

CHAPTER VI.

CALORIMETRY.

57. **Quantity of Heat.**—We have discussed in previous chapters the measurement of temperature, and have seen that it is to a great extent arbitrary, since intervals of temperature which are equal as measured by the expansion of one substance are not equal as measured by the expansion of another.

The measurement of quantities of heat stands upon an entirely different footing. There is nothing arbitrary or conventional in asserting the equality or inequality of two quantities of heat.

58. **Principles Assumed.**—The two following principles may be regarded as axiomatic.

(1) The heat which must be given to a body to raise it through a given range of temperature at constant pressure, is equal to that which the body gives out in falling through the same range of temperature under the same pressure. For instance, the heat which must be given to a gramme of water, to raise its temperature from 5° to 10°, is equal to that which is given out from the same water when it falls from 10° to 5°.

(2) In a homogeneous substance equal portions require equal quantities of heat to raise them from the same initial to the same final temperature; so that, for example, the heat required to raise two grammes of water from 5° to 10° is double of that which is required to raise one gramme of water from 5° to 10°.

59. **Cautions.**—We are not entitled to assume that the quantities of heat required to raise a given body through equal intervals of temperature—for example, from 5° to 10°, and from 95° to 100°—are equal. Indeed we have already seen that the equality of two intervals of temperature is to a considerable extent a matter of mere

convention; temperature being conventionally measured by the expansion (real or apparent) of some selected substance.

It would, however, be quite possible to adopt a scale of temperature based on the elevation of temperature of some particular substance when supplied with heat. We might, for instance, define a degree (at least between the limits 0° and 100°) as being the elevation of temperature produced in water of any temperature by giving it one hundredth part of the heat which would be required to raise it from 0° to 100°.

Experiments which will be described later show that if air or any of the more permanent gases were selected as the standard substance for thus defining equal intervals of temperature, the scale obtained would be sensibly the same as that of the air-thermometer; and the agreement is especially close when the gases are in a highly rarefied condition.

60. **Unit of Heat.**—We shall adopt as our unit, in stating quantities of heat, the heat required to raise a gramme of cold water through one degree Centigrade. This unit is called, for distinction, the gramme degree. The kilogramme-degree and the pound-degree are sometimes employed, and are in like manner defined with reference to cold water as the standard substance.

There is not at present any very precise convention as to the temperature at which the cold water is to be taken. If we say that it is to be within a few degrees of the freezing-point, the specification is sufficiently accurate for any thermal measurements yet made.

61. **Thermal Capacity.**—If a quantity Q of heat given to a body raises its temperature from t_1° to t_2° , the quotient

$$\frac{Q}{t_2 - t_1}$$

of the quantity of heat given by the rise of temperature which it produces, is called the *mean thermal capacity* of the body between the temperatures t_1° and t_2° .

As t_2 is brought nearer to t_1 , so as to diminish the denominator, the numerator Q will also diminish, and in general very nearly in the same proportion. The limit to which the fraction approaches as t_2 is brought continually closer to t_1 is called the *thermal capacity* of the body at the temperature t_1° . That is, in the language of the differential calculus, the thermal capacity at t° is $\frac{dQ}{dt}$.

From the way in which we have defined our unit of heat, it fol-

lows that the thermal capacity of any quantity of cold water is numerically equal to its mass expressed in grammes; and that the number which expresses the thermal capacity of any body may be regarded as expressing the quantity of water which would receive the same rise of temperature as the body from the addition of the same quantity of heat. This quantity of water is often called the *water-equivalent* of the body.

62. Specific Thermal Capacities.—The thermal capacity of unit mass of a substance is called the *specific heat* of the substance; and it is always to be understood that the same unit of mass is employed for the substance as for the water which is mentioned in the definition of the unit of heat. Specific heat is therefore independent of units, and merely expresses the ratio of the two quantities of heat which would raise equal masses of the given substance and of cold water through the same small difference of temperature. Or we may regard it as the ratio of two masses, the first, of cold water, and the second of the substance in question, which have the same thermal capacity.

