PART TWO

Heat

chapter eight

Introduction

Temperature

WE are interested in heat because it is the commonest form of energy, and because changes of temperature have great effects on our personal comfort, and on the properties of substances, such as water, which we use every day. *Temperature* is a scientific quantity which corresponds to primary sensations—hotness and coldness. These sensations are not reliable enough for scientific work, because they depend on contrast—the air in a thick-walled barn or church feels cool on a summer's day, but warm on a winter's day, although a thermometer may show that it has a lower temperature in the winter. A thermometer, such as the familiar mercury-in-glass instrument (Fig. 8.1), is a device whose readings depend on hotness or coldness, and which we choose to consider more reliable than our senses. We are justified in considering it more reliable because different thermometers of the same type agree with one another better than different people do.

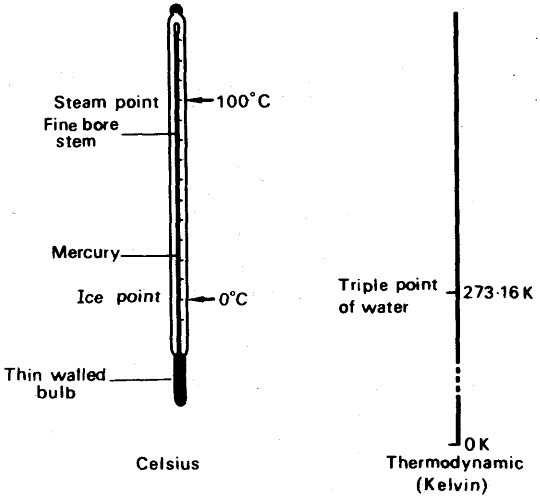


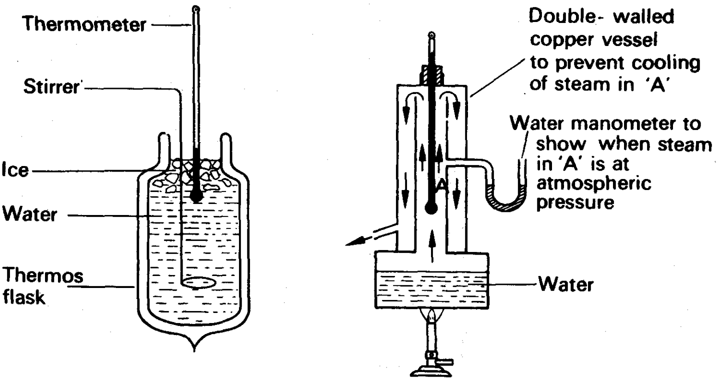
FIG. 8.1. Mercury-in-glass thermometer (left); °C and K scales.

The temperature of a body, then, is its degree of hotness, as measured on a thermometer. The thermometer was invented in Italy about 1630: it consisted of an open-ended tube, with a bulb full of water at its lower end. The water rose in the tube when the bulb was warmed, and fell when it was cooled.

As a liquid for use in thermometers, water soon gave way to linseed oil or alcohol, and by about 1660 thermometer-makers had begun to seal the top of the tube. Early thermometers had no definite scale, like that of a modern thermometer; some of them were used for showing the temperatures of greenhouses, and were mounted on wooden backboards, which were carved with grapes and peaches for example, to indicate the correct temperatures for growing the different fruits. The thermometer as we know it to-day, containing pure mercury and graduated according to a universal scale, was developed by Fahrenheit in 1724.

Temperature Scales. Celsius

When a mercury thermometer is to be graduated, it is placed first in melting ice, and then in steam from boiling water (Fig. 8.2). The temperature of the steam depends on the atmospheric pressure, as we shall see in Chapter 12; for calibrating thermometers, an atmospheric pressure of 76 cm mercury is chosen. In both steam and ice, when the level of the mercury has become steady, it is marked on the glass: the level in ice is called the *lower fixed point*, or ice-point, and the level in steam is called the *upper fixed point*, or steam-point. The distance between the fixed points is called the *fundamental interval* of the thermometer. For scientific work, the fundamental interval is divided into 100 equal parts (Fig. 8.1). This division was first proposed by Celsius in 1742, and the graduations are called degrees Centigrade or, in modern nomenclature, degrees Celsius (°C); the ice-point is 0°C and the steam-point 100°C.



(a) Ice point (b) Steam point

FIG. 8.2. Determination of fixed points.

