

CHAPTER 18

EXPERIMENTAL MEASUREMENTS

18.1 *Introduction*

Most of these notes on heat and thermodynamics have been largely theoretical, and almost no attention has been given to laboratory measurements of the various quantities discussed. This is not because experiment is any less important than theory. Rather it is more the consequence of my own interests and personal lack of expertise in experiment. Indeed, laboratory physics equipment has a tendency to disintegrate as soon as I approach it. However, in this chapter we shall endeavour to describe, however inadequately, some of the early classical experimental measurements.

I am under the impression that today, in order to measure *any* physical quantity, you purchase some expensive equipment, attach one end of it to the thing to be measured, and the other end to a computer, and one instantaneously obtains a digital readout of the quantity in question, without necessarily having any idea how the equipment works. And I, certainly, have little idea how much of modern high technology works. Consequently I shall restrict this chapter to brief descriptions of some of the earlier classical historical determinations of thermal quantities, many of which were performed during the nineteenth century or the early twentieth century.

Of all the many experimental determinations of physical quantities in various branches in physics, accurate determinations in the laboratory of thermal quantities are among the most difficult classical measurements of all. It would be easy to dismiss the various early experiments that I shall describe in this chapter as quaint, crude and of no modern interest. Far from it. Some of these experiments were extremely difficult to carry out accurately, and it is astonishing how accurate many of the early measurements were, as a result of the careful design, attention to detail and allowance for heat losses. The early experimenters deserve our great admiration and our gratitude for the important fundamental contributions they made to our understanding of physical science.

18.2 *Thermal Conductivity*

18.2.1 *Solid Good Conductors (Metals)*

The difference between the thermal conductivities of metals and non-metals is so large that different experimental approaches are needed for the two classes of solids, and in this subsection we deal with metals.

I remember as long ago as when I was in high school one of the experiments we had to do was to measure the conductivity of a metal rod, which, as far as I remember, was about a foot (30 cm) long and maybe two centimetres in diameter. The experiment was called Searle's Rod, or Searle's Bar, after an experimenter in the early years of the twentieth century. The experiment was simple in principle, but very difficult in practice to do accurately, and we were always advised to avoid doing heat experiments in our matriculation examinations. Heat was supplied by an electrical coil wrapped around one end of the rod, and the rate of supply of heat was determined from the current

through the wire and the potential difference across it, measured with an ammeter and voltmeter respectively. Heat was collected at the other end of the rod by means of a stream of water flowing through a helical tube wrapped around that end of the rod. Thermometers at the beginning and end of this helical tube measured the rise in temperature of the water. Hence one could determine the rate of flow of heat out of the cool end of the rod. If no heat were lost from side of the rod, the rate of flow of heat into the rod (determined electrically) should equal the rate of flow out of it (measured by the rise in temperature of the stream of water through the helical tube). The difference between the two would be a measure of how much heat was lost from the side of the rod. The rod was supposedly well lagged with cotton wool to keep the heat loss small. (I am talking of a high-school experiment here. One could improve on this in a more advanced laboratory by having the rod in a vacuum – so there is no loss of heat by conduction or convection, and highly polished to reduce heat loss by radiation). The temperature gradient along the length of the tube was determined by drilling pits at two points along the rod, filling these with mercury (for good thermal contact), and sticking mercury-in-glass thermometers into these little pools of mercury. One can easily imagine how difficult such an experiment was! At any rate, there was by then enough information to determine the thermal conductivity, for one knew the temperature gradient, from the thermometers stuck into the little mercury pools, and one knew the rate of flow of heat into and out of the rod, and of course one knew the cross-sectional area of the rod. In a more advanced laboratory today, rather than sticking mercury-in-glass thermometers into two mercury-filled holes, one could measure the temperature at several points along the length of the rod by means of thermocouples or thermistors welded into the rod. If there were no heat losses along the length of the rod, the temperature gradient would be uniform along the rod. In practice, the thermistors would show a nonuniform temperature gradient, and from this one could calculate and allow for the heat loss along the rod. Likewise the temperatures at the inflow and outflow ends of the little helical tube could be measured with some tiny modern device, and all of these electrical connections today would be connected to a computer, which would immediately do all the necessary calculations, including correction of heat loss, and the thermal conductivity would be instantly displayed!