There is another specific thermal capacity which it is often necessary to consider, namely, the *thermal capacity of unit volume* of a substance. It has not received any brief name. It is equal to the mass of unit volume multiplied by the thermal capacity of unit mass; in other words, it is equal to the *product of the density and the specific heat* of the substance.

It is evident, from what precedes, that the heat required to raise m grammes of a substance through t degrees is mst , where s denotes the mean specific heat between the initial and the final temperature; and the same expression denotes the quantity of heat which the body in question loses in cooling down through t degrees.

63. Method of Mixtures.—Let m_1 grammes of a substance of specific heat s_1 and temperature t_1° be mixed with m_2 grammes of a substance of specific heat s_2 and temperature t_2° , the mixture being merely mechanical, so that no heat is generated or absorbed by any action between the substances, and all external gain or loss of heat being prevented. Then the warmer substance will give heat to the colder, until they both come to a common temperature, which we will denote by t . The warmer substance, which we will suppose to be the former, will have cooled down through the range $t_1 - t$, and will have lost $m_1 s_1 (t_1 - t)$ units of heat. The colder substance will have risen through the range $t - t_2$, and will have gained $m_2 s_2 (t - t_2)$

units of heat. These two expressions represent the same thing, namely, the heat given by the warmer body to the colder. We may therefore write

$$m_1 s_1 (t_1 - t) = m_2 s_2 (t - t_2), \quad (1)$$

that is,

$$m_1 s_1 t_1 + m_2 s_2 t_2 = (m_1 s_1 + m_2 s_2) t, \quad (2)$$

whence

$$t = \frac{m_1 s_1 t_1 + m_2 s_2 t_2}{m_1 s_1 + m_2 s_2}. \quad (3)$$

If there are more than two components in the mixture, similar reasoning will still apply; thus, if there are three components, the resulting temperature will be

$$t = \frac{m_1 s_1 t_1 + m_2 s_2 t_2 + m_3 s_3 t_3}{m_1 s_1 + m_2 s_2 + m_3 s_3}. \quad (4)$$

Strictly speaking, s_1 in these formulæ denotes the *mean* specific heat of the first substance between the temperatures t_1 and t , s_2 the mean specific heat of the second substance between t_2 and t , and so on.

It is not necessary to suppose the two bodies to be literally *mixed*. One of them may be a solid and the other a liquid in which it is plunged. The formulæ apply whenever bodies at different temperatures are reduced to a common temperature by interchange of heat one with another.

64. Practical Application.—The following is an outline of the method most frequently employed for determining the specific heats of solid bodies.

The body to be tested is raised to a known temperature t_1 , and then plunged into water of a known temperature t_2 contained in a thin copper vessel called a *calorimeter*. If m_1 be the mass of the body, m_2 that of the water before immersion, and t the final temperature, all of which are directly observed, we have

$$m_1 s_1 (t_1 - t) = m_2 (t - t_2), \quad (5)$$

since s_2 , the specific heat of the water, may be taken as unity. Hence we have

$$s_1 = \frac{m_2 (t - t_2)}{m_1 (t_1 - t)}. \quad (6)$$

65. Corrections.—The theoretical conditions which are assumed in the above calculation, cannot be exactly realized in practice.

I. The calculation assumes that the only exchange of heat is between the body and the water, which is not actually the case; for

1. The body is often contained in an envelope which cools along with it, and thus furnishes part of the heat given up.

2. The heat is not given up exclusively to the water, but partly to the calorimeter itself, to the thermometer, and to such other instruments as may be employed in the experiment, as, for instance, a rod to stir the liquid for the purpose of establishing uniformity of temperature throughout it.

In order to take account of these disturbing circumstances, it is only necessary to know the thermal capacity of each of the bodies which takes part in the exchange of heat. We shall then have such an equation as the following:—

$$(m_1 s_1 + c_1) (t_1 - t) = (m_2 + c_2 + c_3 + c_4) (t - t_2),$$

where c_1 denotes the thermal capacity of the envelope, and c_2, c_3, c_4 are the thermal capacities of the calorimeter, thermometer, and stirring rod.

