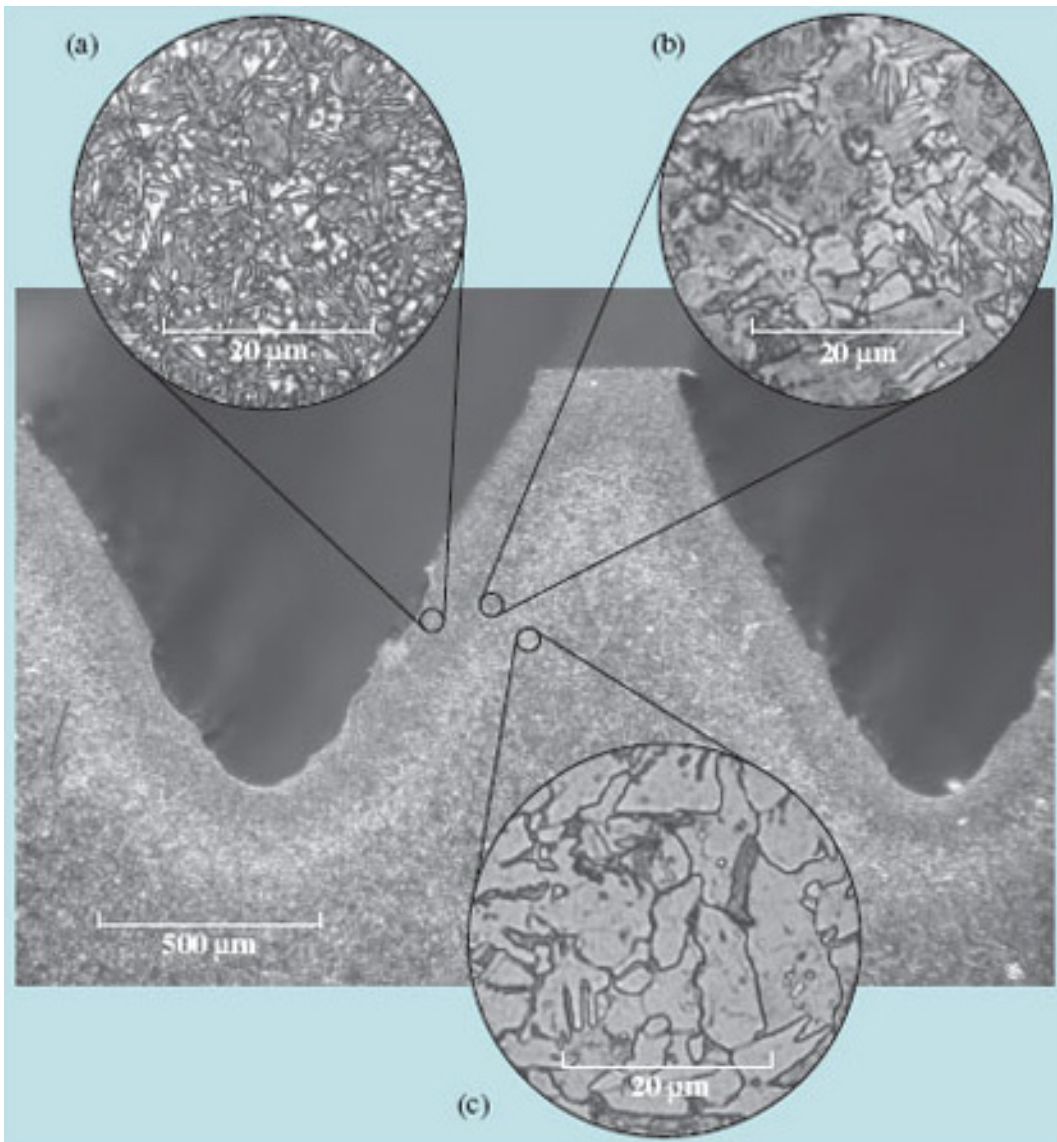


Figure 18 Cross-section through a steel screw thread that has been surface-hardened by carbonitriding, a process in which gaseous carbon and nitrogen atoms are allowed to diffuse at high temperature into the surface of a low-carbon steel component. The variation in carbon (and nitrogen) content enables the subsequent quenching operation to produce a desirable hardness gradient from the hard surface inwards. The magnified sections show: (a) high carbon content iron at the surface, which when quenched produces very hard, brittle martensite, (b) lower carbon content steel, approximately 160 micrometres beneath the surface, which when quenched forms pearlite, a constituent of lesser hardness, (c) interior of low carbon content steel, which when quenched forms relatively soft and ductile ferrite

Whether or not there is any net flow by diffusion within the solid depends upon concentration gradients which lead to more hoppings in one direction than another.

Technologists are particularly interested in diffusion in non-uniform compositions, where the process is one of slowly changing concentrations at all places. Starting with an abrupt interface between two solids, the concentration profile after some time of diffusion must follow the trends of [Figure 19](#).

