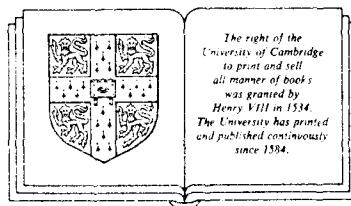# An introduction to thermal physics

C. J. ADKINS

An introduction to thermal physics

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Preface

In recent years there have been marked changes in both the style and the content of physics courses at all levels. The general trend has been towards an increased emphasis on fundamental principles and microscopic explanations. As a consequence, the relative importance attached to various topics has changed, some new ones have been introduced and others, such as geometrical optics, virtually eliminated. Another consequence is that less detailed knowledge of numerous experimental techniques is now expected; in general, only a familiarity with the principles of various methods is required. These changes are reflected in revised syllabuses and call for a new generation of textbooks. It is in the spirit of these changes that this book is written.

The area covered corresponds very roughly to the traditional topics of *heat* and *kinetic theory* together with those parts of *properties of matter* for which there are simple explanations in terms of interatomic forces.

In level, the book is intended for use at universities and technical colleges in physics, engineering, chemistry or other science courses that require an elementary knowledge of thermal physics. It can be used in two ways: either as an introductory text, setting a firm foundation for further work in more specialized courses, or as an account, sufficient in itself for those requiring only a basic knowledge of the subject. It should also be useful in the science libraries of school sixth forms as a reference book that can help to point the way from school physics to the more mature approach of tertiary study. A familiarity with elementary calculus is assumed as its use is essential in the derivation of some of the fundamental results. However, when a result may also be derived without the use of calculus, an alternative derivation is generally given.

SI units are now essentially universal throughout science teaching and the text uses the system exclusively. It also generally follows the current recommendations of the Symbols Committee of the Royal Society as regards conventions for showing physical quantities and their units, and it incorporates the modern definitions of temperature scales.

The development of a sensibility towards the nature and magnitude of physical processes is an essential part of an education in physics and I consider the use of quantitative problems and exercises an essential means to this end. At the end of each chapter I have assembled a collection of problems. Many are original and some are inspired by ideas which have appeared in examination questions and in other texts. The problems are grouped according to the chapter subsections and, in each case, follow a brief summary of the key ideas of the relevant subsection. This makes it possible to work through the problems in parallel with the study of the text, so using them as an aid to learning. The arrangement is also useful for revision purposes. Generally I have avoided the inclusion of discursive questions, except where they are essential to cover certain key topics which cannot be tested quantitatively at that stage of the book. I have not included explicit worked examples separated out within the text. There are several reasons for this, among which is the fact that numerical examples are worked out as part of the narrative, and also, in many cases, the quantitative development of a key result serves to illustrate how that key result may be used.

Despite its title, this is not an easy book, for although it only deals with the *foundations* of thermal physics, the text challenges the reader to think deeply and carefully about the concepts and methods of the subject. It also seeks to show the relevance of the subject by relating these concepts and methods to the everyday physical world. Thus, although a simplistic reading will yield some understanding of thermal physics, more thoughtful study will bring extra rewards.

I should like to thank my wife, Tessara, for her suport and encouragement while I was writing this book, and to thank her and Jean Millar for their help with some of the illustrations. I am also most grateful

My objective throughout the detailed writing of this book has been to achieve a clear and stimulating exposition: to write a book which is easy to learn from. Those who use it must judge whether I have been successful.

C. J. Adkins
Cambridge, 1986

Units, Symbols and Conventions

This book uses SI (Système International) units and generally follows the current recommendations of the Symbols Committee of the Royal Society as regards symbols and conventions of notation.*

The names and symbols for the SI base units are:

Physical quantity	Name of SI unit	Symbol for SI unit
length	metre	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
thermodynamic temperature	kelvin	K
luminous intensity	candela	cd
amount of substance	mole	mol

The SI units of certain common physical quantities have special names. Some of those used in this book are listed in the table below.

Angles, though formally defined so as to be dimensionless (see Appendix, section A.1), are sometimes considered as supplementary units:

Physical quantity	Name of SI unit	Symbol for SI unit
plane angle	radian	rad
solid angle	steradian	sr

The International System has a set of prefixes which may be used to construct decimal multiples of units.†