Lees developed the details of the equipment so that much smaller specimens could be used – e.g. a rod just a few cm in length and a few mm in diameter – so that he could enclose it in a Dewar flask and make measurements down to the temperature of liquid air. Three small coils of varnished copper wire were wound round the rod. (By varnished copper wire I mean copper wire whose surface was painted with a layer of varnish of sufficient thickness to insulate the coils electrically but sufficiently thin that good thermal contact with the rod was made.) One of these coils was wound round the upper end of the rod, and supplied heat at that end. The other two coils could be slid up and down to any desired positions on the rod, and they served as resistance thermometers. That is, the local temperature of the rod could be measured by measuring the resistance of the coils. This set-up provided in principle what was necessary to determine the thermal conductivity of the rod, for the rate of input of heat to the rod was determined by the current in the uppermost coil, and the temperature gradient down the rod was measured with the two movable thermometer coils.

An interesting method that has been used (using a rod of roughly the same dimensions as in Searle's Rod experiment – that is to say, about a foot (30 cm) long and one or two cm in diameter – is to pass an electrical current along length of the rod, thus heating it. However, the two ends of the rod are kept at the same temperature (T_1) by keeping them in constant-temperature baths. The

temperature of the rod is greatest (T_2) at its mid-point. It can be shown, by a solution of the heat conduction equation, that

$$\sigma_{\text{therm}} = \frac{V^2}{8(T_2 - T_1)} \sigma_{\text{elect}}. \quad 18.2.1$$

Here, V is the electrical potential difference, in volts, across the ends of the rod, σ_{therm} is the thermal conductivity in $\text{W m}^{-1} \text{K}^{-1}$, and σ_{elect} is the electrical conductivity, in S m^{-1} . I haven't derived that equation here (if I can, I may do so later!), but at least you can (I hope!) show that it is dimensionally correct. This method has been used to measure the ratio of the thermal to the electrical conductivity down to temperatures of a few kelvin, as well as at high temperatures.

18.2.2 Solid Poor Conductors (Non-metals)

The most obvious modification that has to be made for the measurement of the thermal conductivity of a poor conductor is in the shape of the sample to be measured. Instead of a long, thin rod, one needs a thin disc. In Lees' Discs experiment, the disc-shaped sample is clamped between two copper discs, one of which is heated with an electrical coil. The temperatures of the two copper discs are measured with thermocouples. This gives enough information, in principle, for the determination of the thermal conductivity, but, as in all thermal experiments, there are numerous refinements both for minimizing heat losses, and for allowing for what heat losses remain.

18.2.3 Liquids and Gases

Several methods have been used. Here I mention one straightforward method that has been used for both liquids and gases (i.e. fluids). The fluid is held in a long cylinder of radius b . A wire, of radius a , down the axis of the cylinder is heated electrically. The temperature T_2 of the wire can be measured by measuring its resistance, and the temperature T_1 the wall of the cylinder can be measured with a thermocouple. The rate of flow of heat \dot{Q} through the fluid is equal to the rate at which electrical energy is supplied to the wire - $I^2 R$. Anyone who has been able to work out the electric field between two coaxial cylinders in an elementary electricity course (see the Electricity and Magnetism section of these Notes) will be able to work out the relevant equations, but here goes, anyway.