Thermodynamic Scale

The *thermodynamic scale* of temperature is adopted as the SI temperature scale. On this scale, the *kelvin* is the unit of temperature. It is defined as 1/273·16 *of the thermodynamic temperature of the triple point of water* (p. 319).

The symbol for temperature is 'K' without a degree sign. Thus the triple point of water, T_{tr}, is 273·16 K exactly. The absolute zero, 0 K, is $-273{\cdot}15°C$. To a good approximation, 0°C = 273 K and 100°C = 373 K. (Fig. 8.1.)

The temperature change or interval of one degree Celsius, 1 degC or 1°C, is exactly the same as the temperature interval of one degree on the thermodynamic scale. On this account the interval 'degC or °C' is written 'K' in SI units. Similarly, 'per degC or per °C' is written 'K^{-1}' in SI units. For example, the linear expansivity (formerly, linear coefficient of expansion) of steel is written '12×10^{-6} K^{-1}' in SI units, in place of '12×10^{-6} per degC'. The use of 'K^{-1}' occurs frequently in units throughout the subject and should be noted by the reader.

Types of Thermometer

The *mercury-in-glass* thermometer depends on the change in volume of the mercury with hotness; it is cheap and simple, but is not reliable enough for accurate work (Chapter 14). Other types of thermometer depend on the change, with hotness, of the pressure of a gas at constant volume or the electrical resistance of a metal (Fig. 8.3). Another type of thermometer depends on the electromotive force change with temperature of two metals joined together. Fig. 8.4 (a) shows two wires, one of copper and one of iron, soldered together at A. The ends of the wires are joined to a galvanometer G. When the junction A is heated, a current flows which deflects the galvanometer. The current usually increases with the temperature difference between the hot and cold ends of the wires. For temperature measurement two junctions are used, as in Fig. 8.4 (b); the second one, called the cold junction, is maintained at 0°C by ice-water.

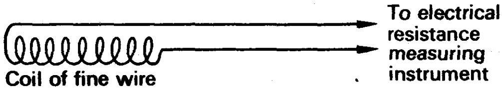


FIG. 8.3. A resistance thermometer; the wire is usually of platinum.

Each of these quantities—e.m.f., resistance, pressure—gives its own temperature scale, and the different scales agree only at the fixed points, where their readings are *defined* as 0°C and 100°C. (When we speak of

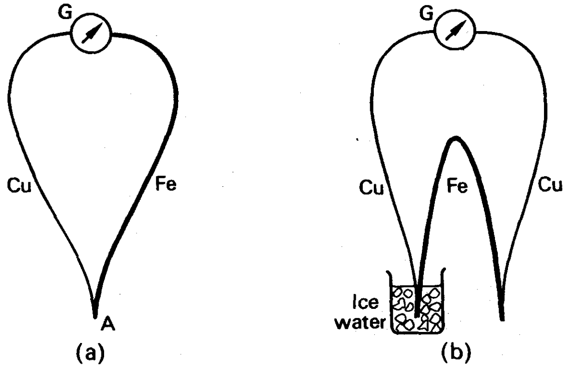


FIG. 8.4. Thermojunctions or thermocouples.

a temperature *scale*, we refer to the quantity used to define it; the difference between °C and K is only a difference in the *graduation* of a given scale.) If, for example, a given platinum wire has resistances R_0 and R_{100} at the ice- and steam-point respectively, then its fundamental interval is $R_{100}-R_0$. And if it has a resistance R at an unknown temperature, the value of that temperature, t_P, on the platinum resistance Celsius scale, is given by

$$t_P = \frac{R-R_0}{R_{100}-R_0} \times 100(°\text{C}).$$

The platinum-resistance scale differs appreciably from the mercury-in-glass scale, as the following table shows:

Mercury-in-glass	0	50	100	200	300	°C
Platinum-resistance	0	50·25	100	197	291	°C

We shall discuss temperature scales again later (p. 366); here we wish only to point out that they differ from one another, that no one of them is any more 'true' than any other, and that our choice of which to adopt is arbitrary, though it may be decided by convenience.

Effects of Temperature

Most bodies, when they are made hotter, become larger; their increase in size is called thermal expansion. Thermal expansion may be useful, as in a thermometer, or it may be a nuisance, as in bridges and railway lines. If the thermal expansion of a solid or liquid is resisted, great forces are set up: that is why gaps are left between railway lines, and why beer-bottles are never filled quite full. If the thermal expansion of a gas is resisted, however, the forces set up are not so great; the pressure of the gas increases, but not catastrophically. The increase of pressure is, in fact, made use of in most forms of engine; it is also made use of in accurate thermometry.