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f			
10^{-18}	atto	a			

Physical quantity	Name of SI unit	Symbol for SI unit	Definition of SI unit	Equivalent forms
force	newton	N	$m\ kg\ s^{-2}$	$J\ m^{-1}$
energy	joule	J	$m^2\ kg\ s^{-2}$	$N\ m$
pressure	pascal	Pa	$m^{-1}\ kg\ s^{-2}$	$N\ m^{-2}, J\ m^{-3}$
power	watt	W	$m^2\ kg\ s^{-3}$	$J\ s^{-1}$
electric charge	coulomb	C	$s\ A$	$A\ s$
electric potential difference	volt	V	$m^2\ kg\ s^{-3}\ A^{-1}$	$J\ A^{-1}\ s^{-1},$ $J\ C^{-1}$
electric resistance	ohm	Ω	$m^2\ kg\ s^{-3}\ A^{-2}$	$V\ A^{-1}$
electric capacitance	farad	F	$m^{-2}\ kg^{-1}\ s^4\ A^2$	$A\ s\ V^{-1}, CV^{-1}$
inductance	henry	H	$m^2\ kg\ s^{-2}\ A^{-2}$	$V\ A^{-1}\ s$
frequency	hertz	Hz	s^{-1}	

* *Quantities, Units and Symbols*, The Royal Society (London, 1975).   † μ, the prefix meaning one millionth, is the Greek letter *mu*.

Symbols for units are always printed in roman (upright) type while symbols for physical quantities such as p for pressure are printed in italic (sloping) type.

The value of a physical quantity is always equal to the product of a numerical value and a unit. Thus, the physical quantity, the mass m_e of the electron is given by

$$m_e = 9.11 \times 10^{-31} \text{ kg}$$

In this equation, the magnitude and unit of the physical quantity are equated across the equals sign. An equivalent dimensionless equation is

$$m_e/\text{kg} = 9.11 \times 10^{-31}$$

Here, the solidus (/) on the left hand side represents division in the usual way: the physical quantity (mass of an electron) is divided by a unit of mass (the kilogram) and the result is a pure number, 9.11×10^{-31}, the number of kilograms in the mass of one electron.

The use of the solidus to represent division of a physical quantity by a unit may be applied in several other ways.

a) *More complex equations* relating physical quantities may often be written concisely and unambiguously using the solidus notation. For example, the molar heat capacity at constant pressure of copper C_{pm} depends on thermodynamic temperature T at low temperatures according to the equation

$$C_{pm}/\text{kJ K}^{-1}\text{ mol}^{-1} = 1.94\,(T/\Theta)^3$$

where $\Theta = 348 \text{ K}$ is the 'Debye Temperature' of copper. Here, kJ K^{-1} mol^{-1} is the unit in which the heat capacity is measured so that the left hand side is a dimensionless number. Similarly, the term in brackets on the right is dimensionless because both T and Θ are temperatures measured in kelvins. Clearly, the number 1.94 is also dimensionless to that the equation is dimensionally homogeneous throughout. An alternative way of giving the same information would be to write

$$C_{pm} = a(T/\Theta)^3$$

where

$$a = 1.94 \text{ J K}^{-1}\text{ mol}^{-1}$$

In this form, dimensional quantities are equated across the equals sign. But it is *wrong* to write

$$C_{pm} = 1.94\,(T/\Theta)^3$$

for this equation is dimensionally inconsistent: the

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left side has dimensions of heat capacity while the right side is dimensionless. The equation only 'works' if C_{pm} is measured in the right units. An equation should express a physical fact; and since a true physical fact is true regardless of how (in what units) it is measured, this last form is unacceptable.

b) *In tables and graphs* the numbers entered or plotted are dimensionless so that the labelling of the table headings or graph axes should also be dimensionless. Thus, a graph of pressure against temperature might have its axes labelled 'pressure/mmHg' and 'temperature/K' respectively. The result of dividing the physical quantity pressure by the unit of pressure mmHg is a pure number, and so is the result of dividing temperature by kelvins. The axes are therefore calibrated in pure numbers and it is the relationship between two pure numbers which the graph displays. It is *not* correct to label the axes 'pressure (mmHg)' and 'temperature (K)' because, following normal notation, these would mean either pressure multiplied by mmHg and temperature multiplied by kelvins, or pressure, a function of the unit mmHg, and temperature, a function of the kelvin. Either alternative is nonsense. Nevertheless, such forms have been used in the past with the meaning 'the numbers on this axis give the magnitude of the pressure when it is measured in mmHg', etc. Clearly, there is no need to have to adopt a special meaning to the use of brackets when the solidus notation is physically and mathematically correct and totally unambiguous.

c) The solidus notation is also useful for *changing the units in which a physical quantity is measured*. It reduces conversion of units to routine algebra. Suppose the speed u of a car is 90 km h^{-1} and we wish to find its speed in m s^{-1}. We are given $u/\text{km h}^{-1} = 90$ and we want $u/\text{m s}^{-1}$. Following the normal rules of algebra we may write

$$u/\text{m s}^{-1} = (u/\text{km h}^{-1}) \times (\text{km/m}) \times (\text{s/h})$$

The first bracket on the right is the number given, the second is the pure number which results from dividing 1 km by 1 m, namely 1000; and the third term on the right is the pure number which results from dividing the unit of time, 1 s by the unit of time 1 h, namely 1/3600. Thus,

$$u/\text{m s}^{-1} = 90 \times 1000 \times 1/3600 = 25$$

or

$$u = 25 \text{ m s}^{-1}$$

Finally, we list the symbols used in this book.