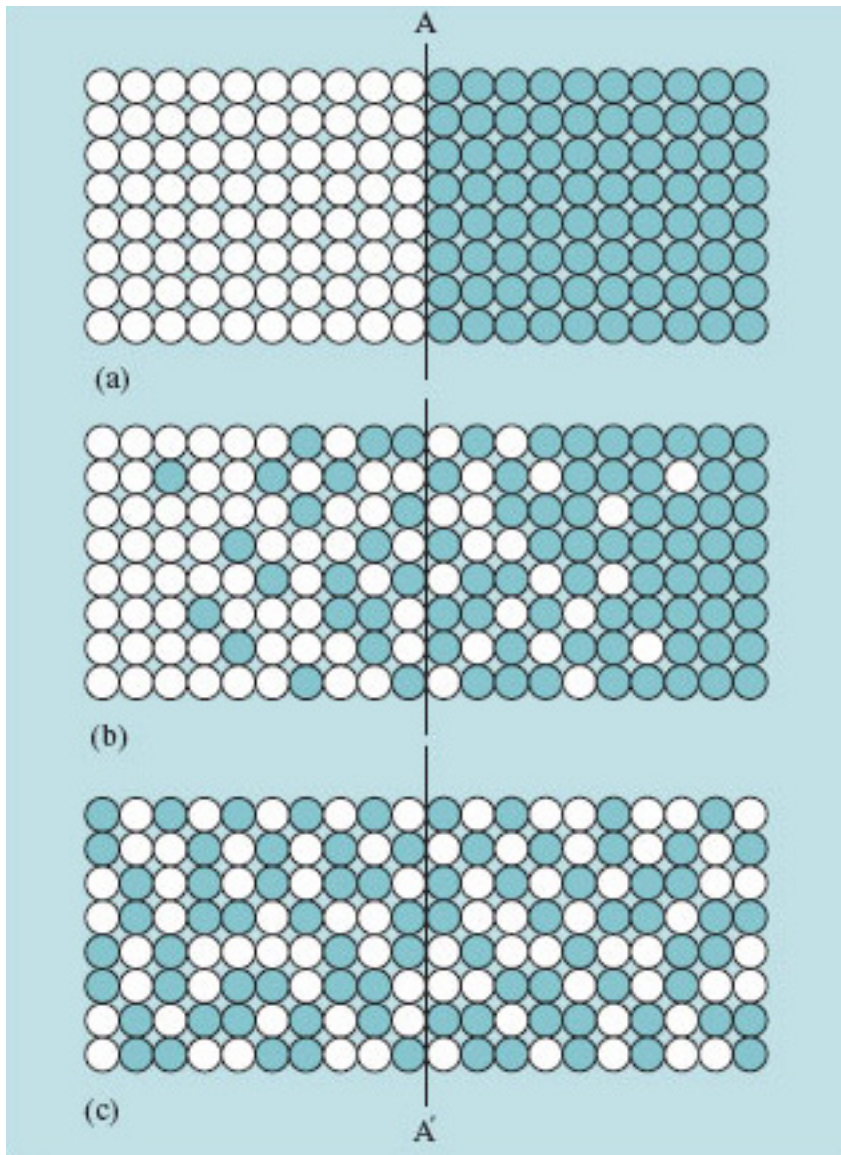


Figure 19 'Coloured' atoms diffuse across the boundary A-A'

It is easy to see that the gradient of concentration encourages the change of composition. In [Figure 19](#) random jumping will move more 'coloured' atoms across the plane A–A' from right to left than the other way, simply because there are more of that species on the right of the plane. That reduces higher concentrations and raises lower ones until uniformity is reached. During the interesting transient phase, differential equations (proposed in the form of two laws by Adolf Fick in 1855) can relate concentrations to time and place via a diffusion coefficient:

$$D = D_0 \exp(-E_a/kT)$$

in which  $E_a$  is the activation energy for the mechanism by which the atoms get to another site in the crystal, and  $D_0$  is the material property which converts the mere possibility of jumps (the exponential term) into an effect. The *number* of particles that are jiggling about with energies in excess of the strength of the bonds varies with the Arrhenius exponential.

To design a technical diffusion process an engineer has to determine how the concentration profile varies with time from some initial distribution. That involves solving Fick's Differential Equations. I'm not going to go into any more detail here, but what emerges are useful

mathematical expressions for the concentration profile of the diffusing material. A useful rule of thumb coming from this solution is that the diffusing material has penetrated a distance  $x \sim \sqrt{Dt}$  after time  $t$ . But to use this result requires knowledge of  $D$  and of its temperature dependence; such data are catalogued for carbon diffusing in steel and for hundreds of other technically important combinations.

## Box 10 Thermistors

When metals get hot their electrical resistivity increases according to the linear model outlined in [Section 3](#). Their conductivity (the reciprocal of resistivity) decreases with temperature. When ceramics get hot, although they're not noted for their electrical conductivity, they do the opposite and become better conductors of electricity at higher temperatures. Because they behave oppositely to metals, ceramics are sometimes said to have negative temperature coefficients (NTCs) for electrical resistance.

With a little ingenuity it's possible to make components for the electronics industry that can play the role of resistors while exhibiting this negative temperature coefficient behaviour. They can be used to compensate for thermal changes in the resistance of normal resistors. They can even be used as thermometers. These components are called *thermistors*.

A commonly used basis for thermistors is a mixture of manganese and nickel oxides. By controlling the gross composition and microstructure, components can be made with electrical resistances that change increasingly rapidly with temperature. The initial resistance, the resistance at a particular temperature and the rate of change with temperature can all be engineered to some degree.

'Microstructure' refers here to the size, shape and composition, on a microscopic scale, of distinct regions (such as individual crystals) in the bulk of the material.

[Figure 20](#) shows the reciprocal of the electrical resistance (electrical conductance) of one of a standard range of thermistors. Notice the rapid rise in conductance with temperature – just what you might expect when there's an exponential function involved.

