chapter nine

Calorimetry

Calorimetry is the measurement of heat; here we shall be concerned with the measurement of specific heat capacities and specific latent heats.

Heat (Thermal) Capacity, Specific Heat Capacity

The *heat capacity* of a body, such as a lump of metal, is the quantity of heat required to raise its temperature by 1 degree. It is expressed in *joules per deg K* (J K^{-1}).

The *specific heat capacity* of a substance is the heat required to warm unit mass of it through 1 degree; it is the heat capacity per unit mass of the substance. Specific heat capacities are expressed in *joule per kilogramme per deg K* (J kg^{-1} K^{-1}) or in *joule per gramme per deg K* (J g^{-1} K^{-1}). The specific heat of water, c_w, is about 4·2 J g^{-1} K^{-1}, or 4200 J kg^{-1} K^{-1}, or 4·2 kJ kg^{-1} K^{-1}, where 1 kJ = 1 kilojoule = 1000 J. Formerly, specific heat capacities were expressed in calories per g per deg C—the values in joule are about 4·2 times as great.

From the definition of specific heat capacity, it follows that

heat capacity, C = mass × specific heat capacity.

The specific heat capacity of copper, for example, is about 0·4 J g^{-1} K^{-1} or 400 J kg^{-1} K^{-1}. Hence the heat capacity of 5 kg of copper = 5 × 400 = 2000 J K^{-1} = 2 kJ K^{-1}.

SPECIFIC HEAT CAPACITIES

Substance	Sp. Ht.: J kg^{-1} K^{-1}	Substance	Sp. Ht.: J kg^{-1} K^{-1}
Aluminium	$0·91 \times 10^3$	Ice	$2·1 \times 10^3$
Brass	0·38	Paraffin wax	2·9
Copper	0·39	Quartz	0·7
Iron	0·47	Rubber	1·7
Lead	0·13	Stone	0·9
Mercury	0·14	Wood	1·7
Nickel	0·46	Alcohol	2·5
Platinum	0·13	Brine (25% by wt.)	3·4
Silver	0·24	Carbon tetrachloride	0·84
Solder	0·18	Ether	2·4
Steel	0·45	Glycerine	2·5
Ebonite	1·7	Paraffin oil	2·1
Glass	0·7	Turpentine	1·76

MEASUREMENT OF SPECIFIC HEAT CAPACITY

Method of Mixtures

A common way of measuring specific heat capacities is the method of mixtures, used by Wilcke (p. 193). Fig. 9.1 shows how we may apply it to a solid, such as a metal. We weigh the specimen (m g) and hang it on a thread in a steam jacket, J, fitted with a thermometer. The jacket is plugged with cotton wool to prevent loss of heat by convection. While the solid is warming, we weigh a thin-walled copper vessel A called a calorimeter (m_c g), then run about 50 cm^3 of water into it, and by subtraction find the mass m_1 of this water. We put the calorimeter into a draught-shield S, and take the temperature, θ_1, of the water in it. After we have given the specimen time to warm up—say half an hour—we read its temperature, θ_3; then we slide the calorimeter under the jacket, and drop the specimen into it. After stirring the mixture, we measure its final temperature, θ_2. If no heat leaves the calorimeter by radiation, conduction, or convection, after the hot specimen has been dropped into the calorimeter, we have:

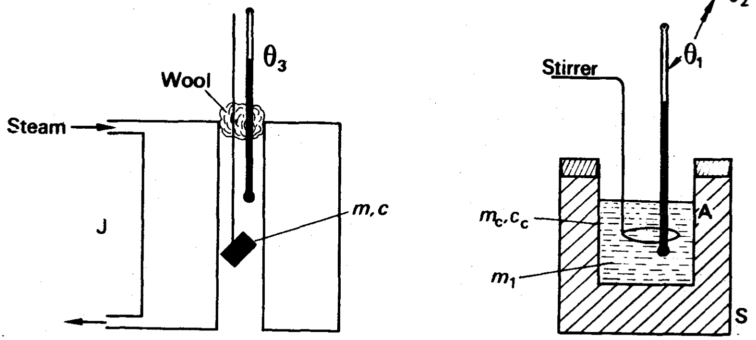


FIG. 9.1. Specific heat capacity by mixtures.

> heat lost by solid in cooling from θ_3 to θ_2 = heat gained by water and calorimeter in warming from θ_1 to θ_2.
> (The heat gained by the thermometer and stirrer may be neglected if high accuracy is not required.)

Therefore, if c is the specific heat of the solid, c_w that of water and c_c that of the calorimeter:

$$mc(\theta_3-\theta_2) = m_1c_w(\theta_2-\theta_1)+m_cc_c(\theta_2-\theta_1)$$

$$= (m_1c_w+m_cc_c)(\theta_2-\theta_1),$$

$$\text{whence} \quad c = \frac{(m_1c_w+m_cc_c)(\theta_2-\theta_1)}{m(\theta_3-\theta_2)} \quad . \quad . \quad (1)$$

Liquids

The specific heat capacity of a liquid can be found by putting some in a calorimeter and dropping a hot solid, of known specific heat capacity c, into it. If m_l, c_l are the mass and specific heat capacity of the liquid, then the product $m_l c_l$ replaces m in equation (1), from which c_l can be calculated.

Calculations

As an illustration of a specific heat capacity determination, suppose a metal of mass 200 g at 100°C is dropped into 80 g of water at 15°C contained in a calorimeter of mass 120 g and specific heat capacity 0·4 kJ kg^{-1} K^{-1}. The final temperature reached is 35°C. Then:

$$\begin{aligned}
&\text{heat capacity of calorimeter} &&= 120\times 0{\cdot}4 = 48\ \text{J K}^{-1}\\
&\text{heat capacity of water} &&= 80\times 4{\cdot}2 = 336\ \text{J K}^{-1}\\
&\therefore\ \text{heat gained by water}+\text{cal.} &&= (336+48)\times(35-15)\ \text{J}\\
&\text{and heat lost by hot metal} &&= 0{\cdot}2\times c\times(100-35)\text{J}\\
&\therefore\ 0{\cdot}2\times c\times 65 &&= 384\times 20\\
&\therefore\ c &&= \frac{384\times 20}{0{\cdot}2\times 65} = 590\text{J kg}^{-1}\ \text{K}^{-1}\ \text{(approx.)}.
\end{aligned}$$

Heat Losses

In a calorimetric experiment, some heat is always lost by leakage. Leakage of heat cannot be prevented, as leakage of electricity can, by insulation, because even the best insulator of heat still has appreciable conductivity (p. 333).