Besides causing a change in size or pressure, a change of temperature may cause a change of state—from solid to liquid, liquid to gas, or vice versa. If we heat some crystals of lead acetate in a crucible, and measure their temperature, with a thermometer reading to 300°C, we find that the crystals warm steadily up to 75°C and then start to melt. Their temperature does not rise further until they have all melted (Fig. 8.5). After it has melted, the lead acetate warms up to 280°C, and

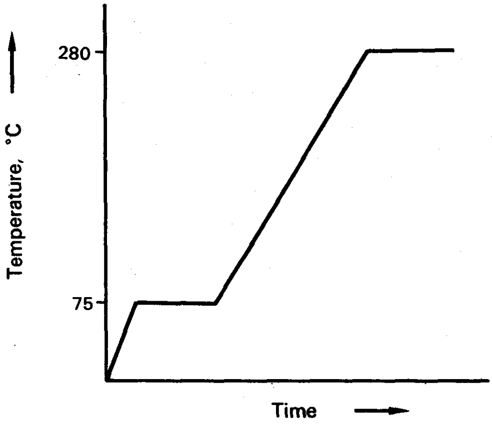


FIG. 8.5. Warming curve of lead acetate.

then keeps a constant temperature until it has all boiled away. We call 280°C the boiling-point of lead acetate; likewise we call 75°C the melting- (or freezing-) point of lead acetate.

HEAT AND ENERGY

Heat and Temperature

If we run hot water into a lukewarm bath, we make it hotter; if we run cold water in, we make it cooler. The hot water, we say, gives heat to the cooler bath-water; but the cold water takes heat from the warmer bath-water. The quantity of heat which we can get from hot water depends on both the mass of water and on its temperature: a bucket-full at 80°C will warm the bath more than a cup-full at 100°C. Roughly speaking, temperature is analogous to electrical potential, and heat is analogous to quantity of electricity. We can perceive temperature changes, and whenever the temperature of a body rises, that body has gained heat. The converse is not always true; when a body is melting or boiling, it is absorbing heat from the flame beneath it, but its temperature is not rising.

Latent Heat and Specific Heat

The heat which a body absorbs, in melting or boiling, it gives out again in freezing or condensing; such heat is called *latent*, or hidden, *heat*, because it does not show itself by a change in temperature. When a body absorbs heat without changing its state, its temperature rises, and the heat absorbed was first called 'sensible heat'.

The term 'latent heat' was used by Black (1728–99); he and a Swede, Wilcke, discovered latent heats independently at about the same date—Black by hanging a bucket of ice in a warm room, Wilcke by pouring boiling water on to snow.

Also independently, Black and Wilcke studied what we now call *specific heats*; the name is due to Wilcke. In his experiments Wilcke dropped various hot bodies into cold water, and measured the temperature rises which they caused. In this way he showed that a given mass of glass, for example, gave out only one-fifth as much heat as an equal mass of water, in cooling through the same temperature range. He therefore said that the specific heat of glass was 0·2.

In the seventeenth and eighteenth centuries the nature of heat was disputed; some thought of heat as the motion of the particles of a body, others thought of it as a fluid, filling the body's pores. Measurements of heat were all relative, and no unit of the quantity of heat was defined. In the nineteenth century, however, the increasing technical importance of heat made a unit of it essential. The units of heat chosen were:

(i) the *calorie* (cal): this is the amount of heat required to warm 1 gramme (g) of water through 1 deg C (see also p. 194);
(ii) the *British Thermal Unit* (Btu): this is the amount of heat required to warm 1 lb of water through 1 deg F.

Heat and Energy

Steam-engines became common in the early part of the eighteenth century; but they were not thought of as heat-engines until the latter part of that century. Consequently the early engines were wasteful of fuel, squandering useful heat in warming and cooling the cylinder at every stroke of the piston. Watt reduced this waste of heat by his invention of the separate condenser in 1769. Trevithick, about 1800, devised an engine which was driven by steam which entered the cylinder at a pressure above atmospheric, and therefore at a temperature above 100°C (p. 304). In this engine, the steam came out of the exhaust at a temperature no higher than in earlier engines, so that a greater fraction of the heat which it carried from the boiler was used in the engine.