ROMAN LETTERS

a	constants
b	constants
c	molecular speed
d	distance
	infinitesimally small change in
e	spectral emissive power
	electronic charge
	base of natural logarithms
f	number of degrees of freedom
	a function
g	acceleration of free fall
h	Planck constant
ι	an integer
k	Boltzmann constant
l	mean free path
m	mass
n	number of moles
	number density
p	pressure
r	radius, distance
t	Celsius temperature
	time
x	a variable
y	a variable
z	coordination number
	a variable
A	area
C	heat capacity
	capacitance
E	Young modulus
	electromotive force
	electric field strength
F	force
H	scale height
I	current
J	joule
	current density
K	kelvin
	bulk modulus
L	length
	latent heat
	inductance
	Lorenz number
M	molar mass
P	power
	probability
Q	heat
	charge

R	resistance
	molar gas constant
S	entropy
	molecular diameter
T	thermodynamic temperature
U	internal energy
V	volume
	potential difference
v	speed
W	work

GREEK LETTERS

Letter	Name	Meanings
α	alpha	spring constant, linear expansivity, absorptivity
β	beta	cubic expansivity
γ	gamma	ratio of principal heat capacities, surface tension
δ	delta	small change in
Δ	delta (cap.)	finite increment of
ϵ	epsilon	energy, emissivity
η	eta	viscosity, efficiency
θ	theta	angle
Θ	theta (cap.)	empirical temperature
κ	kappa	compressibility
λ	lambda	thermal conductivity, wavelength
μ	mu	one millionth
ν	nu	frequency
π	pi	ratio of circumference to diameter of circle
ρ	rho	density
σ	sigma	electrical conductivity, Stefan–Boltzmann constant
ϕ	phi	potential
Φ	phi (cap.)	flux density
ω	omega	angular frequency
Ω	omega (cap.)	solid angle, ohm

MATHEMATICAL NOTATION

$+$	plus
$-$	minus
$=$	equal to
$\neq$	not equal to
$\approx$	approximately equal to
$\propto$	proportional to
$<$	smaller than

$>$	larger than	$\left(\dfrac{\partial f}{\partial x}\right)_y$	partial differential coefficient of $f(x,\ y)$ with respect to x when y is held constant
$\leqslant$	smaller than or equal to		
$\geqslant$	larger than or equal to	$\mathrm{d}f$	total differential of f (infinitesimal change in f)
$\ll$	much smaller than		
$\gg$	much larger than	$\int f(x)\,\mathrm{d}x$	the integral of $f(x)$ with respect to x
$\langle a \rangle, \bar{a}$	mean value of a	$\oint f(x)\,\mathrm{d}x$	the integral of $f(x)$ with respect to x around a closed path
$f(x)$	function of x		
$\lim_{x \to a} f(x)$	the limit to which $f(x)$ tends as x approaches a	$e^x,\ \exp x$	exponential of x
		e	base of natural logarithms
Δ	finite increment of	$\ln x$	natural logarithm (logarithm to the base e) of x
δ	small change of		
$\dfrac{\mathrm{d}f}{\mathrm{d}x}$	differential coefficient of $f(x)$ with respect to x	$\lg x$	common logarithm (logarithm to the base 10) of x

Contents

1 Temperature

1.1 INTRODUCTION

Thermal physics is the study of those properties of materials which are affected by temperature. It is an enormous field, having something to say about subjects as diverse as the expansion of a solid, the internal constitution of stars and why the electrical resistance of some metals vanishes at low temperatures.

The job of the scientist is to observe nature, to try to recognize the regularities in its behaviour and to seek to link those regularities together by laws and principles. For example, it is often found that the current flowing in an electrical conductor is proportional to the applied potential difference; this regularity is called Ohm's law.

When the scientist tries to 'explain' his observations, there are two levels of explanation he can attempt. He may content himself with ideas relating to the behaviour of matter in bulk (e.g. Ohm's law). This is the *macroscopic* approach. In the area of thermal physics it leads to the subject called *thermodynamics*. This branch of physics developed most rapidly during the last century in connection with the study of machines, such as the steam engine, which supplied power for the new industries; but, it was soon realized that the laws of thermodynamics were very fundamental and of importance in areas quite different from power engineering where they were developed. The laws of thermodynamics provide a theoretical framework which is used in many branches of modern science. A typical result which may be derived by thermodynamics is the Clausius–Clapeyron equation (page 111) which connects the variation with temperature of vapour pressure with latent heat.