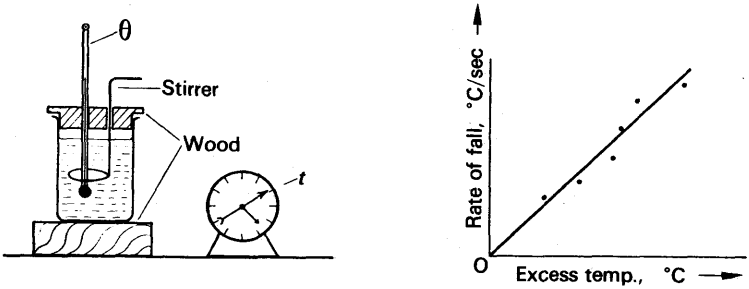
When convection is prevented, gases are the best thermal insulators. Hence calorimeters are often surrounded with a shield S, as in Fig. 9.1, and the heat loss due to conduction is made small by packing S with insulating material or by supporting the calorimeter on an insulating ring, or on threads. The loss by radiation is small at small excess temperatures over the surroundings. In some simple calorimetric experiments the final temperature of the mixture is reached quickly, so that the time for leakage is small. The total loss of heat is therefore negligible in laboratory experiments on the specific heats of metals, but not on the specific heat capacities of bad conductors, such as rubber, which give up their heat slowly. When great accuracy is required, the loss of heat by leakage is always taken into account.

Newton's Law of Cooling

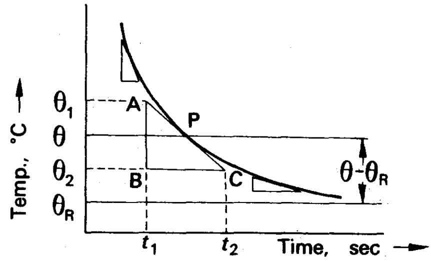
Newton was the first person to investigate the heat lost by a body in air. He found that *the rate of loss of heat is proportional to the excess temperature over the surroundings*. This result, called *Newton's law of cooling*, is approximately true in still air only for a temperature excess of about 20°C or 30°C; but it is true for all excess temperatures in conditions of forced convection of the air, i.e. in a draught. With natural convection Dulong and Petit found that the rate of loss of heat was proportional to $\theta^{5/4}$, where θ is the excess temperature, and this appears to be true for higher excess temperatures, such as from 50°C to 300°C. At low excess temperatures, however, less than 1°C,

G. T. P. Tarrant has pointed out that radiation, not convection, is the major contributing factor to the rate of cooling of an object.

To demonstrate Newton's law of cooling, we plot a temperature (θ)-time (t) cooling curve for hot water in a calorimeter placed in a draught (Fig. 9.2 (*a*)). If θ_R is the room temperature, then the excess temperature of the water is $(\theta - \theta_R)$. At various temperatures, such as θ in Fig. 9.2 (*b*), we drew tangents such as APC to the curve. The slope of the tangent, in degrees per second, gives us the rate of fall of temperature, when the water is at the temperature θ:



(a) Apparatus (c) Treatment of results



(b) Results

FIG. 9.2. Newton's law of cooling.

$$\text{rate of fall} = \frac{\text{AB}}{\text{BC}} = \frac{\theta_1 - \theta_2}{t_2 - t_1}.$$

We then plot these rates against the excess temperature, $\theta - \theta_R$, as in Fig. 9.2 (*c*), and find a straight line passing through the origin. Since the heat lost per second by the water and calorimeter is proportional to the rate of fall of the temperature, Newton's law is thus verified.

Heat Loss and Temperature Fall

Besides the excess temperature, the rate of heat loss depends on the exposed area of the calorimeter, and on the nature of its surface: a dull surface loses heat a little faster than a shiny one, because it is a better radiator (p. 343). This can be shown by doing a cooling experiment twice, with equal masses of water, but once with the calorimeter polished, and once after it has been blackened in a candle-flame. In general, for any body with a uniform surface at a uniform temperature θ, we may write, if Newton's law is true,

$$\text{heat lost/second} = \frac{dQ}{dt} = kS(\theta - \theta_R) \quad . \quad . \quad (2)$$

where S is the area of the body's surface, θ_R is the temperature of its surroundings, k is a constant depending on the nature of the surface, and Q denotes the heat lost from the body.

When a body loses heat Q, its temperature θ falls; if m is its mass, and c its specific heat capacity, then its rate of fall of temperature, $d\theta/dt$, is given by

$$\frac{dQ}{dt} = -mc\frac{d\theta}{dt}.$$

Now the mass of a body is proportional to its volume. The rate of heat loss, however, is proportional to the surface area of the body. The rate of fall of temperature is therefore proportional to the ratio of surface to volume of the body. For bodies of similar shape, the ratio of surface to volume is inversely proportional to any linear dimension. If the bodies have surfaces of similar nature, therefore, the rate of fall of temperature is inversely proportional to the linear dimension: a small body cools faster than a large one. This is a fact of daily experience: a small coal which falls out of the fire can be picked up sooner than a large one; a tiny baby should be more thoroughly wrapped up than a grown man. In calorimetry by the method of mixtures, the fact that a small body cools faster than a large one means that, the larger the specimen, the less serious is the heat loss in transferring it from its heating place to the calorimeter. It also means that the larger the scale of the whole apparatus, the less serious are the errors due to loss of heat from the calorimeter.

Correction for Heat Losses in Calorimetry

Newton's law of cooling enables us to estimate the heat lost in an experiment on the method of mixtures.

In doing the experiment, we take the temperature of the mixture at half-minute intervals, and plot it against time, as in Fig. 9.3. The broken line shows how we would expect the temperature to rise if no heat were lost; we have therefore to estimate the difference, p, between the plateau of this imaginary curve, and the crest of the experimental curve, C. p is known as the 'cooling correction'.

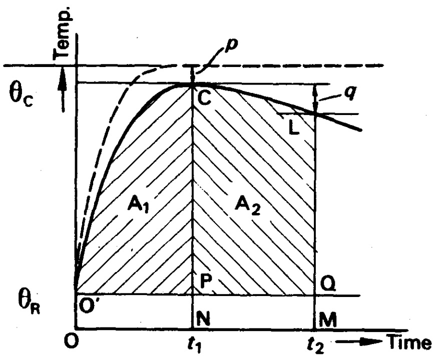


FIG. 9.3. Cooling correction.

We start by drawing an ordinate CN through the crest, and another LM through any convenient point L further along the curve; OM should be not less than twice ON—the greater it is, the more accurate the correction. We next draw an abscissa O′PQ through the room temperature, θ_R; and by counting the squares of the graph paper, we measure the areas O′CP (A_1), PCLQ (A_2). Then, if q is the fall in temperature from C to L:

$$\frac{p}{q} = \frac{\text{O'CP}}{\text{PCLQ}} = \frac{A_1}{A_2}, \qquad . \quad . \quad . \quad (3)$$

or

$$p = q\frac{A_1}{A_2}.$$

Before establishing this equation let us see how to use it. Suppose m_1, c, are the mass and specific heat capacity of the specimen; m, c_w are the mass and specific heat capacity of water; and C the heat capacity of the calorimeter. Then the heat which these lose to their surroundings is the heat which would have raised their temperature by p. Thus

$$\text{heat lost} = (m_1c+mc_w+C)p.$$

Let θ_1 denote the initial temperature of the specimen, θ_c the highest temperature of the mixture; and θ_2 the original temperature of the water and calorimeter. Then we have:

$$\text{heat given out} = \text{heat taken in} + \text{heat lost}.$$

$$\therefore\ m_1c(\theta_1-\theta_c) = (mc_w+C)(\theta_c-\theta_2)+(m_1c+mc_w+C)p,$$

from which $$m_1c(\theta_1-\overline{\theta_c+p}) = (mc_w+C)(\overline{\theta_c+p}-\theta_2).$$

To correct for the heat losses we must therefore add the correction p to the crest temperature θ on each side of the heat balance equation. In equation (1), p. 200, p must be added to θ_2 in both numerator and denominator.