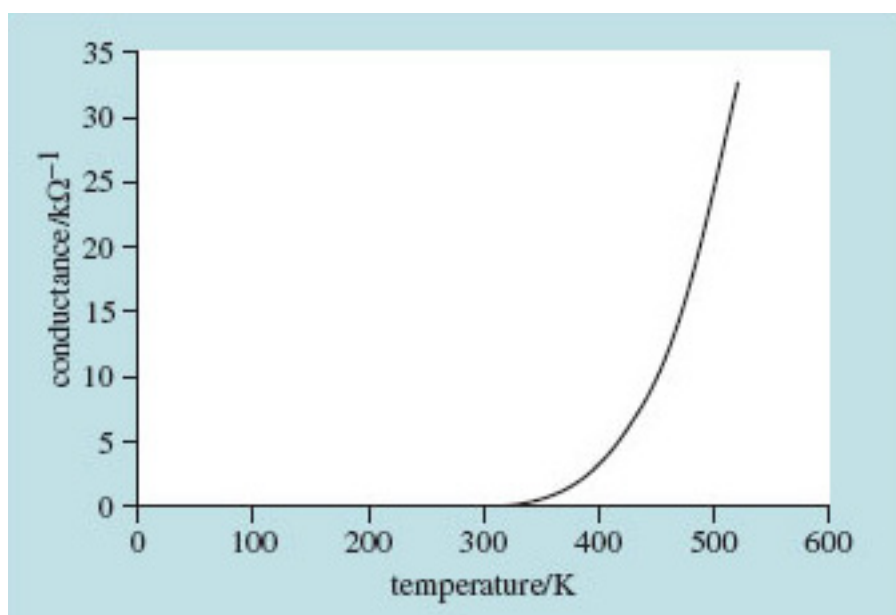


Figure 20 Conductance of a thermistor

### 4.3.3 Getting at the activation energy

The final trick I want to show you with Arrhenius's law is how to extract the constants  $r_0$  and  $E_a$  from experimental data. If the Arrhenius equation ([Section 4.3.1](#)) is 'turned inside out' by taking natural logarithms of both sides it becomes:

$$\ln r = \left( -\frac{E_a}{k} \right) \frac{1}{T} + \ln r_0$$

Comparing the logarithmic equation with the standard equation for a straight line,

$$y = mx + c$$

you can probably see how to get a straight line – if the Arrhenius model is valid,  $\ln r$  (for  $y$ ) against  $1/T$  (for  $x$ ) is what should be plotted.

How do you get the values of  $r_0$  and  $E_a$  from such a graph?

$r_0$  comes from the intercept at  $1/T=0$  and  $-E_a/k$  is the gradient (or slope)  $m$ .

[Box 11 Using Arrhenius plots](#) shows how to do this.

#### Box 11 Using Arrhenius plots

I'm going to describe an epoxy glue, which I'll call TickyTacky. It comes as two tubes of paste that are to be mixed together in equal proportions, and it is cured by heat. The manufacturer's notes say that, once mixed, TickyTacky can be stored in a freezer for several days and that it sets after 6 minutes at 142 °C, 10 minutes at 127 °C, or 30 minutes at 100 °C. That is sufficient data for an Arrhenius plot to be drawn. The rate of reaction is the reciprocal of the setting time, and temperatures need to be in kelvin. [Table 5](#) converts the data to the appropriate form and [Figure 21](#) (a) is the corresponding graph.

**Table 5 Data for TickTacky**

Temperature, $T$		Curing time	Reaction rate, $r$	$T^{-1} / \text{K}^{-1}$	$\ln r$
/ °C	/ K	/ min	/ min <sup>-1</sup>		
142	415	6	0.17	0.00241	-1.8
127	400	10	0.10	0.00250	-2.3
100	373	30	0.033	0.00268	-3.4