At the other level of explanation, the scientist tries to base his understanding on ideas of the nature and properties of matter at the atomic level. This is *microscopic* physics. An example is the kinetic theory of gases (chapter 3) which 'explains' the bulk behaviour of gases in terms of the properties of the molecules of which the gas is composed. While models and laws relating to matter at the atomic level play no direct part in macroscopic physics, they are the essence of microscopic physics. In thermal physics, the microscopic approach leads to the subject called *statistical mechanics*. A typical result of the arguments of statistical mechanics is the Maxwell distribution (page 54), which gives the probabilities of different molecular speeds in a gas.

Both macroscopic and microscopic approaches are of value, as we shall see later in this book, for there are times when we need to explain in terms of fundamental laws operating at the atomic level, while there are other times when to involve ourselves with detailed microscopic models would be a positive encumbrance.

1.2 SOME BASIC IDEAS

We call the object we are investigating the *system*. It could be a volume of gas, or a spring, or a refrigerator, or a solid in the process of melting. We shall often illustrate our arguments by taking as a model system a given mass of gas in a cylinder with a frictionless piston. This is a good model to take because it is easy to visualize what happens when we heat it or do work on it by compressing it.

We describe the *state* of the system in terms of appropriate *parameters* or *variables*, such as mass, pressure, volume, density, temperature. When a system is in a given state, we will always get the same results for any measurements we may make on it. The variables are not all independent; some are related to one another. For example, density is mass/volume. For simple systems of given mass we find that we need to fix the values of *two* variables in order to fix the state of the system. For our given mass of gas, for example, we find that, if we first set the volume, we may still adjust the pressure to any value we please (by varying the temperature), but once the pressure is set also, there is no other property which can be varied. We therefore

say that the gas has two *degrees of freedom*: we are free to choose two of the variables as we like, but then all the other parameters will have taken up definite values which we cannot adjust. This means that any mathematical equation connecting system variables must have at least three variables in it: the values of two must be known in order to determine the state of the system and so fix the value of a third. Thus, the equation of state of an ideal gas (page 40) connects pressure, volume and temperature: $pV/T = $ constant. Again, this is why we have two common heat capacities. A heat capacity is the rate at which heat is absorbed as we change the temperature (section 2.3); but since simple systems have two degrees of freedom, we do not know *how* the system is going to change as the temperature is changed unless more information is given. Two simple cases are that the system should be kept at constant volume or at constant pressure. Such a condition is called a *constraint* because it constrains the system to change in a certain way. Any constraint removes the second degree of freedom so that now a definite amount of heat is absorbed as the temperature is changed.

In developing the ideas of temperature, heat, and so on, we shall be interested in the ways systems interact with one another. There are two kinds of interaction. In *work-like* interactions, one system does work on another (figure 1.1): a force moves through a given distance as in compressing a gas or stretching a spring, or a battery will do work in charging a capacitor because it forces charge to flow against an opposing potential difference. The other kind of interaction is *thermal* and is typified by flow of heat when we place a hot body in contact with a cold one (figure 1.2). In both kinds of interaction,
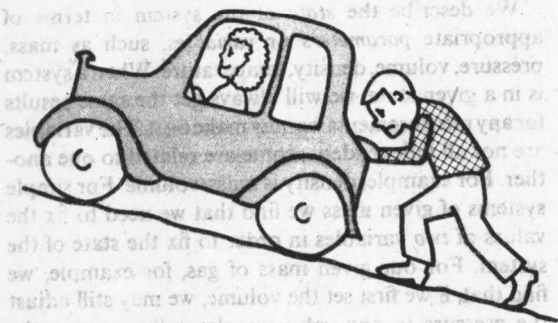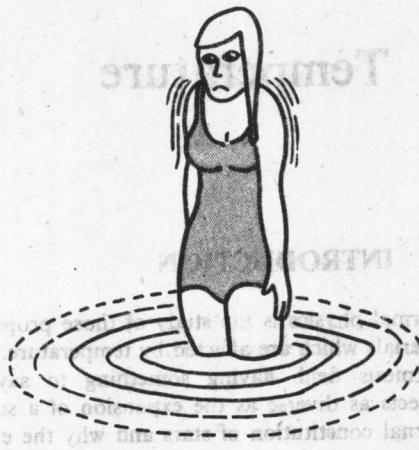

Figure 1.2   A thermal interaction

energy is transferred from one system to another; the difference is that in work-like interactions the process involves some sort of large scale motion (all the molecules of the piston move forward together as the gas is compressed), whereas in thermal interactions the energy is associated with disordered thermal motions of the atoms of which the system is composed: the random motions of the molecules of a gas or the vibrations of the atoms of a solid. When a thermal interaction takes place, the atoms of the cooler system are excited into more violent thermal motion by contact with the hotter (more energetic) atoms of the hotter system.