Theory of the Correction. To establish equation (3), we write down the expression for the heat lost per second from the calorimeter, assuming Newton's law of cooling:

$$\frac{dQ}{dt} = kS(\theta-\theta_R) \qquad . \quad . \quad . \quad . \quad . \quad (4)$$

where k is a constant, and S the exposed area of the calorimeter. Between times $t = 0$ and $t = t_1$, the total heat lost is

$$Q_1 = \int_0^{t_1} kS(\theta-\theta_R)dt$$

$$= kS\int_0^{t_1} (\theta-\theta_R)dt$$

$$= kS \times \text{area O'CP} = kSA_1.$$

This is the heat, which, if it had not been lost, would have warmed the calorimeter and contents by p degrees. Therefore

$$(m_1c+mc_w+C)p = kSA_1 \qquad . \quad . \quad . \quad . \quad (5)$$

Similarly the heat lost between t_1 and t_2 is given by $Q_2 = kSA_2$, and since this loss caused a fall in temperature of q, we have, by the argument above

$$(m_1c+mc_w+C)q = kSA_2 \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

On dividing equation (5) by equation (6), we find

$$\frac{p}{q} = \frac{A_1}{A_2}, \quad \text{or} \quad p = q\frac{A_1}{A_2}.$$

Specific Heat Capacity of Liquid by Cooling

Specific heat capacities of liquids which react with water are often measured by the so-called *method of cooling*. The cooling curve of a calorimeter is plotted, first when it contained a known volume of hot water, and then when it contains an *equal* volume of hot liquid (Fig. 9.4). The volumes are made equal so as to make the temperature distribution, over the surface of the calorimeter, the same in each experiment. From the curves, the respective times t_l and t_w are found which the calorimeter and contents take to cool from θ_1 to θ_2. Whatever the contents of the calorimeter, it gives off heat at a rate which depends only on its excess temperature, since the area and nature of its surface are constant. Therefore, at each temperature between θ_1 and θ_2, the calorimeter gives off heat at the same rate whatever its contents. Thus the average rate at which it loses heat, over the whole range, is the same with water and with liquid. Consequently

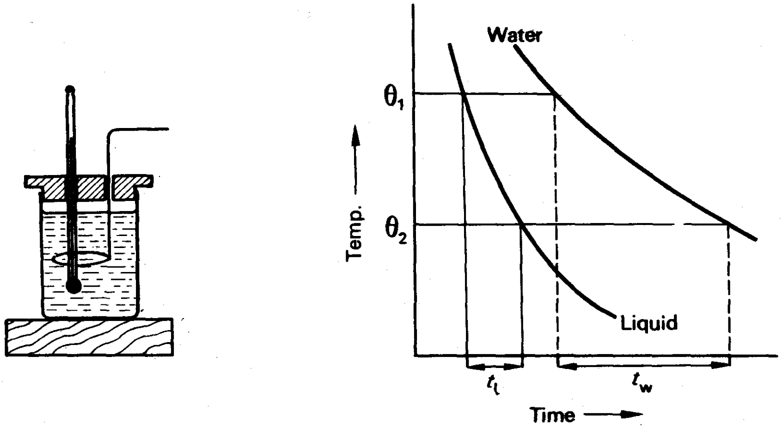


FIG. 9.4. Specific heat capacity by cooling.

$$\frac{(m_1c+C)(\theta_1-\theta_2)}{t_l} = \frac{(mc_w+C)(\theta_1-\theta_2)}{t_w}$$

where m_1, c, are the mass and specific heat capacity of the liquid, m, c_w that of water, and C is the heat capacity of the calorimeter. Thus

$$\frac{m_1c+C}{t_l} = \frac{mc_w+C}{t_w}$$

from which c can be calculated.

Specific Heat Capacity by Electrical Method

The simplest way to measure the specific heat capacity of a liquid in the laboratory is by electrical heating, as illustrated in Fig. 9.5. In this case, the energy supplied = IVt joules, where I is the current in amperes the coil R of resistance wire, V is the potential difference across it in volts and t is the time in seconds for which current flows. The coil may be immersed in a suitable oil of mass m in a calorimeter of heat capacity C.

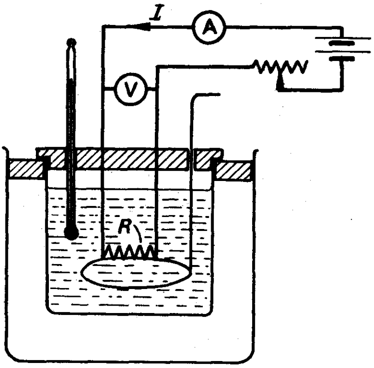


FIG. 9.5. Laboratory electrical method for specific heat capacity.

We pass a steady current I through the coil, and measure the potential difference V across it. Stirring continuously, we plot the temperature of the oil against the time. After a time t long enough to give several degrees rise, we switch off the current and plot the cooling curve. If θ is the corrected rise in temperature, we have

$$IVt = (mc+C)\theta,$$

whence we can calculate c in J kg^{-1} K^{-1}.

Specific Heat Capacity of Water by Continuous Flow Method

In 1899, Callendar and Barnes devised a method for specific heat capacity in which only steady temperatures are measured. They used platinum resistance thermometers, which are more accurate than mercury ones but take more time to read. In the measurement of steady temperatures, however, this is no drawback. As we shall see shortly *the heat capacity of the apparatus is not required*, which is a great advantage of the method.

Fig. 9.6 shows Callendar and Barnes' apparatus. Water from the constant-head tank K flows through the glass tube U, and can be collected as it flows out. It is heated by the spiral resistance wire R, which carries a steady electric current I. Its temperature, as it enters

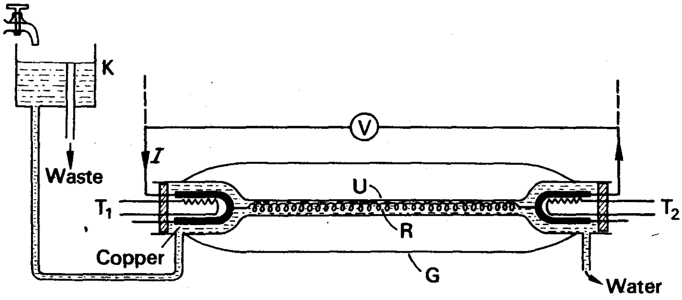


FIG. 9.6. Callendar and Barnes' apparatus (contracted several times in length relative to diameters).

and leaves, is measured by the thermometers T_1 and T_2. (In a simplified laboratory experiment, these may be mercury thermometers.) Surrounding the apparatus is a glass jacket G, which is evacuated, so that heat cannot escape from the water by conduction or convection.