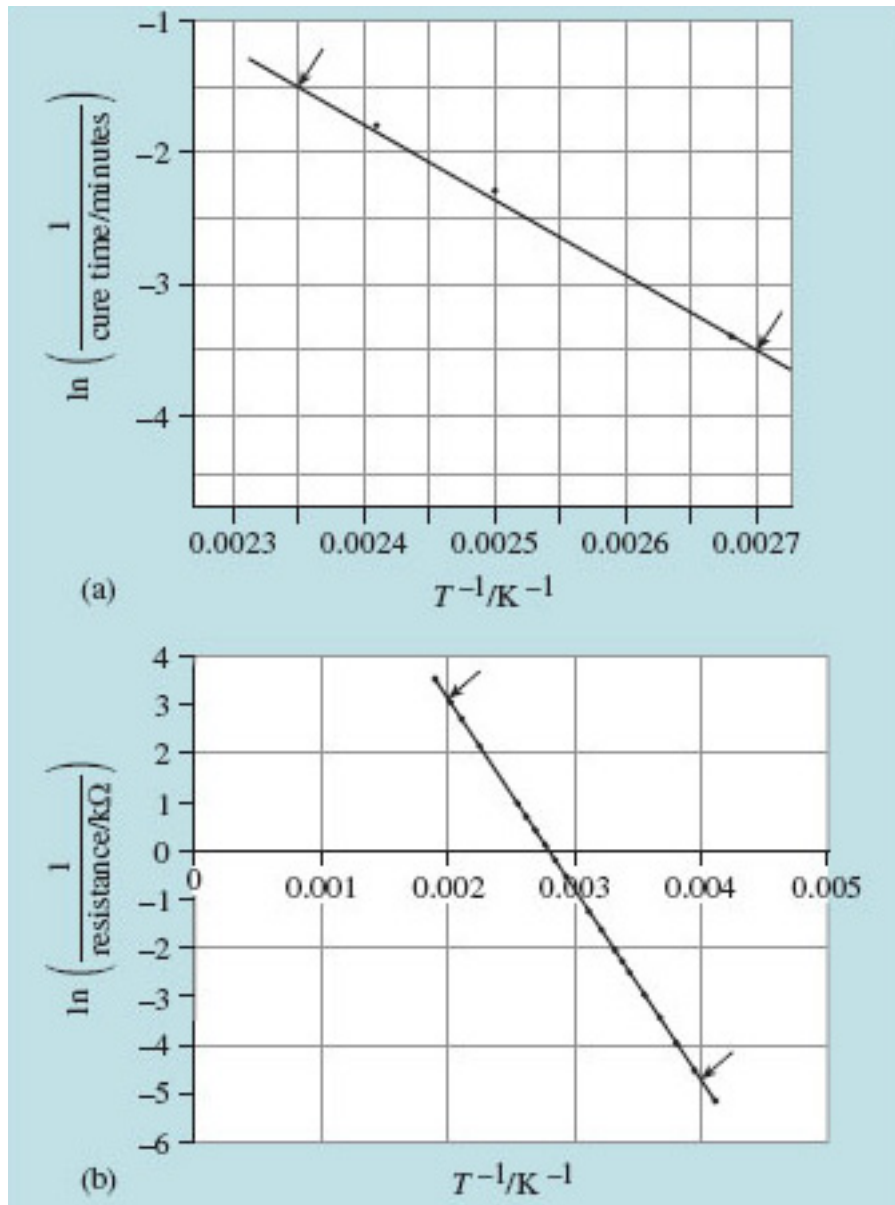


Figure 21 Arrhenius plots: (a) curing curve for TickyTacky, (b) conductance curve for a thermistor. The horizontal axis on both graphs is the reciprocal of temperature  $T$ , measured in kelvins. The vertical axis for (a) is the natural logarithm of the reciprocal of the cure time in minutes, while the vertical axis of (b) is the natural logarithm of the reciprocal of the resistance in kilohms

To find the activation energy for the curing reaction we must calculate the gradient of this logarithmic line. Using the arrowed points in [Figure 21\(a\)](#),

$$\frac{-E_a}{k} = \frac{-3.5 - (-1.5)}{0.00270 - 0.00235} = \frac{-2.0}{0.00035}$$

Taking  $k = 86 \times 10^{-6} \text{ eV K}^{-1}$  gives:

$$E_a = \frac{2.0 \times 86 \times 10^{-6}}{0.00035} = 0.49 \text{ eV}$$

The graph shows a typical awkward feature. Because measurements are over a narrow range of  $T$ , and the  $T^{-1}$  axis is very stretched, the intercept at  $T^{-1} = 0$  is not immediately readable. We need to proceed by calculation instead, taking the data for  $T = 400 \text{ K}$  (that is,  $T^{-1} = 2.50 \times 10^{-3} \text{ K}^{-1}$ ) and  $\ln r = -2.30$ ,

$$\ln r_0 = \ln r + \frac{E_a}{kT}$$

$$= -2.3 + \frac{2.0}{0.00035} \times (2.50 \times 10^{-3})$$

$$= 11.99$$

So  $r_0$  is  $e^{11.99}$ , which is approximately  $160\,000\text{ min}^{-1}$ .

## SAQ 6

(a) You can estimate a shelf-life for the glue 'TickyTacky' by seeing what the curing time would be for room temperature, based on an extrapolation of the Arrhenius plot ([Figure 21a](#)), or by substitution into the above equation; I found the curing time for  $20\text{ }^{\circ}\text{C}$  to be 2000 minutes, which is almost 1.5 days. Check this value for yourself and investigate if storage in a deep freeze at  $-15\text{ }^{\circ}\text{C}$  is worthwhile.

(b) The temperature-dependent conductance of a thermistor was shown in [Figure 20](#). It is plotted again in [Figure 21\(b\)](#) as an Arrhenius plot of  $\ln(1/\text{resistance})$  against  $1/T$ . From the gradient of the line, determine the activation energy for thermally induced conductivity in the material of the thermistor.

## Answer

(a) You need to go as far as  $T^{-1} = 0.00341$  for  $20\text{ }^{\circ}\text{C}$  and  $0.00388$  for  $-15\text{ }^{\circ}\text{C}$ . From that it appears that the straight-line extrapolation passes through  $\ln r = -7.6$  and  $-10.2$ , respectively. To find the reaction rate we need to take  $\exp(\ln r)$ .

Curing times follow from the reciprocal of the rates: 1950 minutes (1.3 days) and 27000 minutes (19 days). Storage in a deep freeze at  $-15\text{ }^{\circ}\text{C}$  is worthwhile for a week or so, after which time the paste will have become unworkable. [Table 6](#) summarises.

**Table 6**

Temperature, $T$		Curing time	Reaction rate, $r$	$T^{-1} / \text{K}^{-1}$	$\ln r$
$^{\circ}\text{C}$	K	/ min	/ $\text{min}^{-1}$		
20	293	1950	0.0005	0.00341	-7.6
-15	25	27000	0.000037	0.00388	-10.2

(b) The gradient of the straight line in the Arrhenius plot of [Figure 21\(b\)](#) is

$$\frac{\Delta_x}{\Delta_y} = \frac{3 - (-5)}{0.002 - 0.004} = \frac{8}{-0.002} = -4000$$

and this is  $-E_a/R$ , so

$$E_a = 86 \times 10^3 \times 4000 \text{ eV} = 0.34 \text{ eV}$$

## 4.4 Summary of Section 4

- Thermal energy is a random thing, so any group of particles possessing it will have a distribution of kinetic energies.
- The fraction of particles with energy greater than an amount  $E_1$  is proportional to  $\exp(-E_1/kT)$ .

- Thermally activated rates follow Arrhenius's law and are characterised by an activation energy.
- Diffusion in solids and electrical conduction in ceramics are thermally activated processes.

## 5 Sudden temperature effects

### 5.1 Sudden changes

The third category of thermal effects identified in [Section 2](#) are those associated with sudden changes. Here are some technically important examples where things change suddenly at a particular temperature:

- Pure water boils at 100 °C (at atmospheric pressure).
- An alloy of neodymium, iron and boron (sometimes written NdFeB, although this is not a quantitative chemical formula) that is widely used for permanent magnets in small, compact motors will lose its magnetisation when heated beyond 450 °C.
- Pure gold melts at 1063 °C (at atmospheric pressure).
- Silver and oxygen spontaneously combine to form silver oxide if the temperature is less than 1530 °C, although the rate of oxidation is extremely slow at ambient temperature. Above 1530 °C the reverse process is spontaneous and silver oxide decomposes into its component parts.
- The compound yttrium-barium-copper oxide (YBCO, pronounced 'ibco') loses all its electrical resistivity below about –180 °C (i.e. it becomes a superconductor).