If two systems are placed in contact in such a way as to allow thermal interaction, they are said to be in *thermal contact* (figure 1.3). If a system is prevented from interacting thermally with its surroundings it is said to be *thermally isolated* (coffee in a vacuum flask), and any change it undergoes is said to be an *adiabatic* change. Put differently, an adiabatic change is one in which no heat enters or leaves the system. We shall discuss the ideas of heat and work more fully in chapter 2.

If you have found these introductory ideas confusing at this stage, it is probably because I have been giving a kind of preview of the things we shall be discussing carefully later in the book. Perhaps you should return to sections 1.1 and 1.2 when you have finished reading it!

Figure 1.1   A work-like interaction

Figure 1.3 Two systems making thermal contact

1.3 TEMPERATURE

The idea of temperature almost certainly originally arose from the physiological sensation of hotness, an unreliable measure of temperature (figure 1.4). We can, however, develop a more exact concept of what temperature means by discussing what happens when bodies are placed in thermal contact.

If we take two systems and place them in thermal contact we generally find that initially changes will occur in both (figure 1.5). Eventually the changes cease, and the systems are then said to be in *thermal equilibrium*. We introduce the idea of temperature by saying that *the condition for the systems to be in thermal equilibrium is that they should be at the same temperature*. Conversely, two systems which are already at the

same temperature will not undergo change when placed in thermal contact. Equality of temperature is therefore the condition for thermal equilibrium.

However, defined like this, it is not clear that the condition for thermal equilibrium might not depend on the nature of the systems concerned. Can the same condition apply when we put a thermometer in our mouth to take our temperature as applies when we put a thermometer in a beaker of concentrated sulphuric acid? Experience shows that the condition for thermal equilibrium does not depend on the nature of the systems concerned. This experimental fact is embodied in the *zeroth law of thermodynamics* (so called because the need for it was not recognized until after the first law had been established).

If two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other.

Since we are free to choose anything we like for the third system, it follows that the condition for thermal equilibrium cannot depend on the nature of the systems concerned: all systems in thermal equilibrium have the same temperature irrespective of their nature. Another way of expressing this is to say that temperature is a universal property. The kind of experiment with which we might illustrate the zeroth law is shown in figure 1.6.

We should note that if we require one system to be in thermal equilibrium with another (i.e. at the same temperature) this represents a constraint on the system and removes one of its degrees of freedom. With our fixed mass of gas, for example, in the absence of any constraint, we are free to choose pressure and volume as we please; however, as soon as we require thermal equilibrium with some other system, the temperature is fixed, and for every value of volume there is only one possible value of pressure. We can put this another way by saying that for each temperature there is a
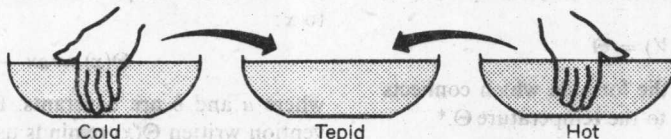

Figure 1.4 **The physiological sensation of hotness is an unreliable measure of temperature.** After one's hand has been in cold water for a time, tepid water feels hot. After it has been in hot water, the tepid water feels cold.
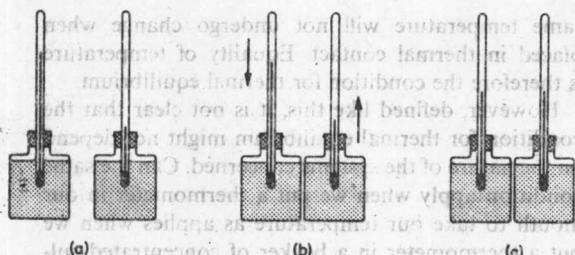
Figure 1.5 When two systems (a), are placed in thermal contact (b), changes generally take place in both systems until they reach thermal equilibrium (c). Here, thermometers indicate the changes (of temperature).
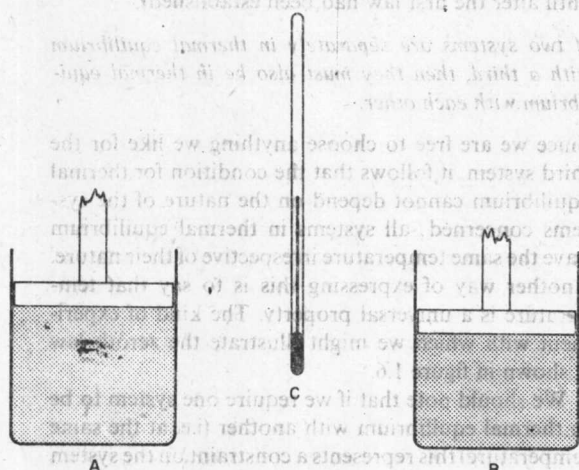