The idea of heat as a form of energy was developed particularly by Benjamin Thompson (1753–1814); he was an American who, after adventures in Europe, became a Count of the Holy Roman Empire, and war minister of Bavaria. He is now generally known as Count Rumford. While supervising his arsenal, he noticed the great amount of heat which was liberated in the boring of cannon. The idea common at the time was that this heat was a fluid, pressed out of the chips of metal as they were bored out of the barrel. To measure the heat produced, Rumford used a blunt borer, and surrounded it and the end of the cannon with a wooden box, filled with water (Fig. 8.6). From the weight of water, and the rate at which its temperature rose, he concluded that the boring operation liberated heat at the same rate as 'nine wax candles, burning with a clear flame'. He showed that the amount of heat liberated was in no way connected with the mass of metal bored away, and concluded that it depended only on the work done against friction. It followed that **heat was a form of energy.**

Rumford published the results of his experiments in 1798. No similar experiments were made until 1840, when Joule began his study of heat and other forms of energy. Joule measured the work done, and the heat produced, when water was churned, in an apparatus which we shall describe on p. 197. He also measured the work done and heat produced when oil was churned, when air was compressed, when water was forced through fine tubes, and when cast iron bevel wheels were rotated one against the other. Always, within the limits of experimental error, he found that the heat liberated was proportional to the mechanical work done, and that the ratio of the two was the same in all types of experiment. His last experiments, made in 1878, showed that about 772 ft-lbf of work were equivalent to one British thermal unit of heat. This ratio Joule called the *mechanical equivalent of heat.* The metric unit of work or energy is the *joule*, J. Since experiment shows that heat is a form of energy, *the joule is now the scientific unit of heat.* 'Heat per second' is expressed in 'joules per second' or *watts*, W.

Today, from definition, about 4·2 J = 1 calorie (more accurately, 4·187 J = 1 calorie). Calories are units still used by chemists, for example. Values in calories met can be converted to joules approximately by multiplying them by 4·2. See p. 199.

In other experiments, Joule measured the heat liberated by an electric current in flowing through a resistance; at the same time he measured the work done in driving the dynamo which generated the current. He obtained about the same ratio for work done to heat liberated as in his direct experiments. This work linked the ideas of heat, mechanical, and electrical energy. He also showed that the heat produced by a current is related to the chemical energy used up.

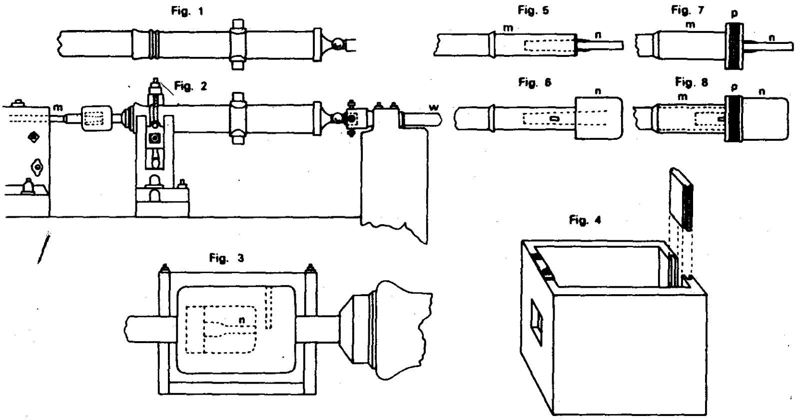


FIG. 8.6. Rumford's apparatus for converting work into heat.

Fig. 1 shows the cannon. Fig. 2 shows the complete apparatus; *w* is connected to machinery driven round by horses, *m* is joined to a blunt borer *n* in a cylinder shown enlarged in Fig. 3 and Fig. 4. Figs. 5, 6, 7, 8 show further details of *m* and *n*.

The Conservation of Energy

As a result of all his experiments, Joule developed the idea that energy in any one form could be converted into any other. There might be a loss of useful energy in the process—for example, some of the heat from the furnace of a steam-engine is lost up the chimney, and some more down the exhaust—but no energy is destroyed. The work done by the engine added to the heat lost as described and the heat developed as friction, it is equal to the heat provided by the fuel burnt. The idea underlying this statement is called the *Principle of the Conservation of Energy*. It implies that, if we start with a given amount of energy in any one form, we can convert it in turn into all other forms; we may not always be able to convert it completely, but if we keep an accurate balance-sheet we shall find that the total amount of energy, expressed in any one form—say heat or work—is always the same, and is equal to the original amount.