When the apparatus is running, it settles down eventually to a steady state, in which the heat supplied by the current is all carried away by the water. *None is then taken in warming the apparatus, because every part of it is at a constant temperature.* The mass of water m, which flows out of the tube in t seconds, is then measured. If the water enters at a temperature θ_1 and leaves at θ_2, then if c_w is its mean specific heat capacity,

$$\text{heat gained by water} = Q = mc_w(\theta_2 - \theta_1)\text{ joules.}$$

The energy which liberates this heat is electrical. To find it, the current I, and the potential difference across the wire V, are measured with a potentiometer. If I and V are in amperes and volts respectively, then, in t seconds:

$$\text{energy supplied to wire} = IVt\text{ joules.}$$

$$\therefore mc_w(\theta_2 - \theta_1) = IVt$$

$$\therefore c_w = \frac{IVt}{m(\theta_2 - \theta_1)}$$

To get the highest accuracy from this experiment, the small heat losses due to radiation, and conduction along the glass, must be allowed for. These are determined by the temperatures θ_1 and θ_2. For a given pair of values of θ_1 and θ_2, and constant-temperature surroundings (not shown), let the heat lost per second be h. Then, in t seconds,

$$\text{heat supplied by heating coil} = mc_w(\theta_2 - \theta_1) + ht,$$

$$\therefore IVt = mc_w(\theta_2 - \theta_1) + ht \quad . \quad (1)$$

To allow for the loss h, the rate of flow of water is changed, to about half or twice its previous value. The current and voltage are then adjusted to bring θ_2 back to its original value. The inflow temperature, θ_1, is fixed by the temperature of the water in the tank. If I', V', are the new values of I, V, and m' is the new mass of water flowing in the same t seconds, then:

$$I'V't = m'c_w(\theta_2 - \theta_1) + ht \quad . \quad . \quad . \quad (2)$$

On subtracting equation (2) from equation (1), we find

$$(IV - I'V')t = (m - m')c_w(\theta_2 - \theta_1),$$

$$\therefore c_w = \frac{(IV - I'V')t}{(m - m')(\theta_2 - \theta_1)} \quad . \quad . \quad . \quad (3)$$

When the temperature rise, $\theta_2 - \theta_1$, is made small, for example, $\theta_1 = 20{\cdot}0$°C, $\theta_2 = 22{\cdot}0$°C, then c_w may be considered as the specific heat at 21·0°C, the mean temperature. If the inlet water temperature is now raised to say $\theta_1 = 40{\cdot}0$°C and θ_2 is then 42·0°C, c_w is now the specific heat at 41·0°C. In this way it was found that *the specific heat capacity of water varied with temperature.* The continuous flow method can be used to find the variation in specific heat capacity of any liquid in the same way.

The '15°C-calorie' was defined as the heat required to raise the temperature of 1 gramme of water from 14·5°C to 15·5°C. The table shows the relative variation of the specific heat capacity of water, taking the 15°C-calorie as 1·0000 in magnitude.

SPECIFIC HEAT CAPACITY OF WATER

Temperature (°C)	5	15	25	40	70	100
c_W	1·0047	1·0000	0·9980	0·9973	1·0000	1·0057

Nernst's Method

Modern methods of measuring specific heat capacities use electrical heating. Nernst's method for the specific heat capacity of a metal is shown in Fig. 9.7. The metal S has a heating coil R of insulated platinum wire wound round the outside, and is covered with silver foil F to minimize heat loss by radiation. It is suspended by the leads to the coil in a glass vessel, which is then evacuated, to prevent losses by convection and conduction. The resistance of the coil is measured, and from it the temperature is calculated. A steady current I, at a known potential difference V, is then passed through the coil for t seconds. After the current has been switched off, the resistance of the coil is again measured, to find the rise in temperature of the specimen. Resistance measurements are made at intervals, and enable the cooling curve to be plotted. If m is the mass of the specimen, C the heat capacity of the coil and foil, and θ the corrected rise in temperature, then the specific heat capacity c of the specimen is given by

$$IVt = (mc+C)\theta.$$

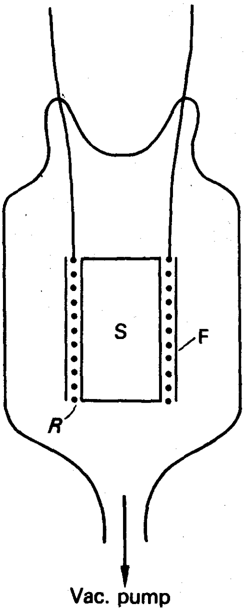


FIG. 9.7. Nernst's calorimeter.

SPECIFIC LATENT HEAT

Fusion

The *specific latent heat of fusion* of a solid is the heat required to convert unit mass of it, at its melting-point, into liquid at the same temperature. It is expressed in joules per kilogramme (J kg^{-1}). High values can be more conveniently expressed in kJ kg^{-1}.

MELTING-POINTS AND SPECIFIC LATENT HEATS OF FUSION

Substance	M.P. °C	S.L.H. J kg^{-1}	Substance	M.P. °C	S.L.H. J kg^{-1}
Aluminium .	658	393 × 10^3	Acetic acid . .	17·5	184 × 10^3
Antimony .	630	163	Beeswax . . .	62	176
Bismuth .	271	58	Brass . . .	900	—
Copper .	1083	180	Naphthalene . .	80	146
Gold . .	1063	67	Paradichlorbenzene (non-flam.)	53	—
Iron . .	1530	205			
Lead . .	327	25	Ice	0	333
Mercury .	—38·9	12·5	Paraffin wax . .	50–60	—
Nickel. .	1452	272	Solder (soft) . .	*c.* 180	50–85
Platinum .	1773	113	Solder (hard) . .	*c.* 900	—
Sulphur .	113–119	38	Steel . . .	1400	—
Silver . .	960·8	109	Glass . . .	300–400	—
Sodium .	97·5	113	Quartz (fused) . .	1,700	—
Tin . .	232	58	Hypo . . .	48·2	*c.* 170
Tungsten .	3380	—			
Zinc . .	419	109			

Ice is one of the substances whose specific latent heat of fusion we are likely to have to measure. To do so, place warm water, at a temperature θ_1 a few degrees above room temperature, inside a calorimeter. Then add small lumps of ice, dried by blotting paper, until the temperature reaches a value θ_2 as much below room temperature as θ_1 was above. In this case a 'cooling correction' is not necessary. Weigh the mixture, to find the mass m of ice which has been added. Then the specific latent heat l is given by:

$$\left.\begin{array}{l}\text{heat given by calori-}\\ \text{meter and water in}\\ \text{cooling}\end{array}\right\} = \left\{\begin{array}{l}\text{heat used in}\\ \text{melting ice}\end{array}\right\} + \left\{\begin{array}{l}\text{heat used in warming}\\ \text{melted ice from }0^\circ\text{C to}\\ \theta_2\end{array}\right.$$

$$\therefore\ (m_1c_w+C)(\theta_1-\theta_2) = ml+mc_w(\theta_2-0),$$

where m_1 = mass of water and c_w = specific heat capacity, C = thermal capacity of calorimeter, and θ_1 = initial temperature.

Hence $$l = \frac{(m_1c_w+C)(\theta_1-\theta_2)}{m} - c_w\theta_2.$$

A modern electrical method, similar to Nernst's for specific heat capacities, gives

$$l = 334\ \text{kJ kg}^{-1} \quad \text{or} \quad 334\ \text{J g}^{-1}.$$

Bunsen's Ice Calorimeter

Bunsen's ice calorimeter is a device for measuring a quantity of heat by using it to melt ice.