Figure 1.6 An illustration of the zeroth law. Systems A and B are fixed masses of gases at particular values of pressure and volume. The third system, C, is a thermometer. If C is in thermal equilibrium separately with A and B, so that its reading does not change when it is placed in thermal contact with either, then no changes will take place when A and B are placed in thermal contact with each other (because they are already at the same temperature).

unique relationship between pressure and volume. This is represented mathematically by an equation of the form

$$f(p, V) = \Theta$$

where $f(p, V)$ stands for the formula which connects the pressure and volume to the temperature Θ.*

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* The Greek letter *theta*. For temperature we use the capital letter. The lower case letter, θ. is generally used for angles.

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For an ideal gas, f is a simple product, pV, and for constant temperature we have

$$f(p, V) = pV = \Theta = \text{constant}$$

which is Boyle's law (page 40). The curve relating p to V for a given value of Θ is called an *isotherm* (figure 1.7).
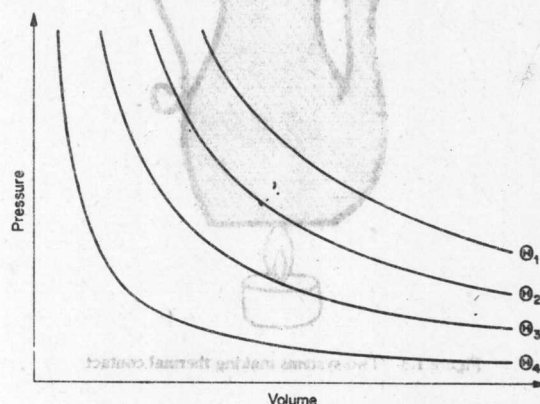

Figure 1.7 Isotherms for an ideal gas. For each temperature, there is only one possible value of pressure for each value of volume.

1.4 SCALES OF TEMPERATURE

We have introduced temperature as a rather abstract concept connected with thermal equilibrium. In practice, we would like to be able to represent temperature by a number whose magnitude changes in some regular way in relation to our ideas of hotness: the hotter the body, the larger the number representing temperature. This is what we do when we set up a *scale of temperature*. The easiest way to do this is to choose a convenient system with a property x which changes with temperature and take the value for temperature as linearly proportional to x:

$$\Theta(x) = ax + b \qquad (1.1)$$

where a and b are constants. Here, again, the convention written $\Theta(x)$ reminds us that Θ is a quantity whose value depends on the value of x: Θ is said to be a *function* of x. The relationship of equation *1.1* is illustrated in figure 1.8.
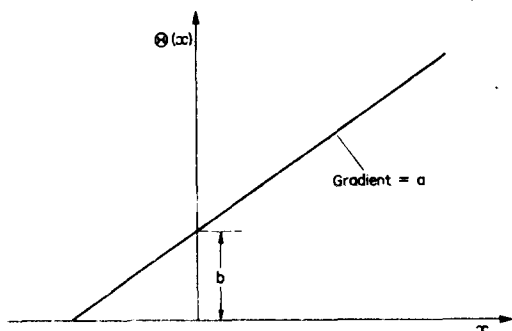
Figure 1.8 A plot of the equation $\Theta(x) = ax + b$

When we set up a temperature scale for everyday use, we want a conveniently placed zero, say low in the range of commonly encountered temperatures, and a sensibly sized unit. Conventionally, the *ice point*, the temperature at which water freezes at one atmosphere pressure, is taken as 0°, and the *steam point*, the temperature at which water boils at one atmosphere pressure, is taken as 100°. A scale so constructed is known as a *centigrade* scale. (Centigrade means one hundred steps.) We may take some examples.

A temperature on a centigrade scale based on the expansion of mercury in a mercury in glass thermometer uses the length of mercury in the capillary as the *thermometric* (temperature measuring) quantity x. The centigrade temperature is given by

$$\Theta(L) = (L - L_i) \times \frac{100}{(L_s - L_i)} \qquad (1.2)$$

where L, L_s and L_i are the lengths of the mercury at the temperature to be measured and at the ice and steam points respectively (figure 1.9). Comparing
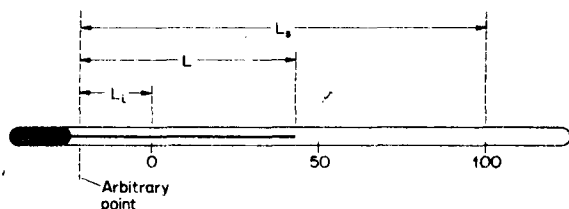

Figure 1.9 Constructing a centigrade scale for a mercury-in-glass thermometer

equation *1.2* with the general linear form, equation *1.1*, we find

$$a = 100/(L_s - L_i)$$

$$b = -100L_i/(L_s - L_i)$$

Again, a temperature on a centigrade scale based on the variation of the resistance R of a coil of copper wire is given by

$$\Theta(R) = 100(R - R_i)/(R_s - R_i) \qquad (1.3)$$

where R, R_i and R_s are the values of the resistance at the temperature to be measured, and at the ice and steam points respectively.