The conservation of energy applies to living organisms—plants and animals—as well as to inanimate systems. For example, we may put a man or a mouse into a box or a room, give him a treadmill to work, and feed him. His food is his fuel; if we burn a sample of it, we can measure its chemical energy, in heat units. And if we now add up the heat value of the work which the man does, and the heat which his body gives off, we find that their total is equal to the chemical energy of the food which the man eats. Because food is the cource of man's energy, food values are commonly expressed in *kilocalories*, which is the heat required to warm 1 kilogramme of water through 1 deg C. A man needs about 3000 kilocalories per day.

Muscles are unique in their capacity to turn chemical energy directly into mechanical energy. When a muscle is stimulated, complex phosphates in its tissues break down; in doing so, they cause the muscle fibres to swell and shorten. Thus, via the bones and joints, the muscle does external work. When the muscle is recovering after contraction, the phosphates are built up again by a series of reactions, involving the oxidation of sugars. The sugars and oxygen are brought to the muscle in the arterial blood; the waste products of the reactions, water and carbon dioxide, are carried away in the venous blood.[1] Recently physiologists have found evidence that muscles may also convert mechanical energy into chemical.[2] For example, when we walk downstairs, gravity does work on our leg-muscles; some of this appears as heat, but some, it now seems, is used in reversing the chemical actions of muscle activity.

All the energy by which we live comes from the sun. The sun's ultra-violet rays are absorbed in the green matter of plants, and make them grow; the animals eat the plants, and we eat them—we are all vegetarians at one remove. The plants and trees of an earlier age decayed, were buried, and turned into coal. Even water-power comes

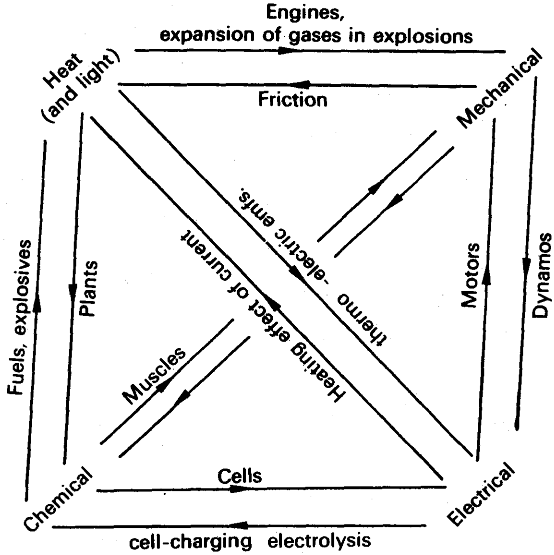


FIG. 8.7. Forms of energy, and their interconversions.

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[1] DAVSON, *General Physiology*, Chap. XVII (Churchill).

[2] ABBOTT, AUBERT and HILL, *Jour. Physiology*, Vol. III.

from the sun—we would have no lakes if the sun did not evaporate the sea and provide the rainfall which fills the lakes. The relationship between all the principal forms of energy are summarized in Fig. 8.7.

Joule's Historic Experiments

About 1847 Joule measured the mechanical equivalent of heat by an apparatus of the form shown in Fig. 8.8. C is a copper cylinder, about 30 cm in diameter, containing water. The water is churned by paddles P, and prevented from whirling round *en masse* by baffles B. The paddles are connected by a coupling K to a drum D, which is rotated by strings S attached to lead weights M. A thermometer T shows the temperature of the water.

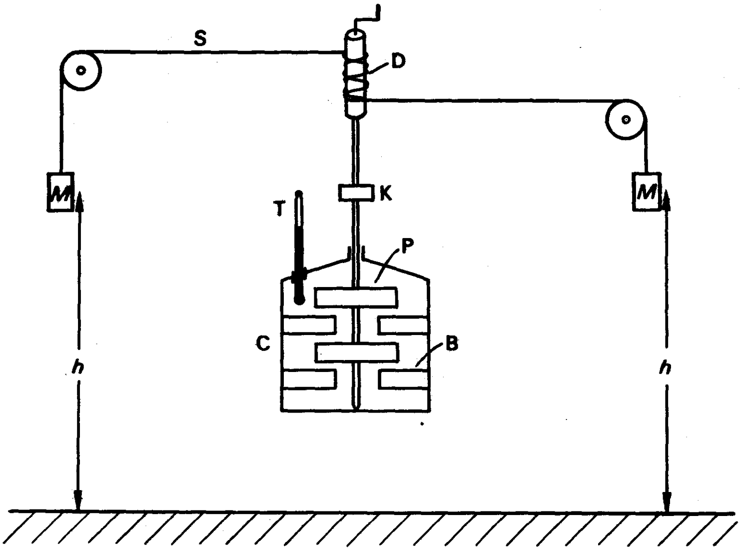

FIG. 8.8. Joule's apparatus for mechanical equivalent.