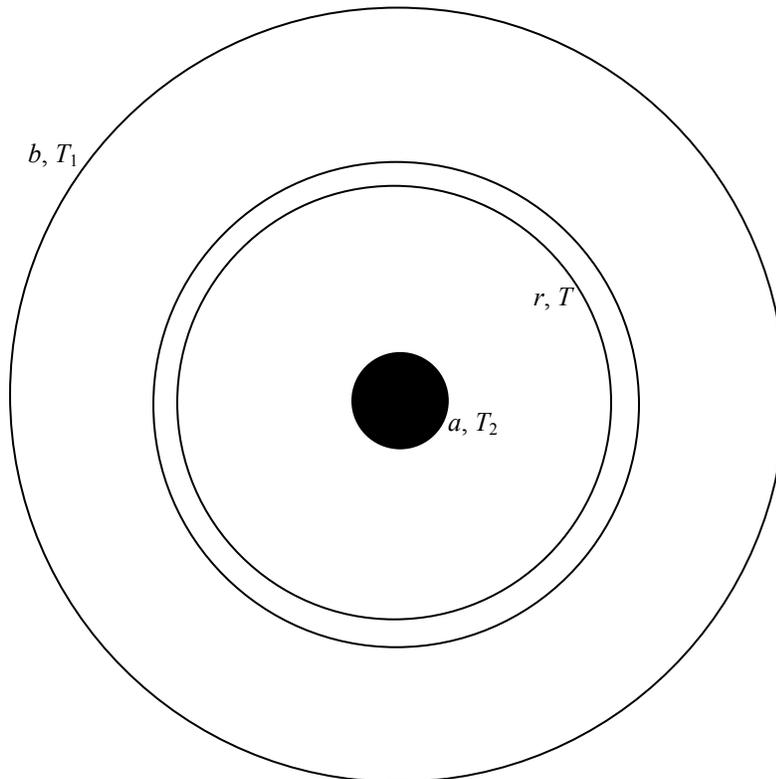
Consider an elemental cylindrical shell, radii r , $r + dr$. Its area is $2\pi r l$, where l is the length of the cylinder. If the temperature gradient there is dT/dr (which is negative), the rate of flow of heat, \dot{Q} (which is known, as explained above) is given by

$$\dot{Q} = -2\pi r l \sigma \frac{dT}{dr}. \quad 18.2.2$$

Integrate this from $r = a$, $T = T_2$ to $r = b$, $T = T_1$, and we get

$$\sigma = \frac{\dot{Q}}{2\pi l(T_2 - T_1)} \ln\left(\frac{b}{a}\right) \quad 18.2.3$$

This assumes a very long cylinder, and ignores end effects. End effects can be kept small by using a long, thin tube, and can be allowed for by experimenting with tubes of several lengths.



18.3 *The Universal Gas Constant.*

If you had an ideal gas, all you would have to do is to measure its pressure, its temperature, and the volume occupied by a mole, for then $PV = RT$. (Measuring P and T is relatively easy. Measuring the volume occupied by a mole is less so.) In real life, however, we have to make measurements on real gases. What has to be done is to measure the product PV (at a given temperature) at progressively lower and lower pressures, and extrapolate the value of PV/T to the limit of zero pressure. (See notes in Chapter 6 on the compression factor.)

18.4 *Avogadro's Number and Boltzmann's Constant.*

Avogadro's number is best determined by electrolytic deposition. That is, you have to measure the quantity of electricity (current times time) that will deposit a mole of a monovalent element from an electrolytic solution on to an electrode. This quantity of electricity is generally called a *faraday*, and is about 96,484 coulombs, and is the product of the electronic charge and Avogadro's number.

Boltzmann's constant is given by $k = R / N_A$.

18.5 Specific Heat Capacities of Solids and Liquids

In elementary instructional methods often used at high school, the *method of mixtures* is generally used. For example, to measure the specific heat capacity of copper, one would need a calorimeter (a small cup) made of copper, and of known mass. Pour a measured mass of boiling water (100 °C) into this. The temperature of the copper rises from room temperature, t_1 °C, to a final temperature, t_2 °C, while the temperature of the water falls from 100 °C to t_2 °C. The specific heat capacity of the copper is then given by $m_{\text{Cu}} C_{\text{Cu}} (t_2 - t_1) = m_{\text{H}_2\text{O}} (100 - t_2)$. Since the specific heat capacity of water is, by definition, $1 \text{ cal g}^{-1} \text{ C}^\circ^{-1}$ (at least to the precision expected at this level of experimentation), the specific heat capacity of the copper is determined.

To determine the specific heat capacity of another liquid, you could pour a measured mass of the hot liquid into the calorimeter (whose heat capacity is now known), and measure the fall in temperature of the liquid and the rise in temperature of the calorimeter, and hence deduce the specific heat capacity of the liquid by means of a similar equation to the above.