Scales constructed in this way are known as *empirical* scales: empirical means based on experiment. The symbol Θ is always used for empirical temperature.

When the scales are set up like this, we find that the value obtained for a temperature depends on what thermometer we use. This is because different properties do not respond in the same way to change of temperature. As a result, centigrade scales based on different systems will not generally agree with one another except, of course, at 0° and 100°, the calibration points, where they must agree by definition. Figure 1.10 shows the differences between centigrade temperatures determined with different thermometers.
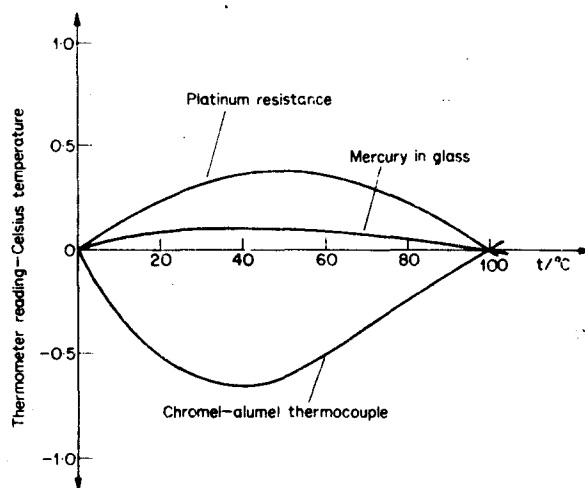

Figure 1.10 Differences between centigrade scales of common thermometers over the temperature range 0–100 °C

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In the search for a scale of temperature which did not depend on the properties of particular substances it was found that disagreement was small among thermometers based on the behaviour of gases. Gases have two degrees of freedom, so that a constraint has to be applied if the pressure or volume is to be uniquely related to temperature. Commonly, volume is kept constant and pressure used as the thermometric property. This is a *constant volume gas thermometer* (page 8) and will give a centigrade temperature

$$\Theta(p) = 100(p - p_i)/(p_s - p_i) \qquad (V = \text{constant})$$

Now while disagreements are generally small when temperatures are determined with different gases at *normal pressures* in this way, it is found that the differences which are present become smaller as the pressures used are reduced. If the measurements are *extrapolated* to find the temperature which would be given if the pressure could be reduced to zero (figure 1.11), it is found that, in this limit, *all* gas thermometers
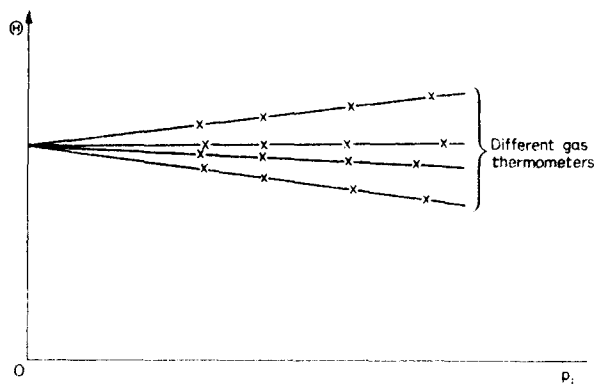
Figure 1.11 All gas thermometers give the same value for a temperature in the low pressure limit. With each thermometer, the temperature is found using different values of p_i. If the lines through the experimental values of temperature are extended back to find the temperature which would be given if the measurements could be made with $p_i = 0$, it is found that all the thermometers give the same value for the temperature.

give the *same* value for a temperature. One thus obtains a temperature scale which is independent of the properties of any particular substance. This scale is called the *perfect gas centigrade scale*. On the perfect gas centigrade scale, the expression for the temperature

is written

$$\Theta_{pgc} = \lim_{p_i \to 0} 100(p - p_i)/(p_s - p_i) \qquad (V = \text{constant})$$

$$(1.3)$$

$\lim_{p_i \to 0}$ means that we take the number given by the formula when the measurements are extrapolated to the limit where $p_i = 0$ (figure 1.11).