Joule would start an experiment by allowing the weights M to fall to the ground and turn the paddles. He would then break the coupling K, and re-wind the weights without disturbing the paddles. In this way he would make the weights fall twenty times or more, in a single experiment, and so increase the work done on the water and consequently the temperature rise.

Suppose n is the number of falls; then the work W' done on the water $= 2nMgh$, where M is the mass of one weight, g is the acceleration of gravity, and h is the height of the fall. The heat Q gained by the cylinder and the water is $(mc_W + C)\theta$, where m is the mass of water, c_W the heat capacity of the cylinder and paddles, and θ is their rise in temperature. The rise θ includes the correction for heat losses. The mechanical equivalent is given by W'/Q

$$= \frac{2nMgh}{(mc_W + C)\theta} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

An experiment of this kind takes a long time—about half an hour—because a great deal of work, by everyday standards, must be done to produce a measurable amount of heat. The cooling correction is therefore relatively great.

Many people refused to accept Joule's work at first, because of the very small temperature differences on which it rested. Nevertheless, Joule's final result differs only by about one part in 400 from the value given by the best modern experiments. In calculating his final result, Joule made corrections for the kinetic energy of the weights as they struck the floor, the work done against friction in the pulleys and the bearings of the paddle wheel, and the energy stored by the stretching of the strings; he even estimated the energy in the hum which the strings emitted, but found it was negligible.

Joule's Large-scale Experiments

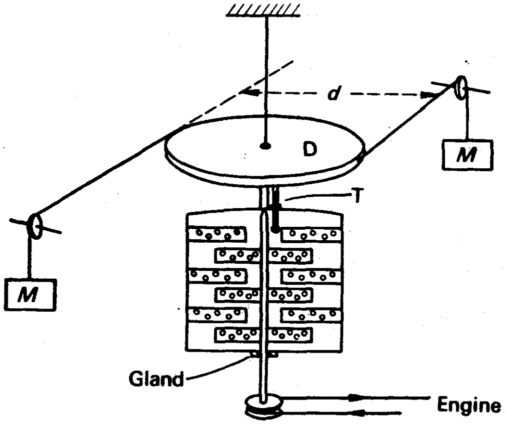

FIG. 8.9. Joule's final apparatus, also Rowland's.

In his last experiments, about 1878, Joule rotated the paddles with an engine, thereby eliminating many of the corrections just mentioned. He suspended the cylinder on a wire, and kept it in equilibrium by an opposing couple, applied by means of the wheel D (Fig. 8.9). This method was repeated in 1880 by Rowland, who had holes drilled in the paddles and baffles, to make their churning action more thorough. The moment, T, of the couple applied by the engine is equal and opposite to that of the couple applied by the masses M. Its value is therefore

$$T = Mgd,$$

where d is the diameter of the wheel. Now the work done by a couple is equal to the product of its moment and the angle θ in radians through which it turns. Hence if the paddles make n revolutions, the work done on the water, since $\theta = 2\pi n$, is

$$\begin{aligned} W' &= 2\pi nT \\ &= 2\pi nMgd. \end{aligned}$$

The number of revolutions was measured on a revolution counter attached to the paddle spindle. If θ is the rise in temperature measured by the thermometer T, corrected for cooling, the heat developed is

$$Q = (mc_W + C)\theta,$$

in our previous notation. Hence the mechanical equivalent

$$= \frac{W'}{Q} = \frac{2\pi nMgd}{(mc_W + C)\theta}.$$

The term 'mechanical equivalent of heat', used in the past, has no meaning nowadays because heat is measured in joules in SI units (p. 194). Experiments in which mechanical energy is converted to heat energy are now regarded as experiments which measure the specific heat capacity of the heated substance in 'joule per kilogramme (or gramme) per deg K' (J kg^{-1} K^{-1} or J g^{-1} K^{-1}). The specific heat capacity of water may be found by the energy conversion method described on p. 206.