In each of these examples matter is undergoing a change of phase. Establishing a little more precisely what that means is the goal of Section 5.2. After that, we'll see if there is any scope here for devising thermal cut-outs.

### 5.2 What's in a phase?

In an engineering and scientific context, a *phase* is an arrangement of atoms that is identifiable through its recurrence – the same pattern is found time and again. For instance, the compound of hydrogen and oxygen that we call water turns up all over the place in the same form as a runny, colourless liquid; this is a specific phase of the compound H<sub>2</sub>O. In water, the atoms apparently organise themselves according to what they are and the ambient conditions of temperature and pressure – there is no need for a separate template or a plan. That 'self-organisation' is the key to defining a phase. Water is a particular phase of hydrogen oxide (H<sub>2</sub>O).

There are three important features of a phase. Changing any one of these three features makes a new, distinct phase.

The first is the physical state of a phase: solid, liquid or gas. Water, ice and steam are different phases of H<sub>2</sub>O. The normal physical state of a phase depends upon both temperature and pressure.

However, there's more to defining a phase than merely the physical state. The second feature that may distinguish a phase is the arrangement of the atoms. For example, diamond and graphite are different phases of carbon owing to the very different crystal structures that the carbon atoms adopt in these materials (see [Figure 22](#)).

Graphite is the normal form for carbon under the conditions of temperature and pressure we are accustomed to, but at extremely high temperature and pressure the diamond

structure is the 'natural' one. We know this because somebody has found this out in the first place; every group of carbon atoms 'knows' this because that's the way the inter-atomic forces and thermodynamics dictate it must be. Given enough time, all diamonds that are not at those extreme conditions of temperature and pressure ought to change to graphite, according to the self-organising drive of thermodynamics. However, the transformation is so incredibly slow that they are a safe investment for a few million years – diamonds almost are 'forever'.

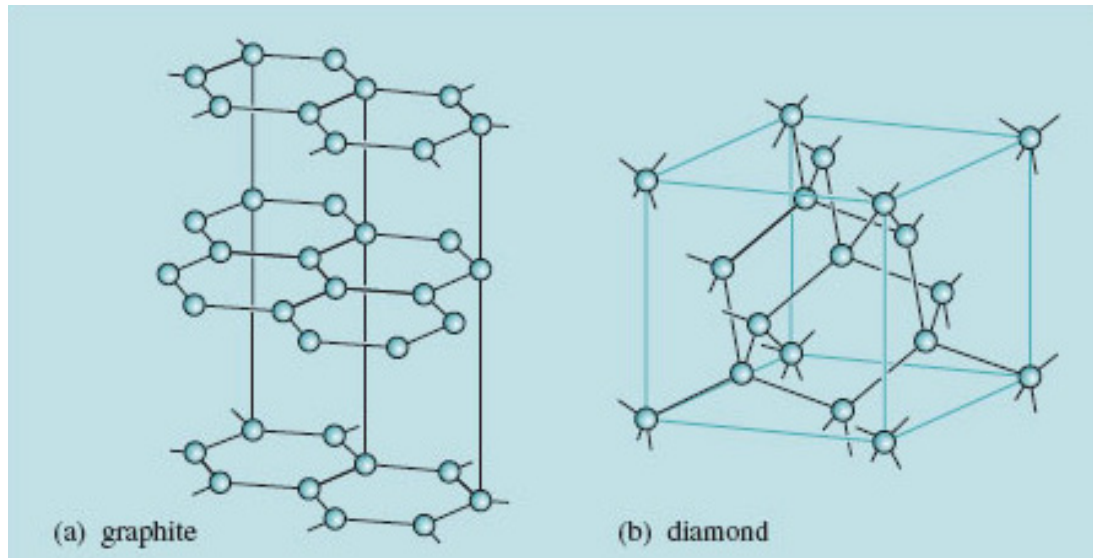


Figure 22 Graphite and diamond

Other structural phase changes can be effected and controlled under more modest conditions of temperature and pressure. In fact, manipulating structural phase changes in solids is at the heart of much metallurgy and materials engineering, and that is the basis of the steel industry in particular.

Structural phase changes are also more subtle. For instance, magnetism and various electronic and opto-electronic phenomena are very sensitive to atomic arrangements and are thereby susceptible to sudden changes of phase triggered by temperature and pressure.

Chemical composition can be a third defining feature of a phase. You may have come across 'phase diagrams' that are maps of the various phases that can be expected in simple two-part (binary) alloys over a range of composition and temperature.

Let's look again at my examples of sudden changes and identify the phases involved. I've started this in [Table 7](#) for you to complete as Exercise 6.

### Exercise 6

Complete the entries in the second column of [Table 7](#).

**Table 7**

Phenomenon	Phase changes
Water boils at 100 °C	.....
NdFeB loses magnetisation above 450 °C	.....
Gold melts at 1063 °C	.....

Silver spontaneously oxidises below 1530 °C    A solid + a gas → another solid

YBCO is superconducting below -180 °C    One solid → another solid

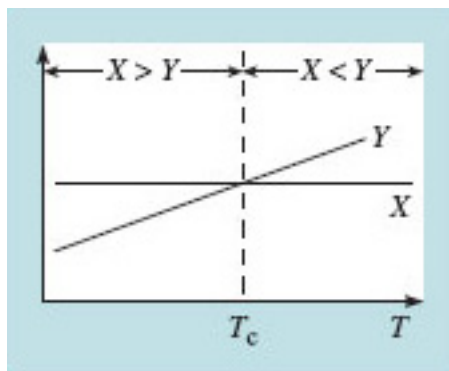
### Answer

**Table 8**

Phenomenon	Phase changes
Water boils at 100 °C	Liquid (water) → gas (steam)
NdFeB loses magnetisation above 450 °C	One (magnetic) solid → another (non-magnetic) solid
Gold melts at 1063 °C	Solid → liquid
Silver spontaneously oxidises below 1530 °C	A solid + a gas → another solid
YBCO is superconducting below -180 °C	One solid → another solid