II. The calorimeter gives out heat to the surrounding air, or takes heat from it. This difficulty is often met by contriving that the heat gained by the calorimeter from the air in the first part of the experiment shall be as nearly as possible equal to that which it loses to the air in the latter part.

This condition will be fulfilled if the average temperature of the calorimeter (found by taking the mean of numerous observations at equal small intervals of time) is equal to the temperature of the air. As the immersed body gives out its heat to the water very rapidly at first, and then by degrees more and more slowly, the initial defect of temperature must be considerably greater than the final excess, to make the compensation exact.

Instead of attempting exact compensation, some observers have determined, by a separate experiment, the rate at which interchange of heat takes place between the calorimeter and the air, when there is a given difference of temperature between them. This can be observed by filling the calorimeter with water in which a thermometer is immersed. The rate of interchange is almost exactly proportional to the difference of temperature between the calorimeter and the air, and is independent of the nature of the contents. The law of interchange having thus been determined, the temperature of the calorimeter must be observed at stated times during the progress of the experiment on specific heat; the total heat lost or gained by interchange with the air will thus be known, and this total heat divided by the total thermal capacity of the calorimeter and its contents gives a correction, which is to be added to or subtracted from t the observed final temperature.

66. Regnault's Apparatus.—The subject of specific heat has been investigated with great care by Regnault, who employed for that purpose an apparatus in which the advantages of convenience and precision are combined. The body whose specific heat is required is divided into small fragments, which are placed in a cylindrical basket G (Fig. 44) of very fine brass wire, in the centre of which

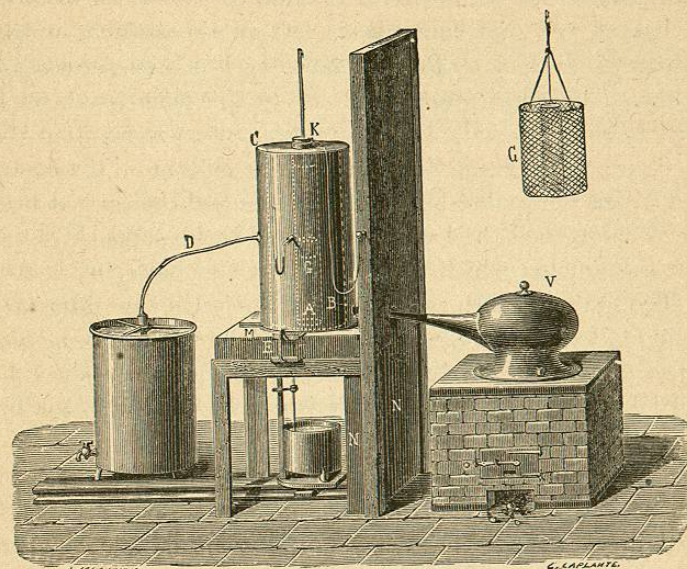


Fig. 44.—Regnault's Apparatus.

is a tube of the same material for the insertion of a thermometer. The basket is shown separately in the figure on a larger scale than the rest of the apparatus. This basket is suspended in the central compartment of the steamer A.B.C, the suspending thread being fixed by the cork K, through which the stem of the thermometer passes. The steamer consists of three concentric cylinders, the two outer compartments being occupied by steam, which is supplied from the boiler V to the second compartment, and finally escapes from the outermost compartment through the tube D into a condenser. In the bottom of the steamer are a pair of slides E which can be drawn out when required.

The steamer rests, by means of a sheet of cork, upon a hollow metal vessel M.N, consisting of a horizontal portion M and a vertical portion N, filled with cold water, and serving as a screen for the calorimeter; the horizontal portion, and the cork above it,

having a hole in the centre large enough for the basket G to pass through.

The calorimeter itself, which is shown beneath the steamer in the figure, is a vessel of very thin polished brass, resting by three points upon a small wooden sled, which runs smoothly along a guiding groove. The thermometer for measuring the temperature of the water in the calorimeter, is carried by a support attached to the sled.