To determine the specific heat capacity of another metal, for example, iron, one can warm an iron specimen (of measured mass) to 100 °C, and then drop it into the copper calorimeter, which contains water at room temperature, t_1 °C, and then measure the final temperature t_2 °C to which the iron cools down and the copper and water heat up. Then

$$m_{\text{Cu}} C_{\text{Cu}} (t_2 - t_1) + m_{\text{H}_2\text{O}} C_{\text{H}_2\text{O}} (t_2 - t_1) = m_{\text{Fe}} C_{\text{Fe}} (100 - t_2).$$

In all such experiments, precautions must be taken to minimize heat losses, and to allow for such heat losses as remain. Most of us will remember such experiments from our schooldays, and will remember how difficult it was to get reliable results, and will be aware that there are much more accurate methods available. Furthermore, the method of mixtures measures the *relative values* of the specific heat capacities of the materials being mixed, rather than their absolute specific heat capacities. This is all right if we accept that the specific heat capacity of water is unity by definition, but, as soon as it is recognized that heat is a form of energy, we want to be able to measure heat capacities in joules rather than in calories, and the method of mixtures does not do this.

It must not be supposed, however, that the method of mixtures is confined to the schoolroom, and is never used in professional research laboratories. It has been found particularly useful in the measurement of heat capacities at high temperatures. While the details of such experiments are much more sophisticated than as described above, the principle of the method of mixtures still remains.

Nevertheless it remains true that the method of mixtures is really a method of *comparing* the specific heat capacities of different materials, or of *comparing* the specific heat capacity of a substance with that of water. The first reasonably accurate direct determination of the amount of energy needed to raise the temperature of a measured mass of water through a measured temperature rise was Joule's famous experiment. In Joule's experiment, water was warmed by stirring it with paddles, which were operated by a set of falling weights, and the amount of work done by these falling weights could be accurately calculated in units of work (which, to Joule, were foot-pounds, but which today, we would calculate in joules.) To Joule, the object of the experiment was to demonstrate that a given amount of work always produced the same amount of heat, and hence to determine what he called the *mechanical equivalent of heat*. Today, we recognize the experiment as a direct measurement, in units of mechanical work, of the specific heat capacity of water, no longer defined to be 1 calorie per gram per degree, but measured to be 4184 joules per kilogram per kelvin. We can look back today at Joule's experiment in amazement – amazement not only at how difficult it must have been and what great experimental skills it entailed, but amazement, too, at how accurate a result he obtained. He wrote: "After reducing the result to the capacity for heat for a pound of water, it appeared that for each degree of heat evolved by the friction of water, a mechanical power equal to that which can raise a weight of 890 lbs to the height of one foot had been expended." Bearing in mind that his "degree of heat" would have been a Fahrenheit degree, this is equivalent to 4790 joules per kilogram per Celsius degree. In addition to his famous paddle-wheel experiment, Joule performed two other experiments - of a quite different nature – to determine the "mechanical equivalent of heat", and he took, as the average of the three experiments, a figure of 817 pounds, which, in modern units, would be equivalent to 4398 joules per kilogram per Celsius degree – only five percent greater than the modern value.

Of course much more accurate measurements of the energy required to raise the temperature of a solid or a liquid can be made by *heating the sample electrically* – that is, in the case of a liquid, immersing a heating coil in the liquid, or, in the case of a solid, wrapping a heating coil around the solid. Admittedly, this does not have the direct frontal approach of heating the sample by mechanical work, but at least the heat input (I^2R) can be accurately measured. Of course, as in all thermal measurements, precautions must be taken to minimize heat losses, and to allow for what heat losses remain, and these considerations must go into the detailed design of the experiment and its procedures. One technique is to surround the calorimeter by an outer vessel, which, by means of suitably-designed thermostats, is kept always at the same temperature as the calorimeter itself, thus (at least in principle) avoiding heat losses from the calorimeter altogether.

Quite precise measurements of the specific heat capacities of solids and liquids (relative to that of water) can be made with the *Bunsen Ice Calorimeter*, which is described in Section 18.7.