When ice turns to water, it shrinks; the volume of 1 g of ice at 0°C is 1·0908 cm^3, whereas that of 1 g of water at 0°C is 1·0001 cm^3 (p. 296). Thus the melting of 1 g of ice causes a contraction of 0·0907 cm^3.

In the Bunsen calorimeter, the contraction due to the melting is measured, and from it the mass of ice melted is calculated. The apparatus is shown in Fig. 9.8. It consists of a test-tube T fused into a wider tube Y. The wider tube leads to a capillary C, and is filled with mercury from X to Y. The space above Y is filled with water from which all dissolved air has been boiled. Except for the capillary, the whole apparatus is placed in ice-water in the vessel V, and, after some time, it all settles down to 0°C. A little ether is then poured into T, and air is blown through it via a thin tube; the ether evaporates and cools the tube T, so that ice forms on the outside of it. A pad of cotton wool is then dropped to the bottom of T and the apparatus is left for some more time, to allow the newly formed ice to settle down to 0°C.

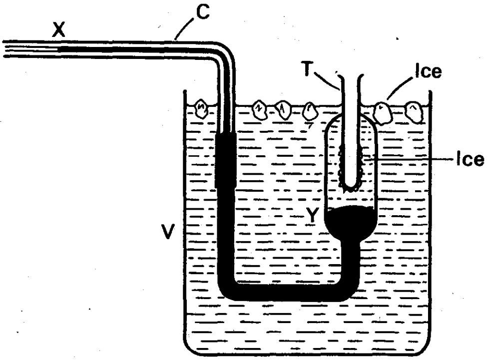


FIG. 9.8. Bunsen's ice calorimeter.

When the apparatus is ready for use, the end of the mercury thread in C is observed by a travelling microscope. If the specific heat capacity of a solid is to be measured, the specimen is weighed (m g) and left to come to room temperature θ. The solid is then gently dropped into the tube T. As it cools, it melts ice, and causes the mercury thread to run back along the capillary. When the thread has ceased to move, its end is again observed. If it has moved through l cm, and the cross-section of the capillary is a cm^2, then the contraction is al cm^3. The mass of ice melted is therefore $al/0{\cdot}0907$ g, and the heat absorbed is $334\ al/0{\cdot}0907$ joules. This heat is given out by m g of solid cooling from θ to 0°C; the specific heat capacity c of the solid is therefore given by

$$mc\theta = \frac{334\,al}{0{\cdot}0907}.$$

In practice, the cross-section is not measured, and the instrument is calibrated by dropping into it a solid of known mass, m_1, and specific heat capacity, c_1. If the room temperature is constant, then

$$\frac{mc}{m_1 c_1} = \frac{l}{l_1},$$

where l_1 is the displacement of the mercury in the calibration experiment. Thus c can be found.

Advantages of the Ice Calorimeter

The advantages of the ice calorimeter are:

(i) no correction for heat capacity of the container: the specimen tube starts at 0°C and finishes at 0°C—all the heat from the specimen is used to melt ice, at constant temperature;

(ii) no heat losses from the apparatus—it is surrounded by a bath at the same temperature as itself, and therefore neither loses heat to the outside, nor gains any from it;

(iii) no loss of heat from the specimen before it enters the calorimeter—the specimen starts at room temperature, and therefore gives up no heat until it enters the specimen tube (contrast the method of mixtures, in which the specimen is heated to 100°C or so): this is a great advantage when the specimen is small;

(iv) easy, and therefore accurate, thermometry—the only temperature to be measured is the room temperature, which is constant and can be determined at leisure.

An advantage sometimes asserted is that specimens can be added one after another, without having to re-set the apparatus. That is true, because each specimen comes to 0°C in turn, and then behaves simply like part of the apparatus, taking no heat from any following specimen. But it does not mean that the calorimeter has the advantage of speed—the time taken to set it up would be enough for half a dozen measurements by the method of mixtures. A disadvantage of this calorimeter is that it never settles down completely—the mercury is always slowly creeping along the capillary, and the creep during an experiment must be estimated and allowed for.

The calorimeter was devised in 1871; it is rarely used nowadays, because electrical methods of calorimetry are more convenient and accurate. However, it has been used for measuring the specific heat capacities of rare earths of which only small specimens were available.

Evaporation

The *specific latent heat of evaporation* of a liquid is the heat required to convert unit mass of it, at its boiling-point, into vapour at the same temperature. It is expressed in joule per kilogramme ($J\,kg^{-1}$), or, with high values, in $kJ\,kg^{-1}$.

BOILING-POINTS AND SPECIFIC LATENT HEATS OF EVAPORATION

Substance	B.P. °C	S.L.H. $J\,kg^{-1}$
Aluminium	1800	—
Acetone	56·7	—
Alcohol (ethyl)	78·3	867×10^3
Alcohol (methyl)	64·7	1120
Benzene	80·2	389
Carbon disulphide	46·2	351
Carbon tetrachloride (non-flam.)	76·7	193
Ether	34·6	370
Glycerine	290	—
Turpentine	161	—
Mercury	357	272
Platinum	3910	—
Sodium	877	—
Sulphur	444·6	—

To find the specific latent heat of evaporation of water, we pass steam into a calorimeter with water (Fig. 9.9). On its way the steam passes through a vessel, T in the figure, which traps any water carried over by the steam and is called a steam-trap. The mass m of condensed steam is found by weighing. If θ_1 and θ_2 are the initial and final temperatures of the water, the specific latent heat l is given by:

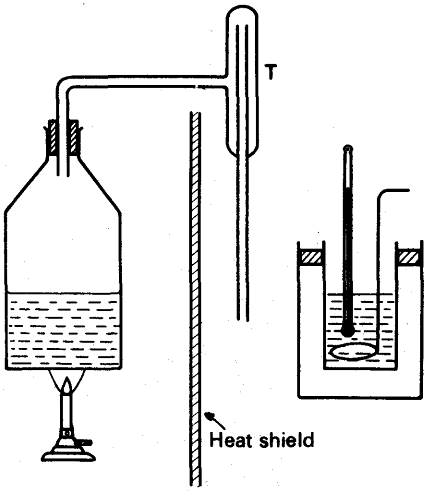


FIG. 9.9. Latent heat of evaporation of water.

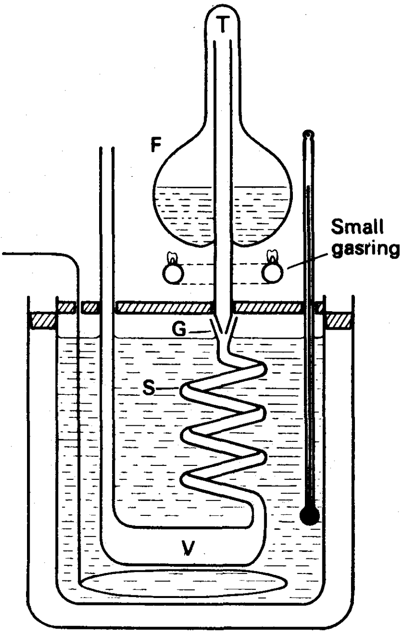


FIG. 9.10. Berthelot's apparatus for latent heat of evaporation.

$$\left.\begin{array}{l}\text{heat given by steam}\\ \text{condensing}\end{array}\right\} + \left\{\begin{array}{l}\text{heat given by con-}\\ \text{densed water cooling}\\ \text{from } 100^\circ\text{C to } \theta_2\end{array}\right\} = \left\{\begin{array}{l}\text{heat taken by}\\ \text{calorimeter and}\\ \text{water}\end{array}\right.$$

$$ml \quad + \quad mc_w(100-\theta_2) \quad = (m_1c_w+C)(\theta_2-\theta_1)$$

where m_1c_w and C have their usual meanings.