## 5.3 Order and chaos

How can we explain a sudden switch of behaviour at a particular temperature? There must be two competing influences (say  $X$  and  $Y$ ) that depend differently on temperature. [Figure 23](#) indicates how a unique temperature (a so-called critical temperature,  $T_c$ ) arises, at which the balance changes from  $X > Y$  to  $X < Y$



**Figure 23** Competing influences with different temperature dependence

Now, if one influence is promoting order and the other is promoting chaos, it clearly matters which wins. Here, perhaps chaos is too strong a word – atoms in a liquid are more *disordered* than the same atoms locked together as a crystalline solid. Likewise, atoms in a gas are more disordered than those same atoms in the liquid state. The factor that promotes order in materials is the formation of cohesive bonds between neighbouring atoms, and the strength of the bonds changes only slowly with temperature. A tendency for disorder, on the other hand, seems to be a fundamental consequence of thermal energy.

Do you want to know more? Further details require an understanding of thermodynamics, and especially the concept of *entropy*, topics beyond the learning outcomes for this block, so I do not propose to delve deeper. What is important for now is that some characteristics

of materials switch abruptly at a critical temperature, whereupon a change of phase occurs.

## 5.4 Critical modelling

Critical phenomena are the simplest to model of the three classes of temperature-dependent changes we have been examining. We don't need a power series such as  $1 + \alpha T + \beta T^2 + \dots$ , nor exponentials such as  $\exp(-E_a/kT)$ . Instead we can describe the behaviour with logical expressions like these:

if  $T < T_c$ , then property=subcritical value (or function)

if  $T > T_c$ , then property=supercritical value (or function).

For example, at atmospheric pressure,

if  $T < 0^\circ\text{C}$ , then the 'natural' state of pure  $\text{H}_2\text{O}$  will be ice.

It follows too that if  $T=T_c$  then both phases co-exist:

if  $T=100^\circ\text{C}$  then pure  $\text{H}_2\text{O}$  may exist as water or steam.

But it's not all ice, water and steam. Magnets, superconductors, aluminium alloys, steels and [Box 12 Shape memory alloys](#) are all solid engineering materials that make much use of critical phase changes. Are there effects here that could be used for making thermal switches for our electric water-boiler?

### Box 12 Shape memory alloys

Components made from shape memory alloys (SMAs) have the ability to adopt a predetermined shape (one that is formed when its temperature is above some transformation temperature). Yet, when an SMA is 'cold', that is below its transformation temperature, it has a relatively low yield strength and can be plastically deformed into some other shape. On crossing above the transformation temperature again, the initial shape is recovered – you can imagine the excitement that must have accompanied the accidental discovery of this effect.

For instance, consider a helical spring formed from an SMA in its higher-temperature state (you can specify that to be anywhere in the range  $-100$  to  $+100^\circ\text{C}$ ). It will keep this shape even when cooler, though in the low-temperature state it will be considerably easier to stretch or squash. Suppose that, while cool, it is 'sprained' by pulling it out beyond its elastic limit so that when relaxed it is now twice the original length. On warming again past the transformation temperature it will begin to return to its original shape.

Can we do anything useful with it? Yes. If it is prevented from recovering the original form, stresses within the material will generate large forces on any external constraints. This phenomenon therefore provides a smart mechanism for remote actuation.

You should recognise that some structural phase change is behind this behaviour. We don't need a complete understanding of the mechanism on an atomic scale to make useful devices. Realising that phase changes are involved is enough, as it tells us to expect that we might be able to exercise some control over the transformation temperature through adjustments to chemical composition and microstructure.

The most common shape memory material is an alloy of almost equal parts nickel and titanium; it's called Nitinol. This particular alloy has very good electrical and mechanical properties, long fatigue life, and high corrosion resistance. The temperature at which the alloy 'remembers' its high-temperature form when heated can be adjusted by slight changes in alloy composition and through heat treatment. Above the transformation temperature, in the 'high' phase, the atoms are arranged in a pattern that metallurgists recognise by calling it face-centred cubic. In the 'low' phase the atoms are slightly displaced to take up a so-called body-centred tetragonal arrangement. In the process of rearrangement, no atoms move very far with respect to surrounding atoms, though as a whole large displacements of material can occur. [Table 9](#) gives some typical physical properties for a nickel-titanium SMA.

**Table 9 Properties of binary Ni-Ti shape memory alloys**

Property	Value
Density / $10^3 \text{ kg m}^{-3}$	6.45
Melting temperature / $^{\circ}\text{C}$	1240–1310
Resistivity / $\mu\Omega \text{ m}$	0.82 ('high' phase), 0.76 ('low' phase)
Ultimate tensile strength / MPa	754–960
Typical elongation to fracture / %	15.5
Typical yield strength / MPa	560 ('high' phase), 100 ('low' phase)
Approximate elastic modulus / GPa	75 ('high' phase), 28 ('low' phase)
Approximate Poisson's ratio	0.3

As an actuator, Nitinol is capable of up to 5% strain recovery and can develop internal restoration stresses of around 300 MPa. If the transition temperature of an SMA is chosen such that room temperature is well below the transformation point of the material, then an electric current passed directly through the SMA is a handy way to initiate the recovery of its shape. The current generates enough heat to trigger the phase transformation. The SMA is heater, sensor and actuator – neat!

### Example 3

Estimate the amount of force and distance of travel that could be triggered by warming a Nitinol wire 0.25 mm in radius and 20 mm long that had been 'permanently' stretched (5% strain) when 'cold'.

#### Solution

5% strain makes the 'cold' wire 1 mm longer. Using the figure of 300 MPa given for the level of stress driving the recovery of the original unstretched length, the force developed over the cross-section of the wire would be:

$$F = 300 \times 10^6 \times \pi (0.25 \times 10^{-3})^2 \approx 60 \text{ N}$$

The recovery stress could lift a 6 kg mass a through a good fraction of 1 mm.