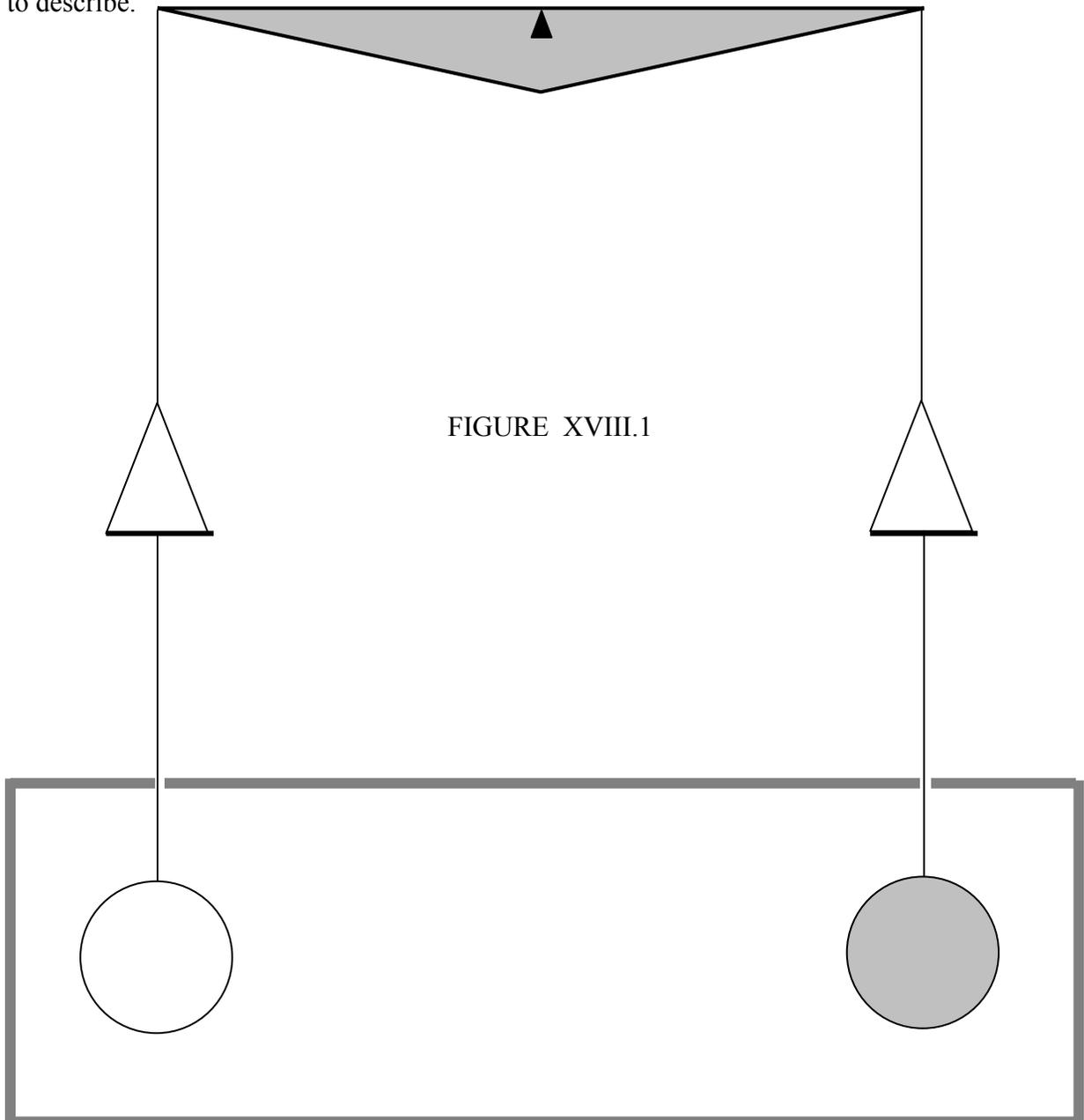
18.6 *Specific Heat Capacities of Gases*

We have to consider the measurement of the specific heat capacity at constant pressure and at constant volume.

The most famous of the early experiments to measure directly the specific heat capacity of a gas at constant pressure were Regnault's experiments of around 1860. Gas from a large storage cylinder was passed at constant pressure (measured with a manometer) through a series of helical copper

tubes. The first helix was immersed in a constant high-temperature bath, which, of course, warmed the gas up. The warm gas then continued its flow through a smaller helix, which was immersed in a small copper calorimeter filled with cold water. The gas, of course, cooled down, and the water in the calorimeter warmed up. The fall in temperature of the gas and the rise in temperature of the water were measured, and hence the specific heat capacity of the gas at constant pressure was calculated. While the principle of the experiment was simple and straightforward, its actual practical execution required an experimental skill of the very highest order.