Hence $$l = \frac{(m_1c_w+C)(\theta_2-\theta_1)}{m} - c_w(100-\theta_2).$$

The accepted value of the specific latent heat of evaporation of water is about $l = 2260 \text{ kJ kg}^{-1}$ or 2260 J g^{-1}.

Berthelot's Apparatus. An apparatus suitable for use with liquids other than water was devised by Berthelot in 1877 (see Fig. 9.10). The liquid is boiled in the flask F, and its vapour passes out through the tube T. This fits with a ground joint G into the glass spiral S, which is surrounded by water in a calorimeter. The vapour condenses in the spiral, and collects in the vessel V, where it can afterwards be weighed. Let

θ_b = boiling-point of liquid.
c = specific heat capacity of liquid.
m = mass of liquid condensed.
θ_1 = initial temperature of water.
θ_2 = final temperature of water, *corrected for cooling.*
m_1 = mass of water of specific heat c_w.
C = thermal capacity of calorimeter + glassware below joint.

Then
$$ml+mc(\theta_b-\theta_2) = (m_1c_w+C)(\theta_2-\theta_1),$$

whence
$$l = \frac{(m_1c_w+C)(\theta_2-\theta_1)}{m} - c(\theta_b-\theta_2).$$

Electrical Method for Specific Latent Heat

A modern electrical method for the specific latent heat of evaporation of water is illustrated in Fig. 9.11 below. The liquid is heated in a vacuum-jacketed vessel U by the heating coil R. Its vapour passes down

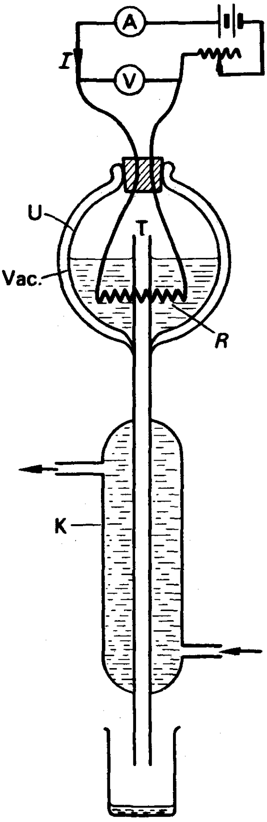


FIG. 9.11. Electrical method for latent heat of evaporation.

the tube T, and is condensed by cold water flowing through the jacket K. When the apparatus has reached its steady state, the liquid is at its boiling-point, and the heat supplied by the coil is used in evaporating the liquid, and in offsetting the losses. The liquid emerging from the condenser is then collected for a measured time, and weighed.

If I and V are the current through the coil, and the potential difference across it, the electrical energy supplied in t seconds is IVt. And if h is the heat lost from the vessel per second, and m the mass of liquid collected in t seconds, then

$$IVt = ml + ht \qquad . \quad . \quad . \quad . \qquad (1)$$

The heat losses h are determined by the temperature of the vessel, which is fixed at the boiling-point of the liquid. Therefore they may be eliminated by a second experiment with a different rate of evaporation (cf. Callendar and Barnes, p. 206). If $I'V'$ are the new current and potential difference, and if m' grammes are evaporated in t seconds, then

$$I'V't = m'l + ht.$$

Hence by subtraction from equation (1)

$$l = \frac{(IV - I'V')t}{(m - m')}.$$

EXAMPLES

1. An electric kettle has a 750 W–240 V heater and is used on a 200 V mains. If the heat capacity of the kettle is 400 J K^{-1} and the initial water temperature is 20°C, how long will it take to boil 500 g of water, assuming the resistance of the heater is unaltered on changing to the new mains.

Firstly, find the new power absorbed on the 200 V mains. Since the resistance R is constant and $P = V^2/R$, it follows that $P \propto V^2$.

$$\therefore \text{ new power} = \left(\frac{200}{240}\right)^2 \times 750 \text{ W} = 520 \text{ W (approx.)}$$

$$\therefore \text{ heat supplied to water} = 520 \text{ J per second} \qquad . \quad . \quad . \quad . \qquad (1)$$

Secondly, assuming 100°C is the boiling point and 4·2 kJ kg^{-1} K^{-1} (4·2 J g^{-1} K^{-1}) is the specific heat capacity of water,

$$\begin{aligned} \text{heat gained by water and kettle} &= 500 \times 4{\cdot}2 \times (100-20) + 400 \times (100-20) \\ &= (500 \times 4{\cdot}2 + 400)(100-20) \\ &= 610 \times 80 \text{ J.} \end{aligned}$$

$$\text{From (1), } \therefore \text{ time, } t = \frac{2500 \times 80}{520} = 385 \text{ seconds (approx.)} = 6{\cdot}4 \text{ min.}$$

2. Water flows at the rate of 150·0 g min^{-1} through a tube and is heated by a heater dissipating 25·2 W. The inflow and outflow water temperatures are 15·2°C and 17·4°C respectively. When the rate of flow is increased to 231·8 g min^{-1} and the rate of heating to 37·8 W, the inflow and outflow temperatures are unaltered. Find (i) the specific heat capacity of water, (ii) the rate of loss of heat from the tube.

Suppose c_w is the specific heat of water in J g^{-1} K^{-1} and h is the heat lost in J s^{-1}. Then, since 1 W = 1 J per second,

$$25{\cdot}2 = \frac{150{\cdot}0}{60}c_w(17{\cdot}4-15{\cdot}2)+h \quad . \quad . \quad . \quad (1)$$

and
$$37{\cdot}8 = \frac{231{\cdot}8}{60}c_w(17{\cdot}4-15{\cdot}2)+h \quad . \quad . \quad . \quad (2)$$

Subtracting (1) from (2),

$$\therefore\ 37{\cdot}8-25{\cdot}2 = \frac{231{\cdot}8-150{\cdot}0}{60}\ c_w(17{\cdot}4-15{\cdot}2)$$

$$\therefore\ c_w = \frac{12{\cdot}6\times 60}{81{\cdot}8} = 4{\cdot}2\ \text{J g}^{-1}\ \text{K}^{-1} = 4{\cdot}2\ \text{kJ kg}^{-1}\ \text{K}^{-1}.$$

Substituting for c_w in (1),

$$\therefore\ h = 25{\cdot}2-\frac{150}{60}\times 4{\cdot}2\times 2{\cdot}2 = 2{\cdot}1\ \text{J s}^{-1}.$$

3. Define *latent heat.* Describe the measurement of the specific latent heat of evaporation of water under school laboratory conditions.