Shape memory alloys, however, are not appropriate for all actuator applications. You've got to take into account the forces, displacements, temperature conditions and cycle rates required in any particular situation. The advantages of Nitinol become more pronounced as the size of the application decreases. Large mechanisms may find solenoids, motors and electromagnets, or even explosive bolts, more appropriate. But in applications where such actuators cannot be used, shape memory alloys provide an excellent alternative.

SMA's also show *superelastic* behaviour when deformed at a temperature which is slightly above the transformation temperature. This effect is caused by stress-induced formation of the 'low' phase above its normal temperature. Because it has been formed above its normal temperature, the 'low' phase reverts immediately to an undeformed 'high' phase arrangement as soon as the stress is removed. This process provides a very springy, 'rubber-like' elasticity in these alloys with as much as 6% elastic strain beyond yield point.

Products containing SMA's have been around for many years, but we are often unaware of their presence because they are out of sight. One of the more visible applications is in 'indestructible' spectacle frames; these can be bent and twisted to a remarkable extent and then regain their original shape.

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## 5.5 Summary of Section 5

- The phase of a material is characterised by its physical state (e.g. solid, liquid or gas), a distinctive arrangement of the atoms, and its chemical composition.
- Material properties can change suddenly as the temperature increases or decreases, corresponding to changes of phase and the degree of order associated with the arrangement of atoms.
- Shape memory alloys are examples of a wide range of useful engineering materials that exploit critical phenomena arising from phase changes.

## 6 The water boiler again

### 6.1 Review

Let's see if we have made any progress in studying thermal effects. The following SAQ is based on [Exercise 3](#), although this time I have a higher expectation of how much you should be able to do.

#### SAQ 7

Here is a list of twelve items to fit into [Table 10](#) as A to L. Place at least *three* in each of the categories – gradual, accelerating and sudden.

1. Creep deformation (slow change in shape of a material under stress)
2. Homogenisation of castings (reduction of non-uniformity of composition)
3. Glass shattering under thermal shock
4. Convection in a domestic water system
5. Quenching (sudden cooling from high temperature) and tempering (reheating to a moderate temperature to allow regrowth of crystals and thereby improve ductility) of steel
6. The temperature dependence of resistivity demands highly uniform cross-section of a lamp filament
7. p–n junctions (regions in a semiconductor where differently doped regions meet) are stable against homogenisation (don't intermix) at room temperature
8. Fuses in electrical circuits
9. Superconducting transitions are all at inconveniently low temperatures (so far!)
10. Provision of surface compressive stress enables 'safety glass' for car windows
11. Onset of unwanted reactions in chemical processes
12. Silicon melts at 1414 °C, so diffusion of dopants to control semiconducting properties cannot be done at arbitrarily high temperatures.

#### Answer

The completed version of the table was given in the answer to [Exercise 3](#).

### 6.2 Refining the specification

The ideas for the boiler cut-out switch can now be based on some real knowledge about temperature effects. You are now ready to tackle the next exercise.

#### Exercise 7

List four temperature-dependent changes in material properties that could be exploited in the automatic cut-out switch for an electric water-boiler.

### Answer

Here are my suggestions:

- Expansion of a solid
- Expansion of a gas
- Phase change in a solid
- Phase change in the water
- Change in electrical conductivity of a metal
- Change in electrical conductivity of a thermistor.

**Table 10 Examples of gradual, accelerating and sudden changes**

		Gradual	Accelerating	Sudden
Service	Opportunity	Electrical resistance thermometer	Heat-curable glues	Onset of ferro-electric properties
		Bimetal switches	Enhanced performance of detergents in hotter water	Can leave cooking to simmer
	Challenge	A	B	C
		Crazed glaze on crockery	High-temperature limit on semiconductor performance	Some permanent magnet materials demagnetise at modest temperatures
		Need to compensate timer in clocks and watches	Excessive corrosion of high-temperature components	Water pipes burst through freezing
Process	Opportunity	D	E	F
		Density variation provides convective mixing in castings	Temperature control of workability of glass	Chemical reaction selection by use of critical temperature
		Metal tyres and bearing sleeves can be shrink-fitted to wheels/shafts	Sintering of powders to continuous solid (a route to near net shape forming)	Melting allows casting processes
	Challenge	G	H	I
		Continuous welded railway lines may buckle in extreme heat or crack in extreme cold	Over-ageing of precipitation-hardened alloys	Upset metallurgy in the heat-affected zones of welds
			Continued diffusion of previously implanted dopants in subsequent processing of microcircuit chips	Cracks in porcelain due to crystal transition in quartz
	J	K	L	

In the specific case of the water-boiler we have been looking at, what is wanted is a cut-out switch (not a thermostat), so our specification is for the switch to operate at a temperature close to the boiling point of water, and to be re-settable manually once triggered. This overall cut-out function requires a kind of irreversibility to be built into the device mechanism. What I mean is that, having reached the operating temperature, the device has to flip into a state where it has caused the current to be switched off, such that, without a manual reset, it will not start to pass current again once the water has started to cool.

All the thermal effects listed in my answer to Exercise 7 are fully reversible – as we would want them to be because the switch is to be reused many times over. For example, when a metal is allowed to cool again after being heated to a given temperature, its electrical resistivity will be the same as it was at that temperature before it was heated (otherwise a platinum resistance thermometer would be pretty useless). This means that to make the device that is wanted, some kind of mechanism has to be introduced to do the flipping, that will not flip back by itself until helped by the user. Another good reason this is needed in this case, where a flow of electric current is being interrupted, is that the switch-off should be done as sharply as possible to avoid arcs and sparks.

### Exercise 8

For the four thermal effects you selected in the last exercise, describe how each could be used in a thermal cut-out switch operating at or near the boiling temperature of water.