The most famous of the early experiments to measure directly the specific heat capacity of a gas at constant volume is *Joly's differential steam calorimeter* of around 1890. Two equal hollow copper spheres were suspended from the arms of a balance. One of the spheres was filled with the gas under investigation; the other was evacuated (or at least as far as the vacuum technology of the day could achieve). The two spheres were surrounded by a chamber into which steam could be pumped. I'm not very good at art, but I'll try to indicate very schematically, in figure XVIII.1, what I am trying to describe.



Steam was pumped into the chamber, and some of it condensed on the two spheres. Naturally, more steam condensed on the sphere that held the gas, and the mass of extra condensate was measured by adding weights to the other scale pan. The mass of extra condensate times its specific latent heat of condensation was equated to the heat required to raise the temperature of the gas inside the filled sphere from its initial room temperature to 100 °C. It was a brilliant experiment requiring superb experimental skill.

18.7 Latent Heat of Fusion

The most straightforward method for measuring the specific latent heat L of ice is to drop a lump of

Ice of mass m and specific latent heat L at its melting point T_0 into a Calorimeter of mass M_C and specific heat capacity C_C and initial (warm) temperature T_2 , which contains a mass M_W of Water of specific heat capacity C_W at the same warm temperature T_2 .

After the ice has melted everything comes to a final (cool) temperature T_1 . Then

$$m[L + C_W(T_2 - T_0)] = (M_C C_C + M_W C_W)(T_2 - T_1). \quad 18.7.1$$

If the temperatures in this equation are supposed to be in degrees Celsius, so that $T_0 = 0$, and if masses are in grams and heat in calories, so that $C_2 = 1$, this equation becomes

$$m(L + T_2) = (M_C C_C + M_W)(T_2 - T_1). \quad 18.7.2$$

For good results, heat losses must be minimized and allowed for, and precautions must be taken to minimize and allow for any water initially clinging to the lump of ice.

Quite precise measurements of the latent heat of fusion of ice can be made with the *Bunsen Ice Calorimeter*, an apparatus that can also be used to measure specific heat capacities of other substances. My limited artistic skills with the computer do not allow me to draw all the minute details of the practical construction of a Bunsen ice calorimeter that makes it a precision instrument, but may, perhaps, suffice to show the general principles, in figure XVIII.2. A test-tube T, is fitted with an outer glass sleeve S, the lower end of which leads to a manometer M. The portion of the sleeve above the level B is filled with air-free pure water at its freezing point. The manometer from level A to level B is filled with mercury. The entire apparatus is generally enclosed in a large ice-box, so that the entire apparatus is at 0°C. Some ice is formed outside the bottom of the test-tube, at I. In order to measure the specific latent heat of fusion of ice, a measured quantity of hot water is poured into test-tube. This water, in cooling down to 0°C, gives up a known amount of heat to the ice, some of which melts. So – how do you know how much ice has melted? Water ice contracts on melting into liquid. Consequently the level B moves up and the level A (which can be in a quite narrow capillary tube) goes down, so the reduction in volume (and hence the mass of ice melted) can be determined quite accurately. Thus the latent heat of fusion of ice can be determined. Once the equipment has been calibrated (i.e. when we know how much movement of level A corresponds to how much transfer of heat), the calorimeter can be used to

measure specific heat capacities of other substances, simply by dropping a known mass of the substance at a known temperature into the test-tube, and measuring the movement of the level A. It will be understood, I think, that, in using the apparatus to measure the specific latent heat of ice, it is necessary to know the densities of ice and of water precisely. To use it for measuring the specific heat capacities of other substances, it is not necessary to know this, or even to know the specific latent heat of fusion of ice. You do have to know the specific heat capacity of water – which is not much of a burden, especially if you are content to express heat in calories!

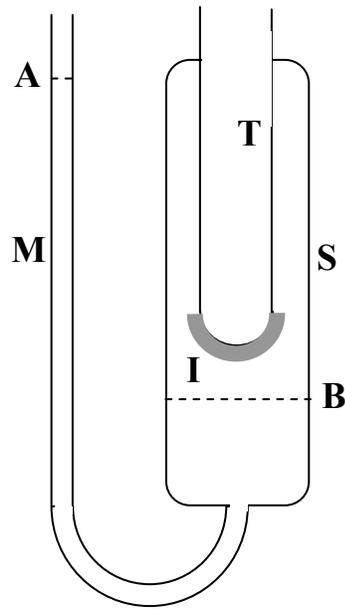


FIGURE XVIII.2

18.8 *Coefficient of Expansion*

If a specimen can be obtained in the form of a long rod, the simplest and most direct method is merely to rest the rod horizontally on some support, immersed in a water bath by which means the temperature can be varied. Two scratches, one at each end of the rod, can be observed with a pair of measuring microscopes held on a support at constant temperature. The measuring microscopes can either be fixed and fitted with a fine scale in the eyepiece of each, or they may be movable by means of a fine precision screw (96 turns to the inch). The movement of the microscopes can be measured either by means of a wheel fitted with a vernier that turns the precision screw, or by