If measurements made on this scale are extrapolated back to find the perfect gas centigrade temperature at which the pressure of the perfect gas would vanish (figure 1.12), the value found is -273.15. This temperature is known as *absolute zero*.
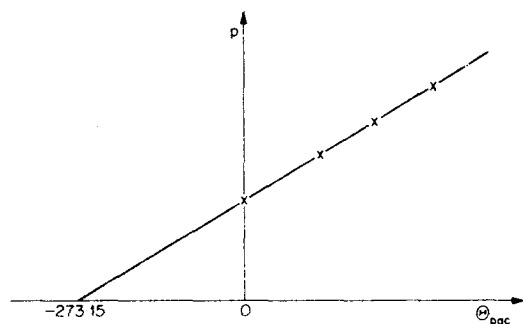

Figure 1.12 The pressure of an ideal gas would vanish at a perfect gas centigrade temperature of -273.15

1.5 THERMODYNAMIC TEMPERATURE

The reason why all gases give the same value for a temperature in the low pressure limit is that, in that limit, their behaviour tends to that of the perfect or ideal gas (chapter 3) whose equation of state is

$$pV/T = \text{constant} \qquad (1.4)$$

where T is *thermodynamic temperature*, the fundamental measure of temperature which comes from the second law of thermodynamics (chapter 7). For the moment the equation must be taken on trust. (When we discuss the ideal gas in chapter 3, we shall show that its equation of state is $pV/\Theta = \text{constant}$, where Θ is temperature on the perfect gas scale. It is not until chapter 7, when we discuss the second law, that we are able to explain the idea of thermodynamic temperature and prove that perfect gas temperature

6

is identical to thermodynamic temperature.) Substituting 1.4 in 1.3, the volume and the constant cancel through numerator and denominator and we get

$$\Theta_{pgc} = (T - T_i) \times \frac{100}{(T_s - T_i)}. \qquad (1.5)$$

This equation shows that perfect gas centigrade temperatures, like thermodynamic temperatures, are independent of the properties of any particular substance.

Thermodynamic temperature is now accepted as the fundamental measure of temperature. Gases are unique in that thermodynamic temperature appears in such a simple way in the equation of state (which holds for real gases in the low pressure limit), and this is why determinations of thermodynamic temperatures are often ultimately based on gas thermometry.

Now we are free to choose the size of the unit of thermodynamic temperature as we please. If we choose to have 100 units between ice and steam points, equation 1.5 becomes

$$\Theta_{pgc} = (T - T_i)/\text{K} \qquad (1.6)$$

However, there are disadvantages in fixing the size of the unit in this way. In the first place it is necessary to calibrate a gas thermometer at *two* fixed points: the ice and steam points. Secondly, when measurements made at the fixed points are extrapolated back to very low temperatures, that is to small values of T, the experimental uncertainties become *relatively* large, which could be serious in low temperature work. Now we notice that thermodynamic temperature has a natural zero, namely, the temperature at which the pressure of an ideal gas would vanish (see equation 1.4). If we take this natural zero as a fixed point on the scale, we only need to calibrate the thermometer at *one* fixed point to fix the size of the unit. In effect, we choose the *value* of thermodynamic temperature for *one* fixed point and this sets the scale. This way of fixing the size of the unit of thermodynamic temperature is the one now adopted by the International Committee of Weights and Measures. The fixed point chosen is the *triple point of water* (the temperature at which water, ice and water vapour coexist in equilibrium, a temperature more reproducable than the ice or steam points) and the value of temperature allotted to it is 273.16. The unit so

defined is called the kelvin* for which the symbol K is used. Thus

Thermodynamic temperature is the fundamental temperature; its unit is the kelvin which is defined as the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

Therefore, a thermodynamic temperature determined by gas thermometry would be given by

$$T/\text{K} = \lim_{p \to 0} (pV) \times \frac{273.16}{\lim_{p \to 0} (pV)_{tr}} \qquad (1.7)$$

where pV is the value of the product of pressure and volume at the temperature to be determined and $(pV)_{tr}$ is the value of the product at the triple point. Absolute zero is 0 K by definition. When we discuss the ideal gas we shall see that absolute zero is the temperature at which all thermal motion would cease.

Figure 1.13 shows schematically how the triple point is achieved for thermometer calibration.
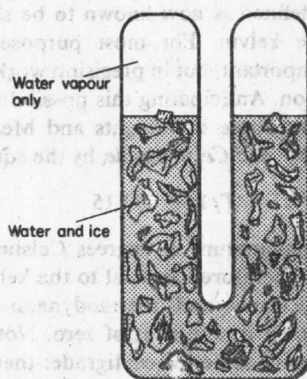

Figure 1.13 A triple point cell. The cell is cooled until some ice is present as well as water and water vapour. When all three are in equilibrium with one another, the temperature is 273.16 K by definition. The thermometer to be calibrated is inserted into the central tube.

1.6 THE CELSIUS TEMPERATURE SCALE

The reason for the choice of 273.16 K for the thermodynamic temperature of the triple point of water

* After Lord Kelvin (William Thompson), 1824–1907.