A copper calorimeter of mass 70·5 g contains 100·0 g of water at 19·5°C. Naphthalene (M.P. 79·9°C) is melted in a test tube, cooled to 80·0°C, and then poured into the calorimeter. If the highest temperature reached by the water after stirring is 28·7°C and the final mass of the calorimeter and its contents is 188·3 g calculate the latent heat of fusion of naphthalene. (Specific heat capacity of copper 0·4, of naphthalene 1·3 kJ kg^{-1} K^{-1}.) (*L.*)

First part. The specific latent heat of a substance is the heat required to change unit mass of the solid at the melting-point to liquid at the same temperature (fusion), or the heat required to change unit mass of the liquid at the boiling-point to vapour at the same temperature (vaporization).

The measurement of the specific latent heat of evaporation of water requires the following, among other points: (i) use of a steam trap, (ii) a rise in temperature of the water in the calorimeter of about 10°C, (iii) a 'correction' to 100°C as the steam temperature, if the barometric pressure is not 76 cm mercury, (iv) a cooling correction.

Second part. The mass of naphthalene = 188·3 − 170·5 = 17·8 g.

Heat lost by naphthalene = heat gained by water and calorimeter.

$$\therefore\ 17{\cdot}8l+17{\cdot}8\times 1{\cdot}3\times(79{\cdot}9-28{\cdot}7)$$
$$= 100\times 4{\cdot}2\times(28{\cdot}7-19{\cdot}5)+70{\cdot}5\times 0{\cdot}4\times(28{\cdot}7-19{\cdot}5).$$

Solving, $\therefore\ l = 164\ \text{J g}^{-1}$ (approx.) $= 164\ \text{kJ kg}^{-1}$.

4. In an X-ray tube, 10^{18} electrons per second arrive with a speed of 2×10^6 m s^{-1} at a metal target of mass 200 g and specific heat capacity 0·5 J g^{-1} K^{-1}. If the mass of an electron is $9{\cdot}1\times 10^{-31}$ kg, and assuming 98% of the incident energy is converted into heat, find how long the target will take to rise in temperature by 50°C assuming no heat losses.

The kinetic energy of a moving object is $\frac{1}{2}mv^2$ joules, where m is the mass in kg and v is the speed in m s^{-1}. Assuming the initial speed is zero,

$$\therefore\ \text{energy per second of incident electrons} = \tfrac{1}{2}\times(10^{18}\times 9{\cdot}1\times 10^{-31})\times(2\times 10^6)^2\ \text{J}$$
$$= 1{\cdot}8\ \text{J (approx.)}.$$

Heat gained by target = 200 × 0·5 × 50 J = 50000 J

$$\therefore\ \text{time} = \frac{50000}{1{\cdot}8} = 2780\ \text{seconds (approx.)} = 46{\cdot}3\ \text{min}.$$

EXERCISES 9

1. Describe, with the aid of a labelled diagram, how you would find the specific heat capacity of a liquid by the method of continuous flow.

Discuss the advantages and disadvantages of the method compared with the method of mixtures.

The temperature of 50 g of a liquid contained in a calorimeter is raised from 15·0°C (room temperature) to 45·0°C in 530 seconds by an electric heater dissipating 10·0 watts. When 100 g of liquid is used and the same change in temperature occurs in the same time, the power of the heater is 16·1 watts. Calculate the specific heat capacity of the liquid. (*N.*)

2. Distinguish between *specific* heat capacity and *latent* heat capacity. With what physical changes is each associated? Describe the processes involved in terms of simple molecular theory.

A thin-walled tube containing 5 cm^3 of ether is surrounded by a jacket of water calibrated so that changes in the volume of the water can be read off. The whole apparatus is cooled down to 0°C and all the ether is then evaporated by blowing a rapid stream of air pre-cooled to 0°C through it. The change of volume as ice forms in the water is 0·35 cm^3. Calculate the specific latent heat of evaporation of the ether.

(Use the following values: specific latent heat of fusion of ice = 334 J g^{-1}. Densities at 0°C: water, 1·000 g cm^{-3}; ice, 0·917 g cm^{-3}; ether, 0·736 g cm^{-3}.) (*O. & C.*)

3. Give an account of an electrical method of finding the specific latent heat of vaporisation of a liquid boiling at about 60°C. Point out any causes of inaccuracy and explain how to reduce their effect.

Ice at 0°C is added to 200 g of water initially at 70°C in a vacuum flask. When 50 g of ice has been added and has all melted the temperature of the flask and contents is 40°C. When a further 80 g of ice has been added and has all melted the temperature of the whole becomes 10°C. Calculate the specific latent heat of fusion of ice, neglecting any heat lost to the surroundings.

In the above experiment the flask is well shaken before taking each temperature reading. Why is this necessary? (*C.*)

4. The specific heat capacity of gallium metal is 0·33 kJ kg^{-1} K^{-1}. Explain carefully how this result may be determined experimentally. Indicate the sources of error in your method and estimate the accuracy which could be achieved.

[Melting point of gallium = 30°C.]

A ball of gallium is released from a stationary balloon, falls freely under gravity and on striking the ground it just melts. Calculate the height of the balloon assuming that the temperature of the gallium just before impact is 1°C and that all the energy gained during its free fall is used to heat the gallium on impact. Why are the conditions specified in this problem unrealistic?

[Specific latent heat of fusion of gallium = 79 kJ kg^{-1}.] (*O. & C.*)

5. Explain what is meant by the specific latent heat of vaporization of a liquid, and describe an experiment for an accurate determination of this quantity for carbon tetrachloride, which boils at 77°C.

A thermally insulated vessel connected to a vacuum pump contains 10·0 g of water at a temperature of 0°C. As air and water vapour are exhausted from the vessel, it is observed that the water remaining in the vessel freezes. Explain why this happens, and find the mass of water which is converted into ice.

[Specific latent heat of vaporization of water at 0°C = 2520 kJ kg^{-1}; specific latent heat of fusion of ice at 0°C = 336 kJ kg^{-1}.] (*C.*)

6. Discuss the nature of the heat energy (*a*) of a solid, (*b*) of a gas, (*c*) of the sun during the transmission of this energy to the earth.

265430 joules of heat are produced when a vehicle of total mass 1270 kg is brought to rest on a level road. Calculate the speed of the vehicle in km per hr just before the brakes are applied. (*L.*)

7. State *Newton's law of cooling* and describe how to obtain observations and how to use them in order to test the validity of the law.

A solid of mass 250 g in a vessel of thermal capacity 67·2 J K^{-1} is heated to a few degrees above its melting point and allowed to cool in steady conditions until solid again. Sketch the graph of its temperature plotted against time. If this graph shows that immediately before solidification starts the rate of cooling is 3·2 deg C min^{-1}, while immediately after solidification it is 4·7 deg C min^{-1}, calculate the specific heat capacity of the solid taken by the solidifying process. (The specific latent heat of fusion of the substance may be taken as 146·6 kJ kg^{-1} and its specific heat capacity in the liquid state as 1·22 kJ kg^{-1} K^{-1}.) (*L.*)

8. What do you understand by the *specific heat capacity* of a substance? Describe how you would measure the specific heat capacity of a sample of rock, describing the precautions that you would take to obtain an accurate result.