attaching a corner reflector to each moving microscope, and reflecting a laser beam off the reflector and counting the number of half wavelengths traversed by the microscope.

If the specimen cannot be obtained in the form of a long rod, but can be obtained in the form of a thin, flat plate with parallel faces, another method can be used. A hole might be cut in the flat specimen, and the specimen can be rested on top of a flat glass plate. A second flat glass plate rests on the upper face of the specimen. The arrangement can be illuminated with an extended monochromatic light source, to create a system of interference fringes. When the temperature is raised, the specimen expands and the distance between the glass plates increases by an amount that can be measured by measuring the movement of the interference fringes.

Some materials may not be easily obtainable either in the form of a long rod or a thin plate, but perhaps they can be obtained in the form of a small cube. The specimen is placed side-by-side with a similar cube of quartz, whose expansion coefficient is very small, the two resting on the horizontal surface of a polished shiny metal or glass block. On top of the two specimens rests a thin, flat glass plate. A narrow beam of light, preferably from a laser, is directed from above to the arrangement, and two reflections are observed, one from the thin glass plate that rests on top of the specimen and its quartz companion, the other from the upper surface of the block on which the specimens are resting. When the specimen and the quartz are warmed, the specimen expands more than the quartz does, and so the upper thin glass plate tilts, and the reflection from it is deflected. The displacement of one reflected beam from the other can be measured with a microscope, and hence the tilt of the upper glass plate can be calculated, and hence the excess of expansion of the specimen over that of the quartz can be determined. The experiment gives the difference in expansion coefficient between the specimen and the quartz. The latter is very small, and its exact value need not be known with great precision in order to obtain the absolute coefficient of expansion of the specimen.

For nonvolatile liquids, a *weight thermometer* can be used. This is a glass (or, better, fused quartz) bulb fitted with a narrow capillary tube as shown in figure XVIII.3.

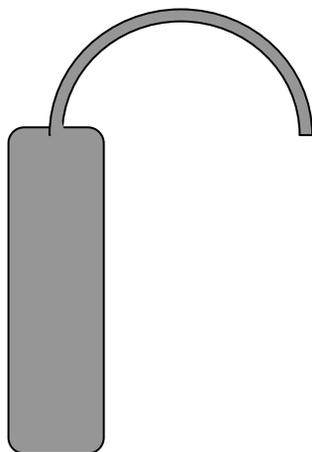


FIGURE XVIII.3

The bulb (whose weight empty is known) is completely filled (including the capillary to the very tip) with the liquid, and weighed, so that the weight, hence mass, of the liquid is known. The temperature is increased, so some liquid escapes, and the bulb is weighed again. Thus we know the weight of the liquid held by the bulb at two temperatures. If we assume that the volume is constant

(the bulb being made of fused quartz) this enables us to calculate the coefficient of expansion of the liquid. Of course, the bulb does expand a little, so what we have determined is the difference between the volume expansions of the liquid and the quartz. If we know the volume expansion of the quartz (which need not be known to high precision, since it is small), we can then determine the absolute coefficient of expansion of the liquid.

In another method for measuring the coefficient of expansion of liquids, the liquid is contained in a U-tube, the two arms of which are maintained at different temperatures, as shown in figure XVIII.4. The upper ends of the two arms of the U-tube are connected to vertical tubes containing mercury for controlling and measuring the pressure. The apparatus is maintained so that the volumes of the liquids in the two arms of the U-tube are equal – but because the two arms are at different temperatures, their densities (hence specific volumes) are different, so a little extra mercury is needed to balance the hot arm against the cold arm. Thus it is possible to determine the difference in densities at the two temperatures, and hence to determine the volume coefficient of expansion. The figure shows the principle of the method; some practical refinements are needed in the actual equipment.