#### Answer

Here are my suggestions, based on my answer to Exercise 7. They are not necessarily the best ways of using each effect. The fun is in trying to think up a really neat way of getting the result you want.

- *Expansion of a solid:* Two metals with different expansion coefficients are joined together to form a bimetallic strip. This bends as the temperature changes. At the right temperature, the strip has bent far enough to act on an over-centre latch to open a switch.
- *Expansion of a gas:* A sealed capsule of gas exerts a temperature-dependent pressure on a diaphragm, which has been formed to be domed slightly inwards. At the right temperature this dome snaps outwards, opening the switch.
- *Phase change in a solid (shape memory alloy):* This works in the same way as the bimetallic strip, except that the deformation of the shape memory is caused by a phase change, not a linear expansion, and so will happen all at once at a sharply defined temperature.
- *Phase change in the water:* This could be a microphone picking up the sound of the steam bubbles as the water boils. This is detected in an electronic circuit that opens either a transistor switch or an electromechanical relay.
- *Change in electrical conductivity of a metal:* This could be detected by an electronic circuit which then operates a switch, as in the microphone system above.
- *Change in electrical conductivity of a thermistor:* This would be similar to the resistor-based system, but with the difference that the sensor output would be an exponential function of temperature.

The next step of selecting and modelling the most suitable solution has to be taken with reference to the specification and other considerations, such as whether the company wants to manufacture the devices itself, perhaps making use of equipment it already has and techniques it already knows.

One part of the functional specification that could be of importance to the user is the repeatability with which the device trips at the set-point temperature. This might be wanted where the water is to be used in a temperature-dependent process, and product consistency is a requirement, or if the water has to have reached a temperature very close to boiling. On the other hand, there may be a market for switches that can be set to trigger at any temperature chosen by the user.

### SAQ 8

Identify a type of thermal effect (gradual, accelerating, or sudden) likely to give:

- (a) a repeatable switching temperature;
- (b) an adjustable switching temperature.

For each, explain why.

#### Answer

*Sudden:* These effects produce dramatic changes in material properties over very small temperature ranges, determined by the physical process itself.

*Gradual:* These effects are linear or nearly linear changes in the properties. The device can be arranged to be adjustable by having a movable set-point.

### Exercise 9

[Table 11](#) lists the candidate solutions from my answer to the previous exercise, against some of the criteria for the water-boiler listed in the example at the beginning of this course. If you had some candidate solutions of your own, add these to the table. Devise a rating or scoring system, and obtain a rank-ordering of the candidate solutions.

**Table 11**

	Accuracy	Reliability	Ruggedness	Cheapness
Bimetallic				
Gas capsule				
Shape memory				
Microphone				
Metal resistance				
Thermistor resistance				

### Answer

Here is a simple rating scheme in which I have given scores of 1, 2 or 3 and simply added together the scores for each candidate. It takes no account of the relative importance of each criterion. If it had, the rating scheme would have looked more like the example in OpenLearn course T207\_1 *The engineer as problem-solver: the nature of problems* of choosing a TV set, where each score against a particular criterion is multiplied by an 'importance factor'. So the answer here rates shape memory as the winner, ahead of bimetallic, whereas the bimetallic solution is in fact the commonest. This is probably because in most real-life applications, accuracy is less important than cost.

**Table 12**

	Accuracy	Reliability	Ruggedness	Cheapness	Score (higher=better)
Bimetallic	1	3	3	3	10
Gas capsule	1	2	2	2	7
Shape memory	3	3	3	2	11
Microphone	3	1	1	1	6
Metal resistance	3	2	2	3	10
Thermistor resistance	3	2	2	3	10

You will have realised when trying the last exercise that much of the information you supplied to perform the ranking task was largely guesswork – for instance, off the top of your head you can't be really sure whether the gas capsule approach will be cheaper or more expensive than the shape memory solution. Another example is the comparison of the accuracy of the thermistor and the metal. At or near the boiling point of water, the percentage change of resistance of the metal per degree centigrade is the same as at lower temperatures – at least that's what our linear model presumes. But for the thermistor, the change is an accelerating one, and its rate of change at a given temperature depends both on the value of the activation energy of the electrical conduction process,  $E_a$ , and on the temperature itself. Without doing the calculations for specific materials, you don't know which approach will provide the greater accuracy.

Therefore we can say that to make a good decision, more work needs to be done. But at least now, the tasks are very specific fact-finding or mathematical modelling exercises. It leads me on to an observation that is true of any solution-finding undertaking. Whatever the details of the decision-making process used to select the preferred solution from the candidates presented, none of it is of much value unless the information that informs that process is of the highest possible quality. For the engineer, that information is:

- the identification and expression of the need
- the detailed specification
- good-quality ideas, based on a sound understanding of the underlying principles
- facts and figures (accurate and reliable data) relevant to the selection criteria.

## 6.3 Summary of Section 6

- In trying to find solutions to the specific problem of the water-boiler, where the need was for a particular response to a certain temperature change, we have gone into the principles behind the three classes of temperature effect – gradual, accelerating and sudden. This has provided you with mathematical models that are of real use in putting definite numbers to the magnitudes of these effects in any designs that are proposed. The ability to do this is just as important where temperature effects are an unwanted complication, as when the aim is to exploit them.
- Since temperature is an agent of change that may act throughout our engineered world, it is important to realise that knowledge gained here about temperature effects is generally applicable.
- The topic of this course was also a worked example of the problem-solving methodology described in OpenLearn course T207\_1 *The engineer as problem-solver: the nature of problems*. As a practical embodiment of the approach described in more abstract terms before, it helps to demonstrate by experience the logic of the progression from need towards solution.

## Conclusion

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This free course provided an introduction to studying Technology. It took you through a series of exercises designed to develop your approach to study and learning at a distance, and helped to improve your confidence as an independent learner.

## Acknowledgements

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This free course is adapted from a former Open University course called 'Engineering: mechanics, materials, design (T207).'

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