A room is heated during the day by a 1 kW electric fire. The fire is to be replaced by an electric storage heater consisting of a cube of concrete which is heated overnight and is allowed to cool during the day, giving up its heat to the room. Estimate the length of an edge of the cube if the heat it gives out in cooling from 70°C to 30°C is the same as that given out by the electric fire in 8 hours.

[Density of concrete = 2700 kg m^{-3}; specific heat capacity of concrete = 0·85 kJ kg^{-1} K^{-1}.] (*O. & C.*)

9. An experiment was performed to determine the specific latent heat of vaporization of a volatile liquid at the prevailing boiling point by the method of electrical heating. The results are summarized in the following table:

Rate of supply of energy to boiling liquid (watt)	Mass of liquid vaporized in 200 seconds (g)
10	1·6
20	6·4
30	11·2
40	16·0

Use the data to plot a graph (using the graph paper available) and hence determine the latent heat of vaporization of the liquid and the rate of loss of heat from the calorimeter containing the boiling liquid.

Draw a labelled diagram of a suitable apparatus for use in the experiment and indicate how the above results would have been obtained.

Give *two* advantages of this method over the method of mixtures. (*N.*)

10. In 1948 the International Conference on Weights and Measures recommended that the calorie should no longer be regarded as the basic unit of heat, but that it should be replaced by the joule. Discuss the reasons for, and the advantages and possible disadvantages of, this recommendation.

Give a labelled diagram of a continuous flow calorimeter suitable for the determination of the specific heat capacity of a liquid. What measurements would you make in such a determination, and how would the result be obtained from them? State the precautions which you would adopt to ensure an accurate result. (*C.*)

11. Give an account of a method of determining the specific latent heat of evaporation of water, pointing out the ways in which the method you describe achieves, or fails to achieve, high accuracy.

A 600 watt electric heater is used to raise the temperature of a certain mass of water from room temperature to 80°C. Alternatively, by passing steam from a boiler into the same initial mass of water at the same initial temperature the same temperature rise is obtained in the same time. If 16 g of water were being evaporated every minute in the boiler, find the specific latent heat of steam, assuming that there were no heat losses. (*O. & C.*)

12. 300 g of a certain metal of density about 19 g cm^{-3} is available in the form of a coarse powder, together with a calorimeter of heat capacity about 33·6 J K^{-1} and volume about 160 cm^3, and a 50°C thermometer reading to $\frac{1}{5}$ deg.

Using this and other necessary apparatus, how would you verify, by the method of mixtures, that the specific heat of the metal is 0·13 kJ kg^{-1} K^{-1}?

In the experiment you describe why is it (*a*) unnecessary to apply a correction for heat exchange with the surroundings, (*b*) necessary to decide on a suitable maximum temperature of the mixture? How would you ensure that such a temperature is realized? (*N.*)

13. Describe an *electrical* method for the determination of the *specific latent heat of steam.* State the probable sources of error in the experiment and suggest how they may be minimised.

In one method for storing solar energy, Glauber's salt can be allowed to warm up to 45°C in the sun's rays during the day and the stored heat is used during the night, the salt cooling down to 25°C. Glauber's salt melts at 32°C. Calculate the mass of salt needed to store 1 million joules.

(Specific heat capacity of Glauber's salt, solid = 0·11 kJ kg^{-1} K^{-1}; specific heat capacity of Glauber's salt, molten = 0·16 kJ kg^{-1} K^{-1}. Specific latent heat of fusion = 14 kJ kg^{-1}.) (*O. & C.*)

14. What is meant by the *specific heat capacity* of a substance? Give a brief account of **two** methods, one in each case, which may be used to find the specific heat capacity of each of the following: (*a*) a specimen of a metal in the form of a block a few cm in linear dimensions, and (*b*) a liquid which is available in large quantities. Indicate whether the methods you describe involve a cooling correction.

An electrical fuse consists of a piece of lead wire 1·5 mm in diameter and 5 cm long, which has a resistance of $6{\cdot}5 \times 10^{-3}$ ohm. Owing to a fault a constant current of 800 A passes through the fuse. If the wire is initially at 10°C and melts at 330°C, find the time interval before it starts to melt, assuming that its specific heat capacity and its electrical resistance are constant and that there are no heat losses.

[Specific heat capacity of lead = 0·13 kJ kg^{-1} K^{-1}. Density of lead = 11000 kg m^{-3}.] (*O. & C.*)

15. Describe the determination of the latent heat of fusion of ice by the method of mixtures and, in particular, show how allowance is made for heat interchange with the surroundings.

A calorimeter of heat capacity 84 J K^{-1} contains 980 g of water supercooled to −4°C. Taking the latent heat of fusion of ice at 0°C as 336 kJ kg^{-1}, find the amount of ice formed when the water suddenly freezes. Calculate also the specific latent heat of fusion at −4°C if the specific heat capacity of ice is 2·1 kJ kg^{-1} K^{-1}. (*N.*)

16. State Newton's law of cooling, and describe an experiment by which you would verify it. A calorimeter containing first 40 and then 100 g of water is heated and suspended in the same constant-temperature enclosure. It is found that the times taken to cool from 50° to 40°C in the two cases are 15 and 33 minutes respectively. Calculate the heat capacity of the calorimeter. (*O. & C.*)

17. Oil at 15·6°C enters a long glass tube containing an electrically heated platinum wire and leaves it at 17·4°C, the rate of flow being 25 cm^3 per min and the rate of supply of energy 1·34 watts. On changing the rate of flow to 15 cm^3 per min and the power to 0·76 watt the temperature again rises from 15·6° to 17·4°C. Calculate the mean specific heat capacity of the oil between these temperatures. Assume that the density of the oil is 870 kg m^{-3}. (*N.*)

18. In the absence of bearing friction a winding engine would raise a cage weighing 1000 kg at 10 m s^{-1}, but this is reduced by friction to 9 m s^{-1}. How much oil, initially at 20°C, is required per second to keep the temperature of the bearings down to 70°C? (Specific heat capacity of oil = 2·1 kJ kg^{-1} K^{-1}; $g = 9{\cdot}81$ m s^{-2}. (*O. & C.*)

19. A heating coil is embedded in a copper cylinder which also carries a thermocouple. The whole is thermally equivalent to 25 g of copper. The cylinder is suspended in liquid air until the thermocouple reading is constant. The cylinder is taken out and rapidly transferred into a beaker of water at 0°C. A coating of ice forms on the cylinder and when its temperature is again constant it is taken out of the water and suspended in a space maintained at 0°C. The heating coil is switched on at a steady energy dissipation of 24 watts. After 1 minute 5 seconds the whole of the ice has just melted. What is the temperature of the liquid air?

What assumptions were made in carrying out the calculations? (Mean specific heat capacity of copper is 0·336 kJ kg^{-1} K^{-1}.) (*L.*)

20. Describe a continuous flow method of measuring the specific heat capacity of a liquid. Explain the advantages of the method.

Use the following data to calculate the specific heat capacity of the liquid flowing through a continuous flow calorimeter: *Experiment I.* Current 2·0 amp, applied p.d. 3·0 volt, rate of flow of liquid 30 g min^{-1}, rise in temperature of liquid 2·7°C. *Experiment II.* Current 2·5 amp, applied p.d. 3·75 volts, rate of flow of liquid 48 g min^{-1}, rise in temperature of liquid 2·7°C. (*L.*)