The basket, with its contents, is left in the steamer until the temperature indicated by the thermometer has been for some time stationary. The calorimeter, which, up to this time has been kept as far away as it can slide, is then pushed into the position shown in the figure, the slides E, which close the bottom of the compartment in which the basket is, are drawn out; and the cork at the top having been loosened, the basket is lowered by its supporting thread into the calorimeter, which is immediately slid back to its former place. The basket is then moved about in it until the water attains its maximum temperature, which is read off on the thermometer.

To determine the specific heats of liquids, a thin glass tube is employed instead of the basket. It is nearly filled with the liquid and hermetically sealed.

For solids which are soluble in water, or upon which water has a chemical action, some other liquid—oil of turpentine, for example—is placed in the calorimeter, instead of water; and the experiment is in other respects the same.

The specific heats of several substances are given in the following table:—

| | | | |
|---------------------------|---------|------------------------------|---------|
| Water, | 1.00000 | | |
| | | SOLIDS. | |
| Antimony, | 0.05077 | Brass, | 0.09391 |
| Silver, | 0.05601 | Nickel, | 0.10860 |
| Arsenic, | 0.08140 | Gold, | 0.03244 |
| Bismuth, | 0.03084 | Phosphorus, | 0.18870 |
| Cadmium, | 0.05669 | Platinum, | 0.03243 |
| Charcoal, | 0.24150 | Lead, | 0.03140 |
| Copper, | 0.09215 | Plumbago, | 0.21800 |
| Diamond, | 0.14680 | Sulphur, | 0.20259 |
| Tin, | 0.05623 | Glass, | 0.19768 |
| Iron, | 0.11379 | Zinc, | 0.09555 |
| Iodine, | 0.05412 | Ice, | 0.5040 |
| | | LIQUIDS. | |
| Mercury, | 0.03332 | Benzine, | 0.3952 |
| Acetic acid, | 0.6589 | Ether, | 0.5157 |
| Alcohol at 36°, | 0.6735 | Oil of turpentine, | 0.4629 |

67. Great Specific Heat of Water.—This table illustrates the important fact, that, of all substances, water has the greatest specific heat; that is to say, it absorbs more heat in warming, and gives out more heat in cooling, through a given range of temperature, than an equal weight of any other substance. The quantity of heat which raises a pound of water from 0° to 100° C. would suffice to raise a pound of iron from 0° to about 900° C., that is to a bright red heat; and conversely, a pound of water in cooling from 100° to 0°, gives out as much heat as a pound of iron in cooling from 900° to 0°. This property of water is utilized in the heating of buildings by hot water, and in other familiar instances, such as the bottles of hot water used for warming beds, and railway foot-warmers.

68. Ice Calorimeters.—In the calorimeters above described, the heat which a body loses in cooling is measured by the elevation of temperature which it produces in a mass of water. In ice calorimeters this heat is measured by the quantity of ice (initially at the freezing-point) which it melts. In some ice calorimeters the water produced by melting is collected and weighed; in Bunsen's, the measurement depends upon the diminution of volume which occurs when ice melts.

The construction of this instrument is shown in Fig. 45. The small thin test-tube A, open to the air at the top, is sealed into the reservoir B, which communicates with the tube C having at its end a movable plug D, through which passes the vertical portion of a fine tube S, whose other portion is horizontal and may be of considerable length. The small body whose specific heat is required

is heated, and dropped into ice-cold water which stands at the level α in A. The surrounding space in the reservoir, from the level β to the top, contains ice and ice-cold water, and some of the ice is melted by the heat emitted from the body in A, the whole apparatus being kept immersed in a mixture of ice and water to prevent loss or gain of heat externally. The diminution in the joint volume of water and ice in B produced by the melting is indicated by the movement of the end of a mercurial column in the horizontal part of S, the whole space from B to S being occupied by mercury.

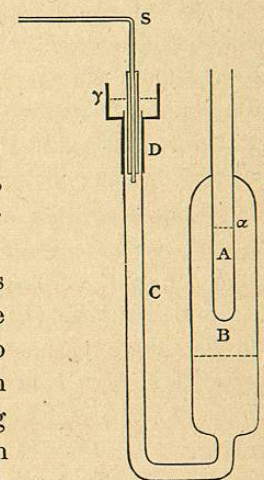


Fig. 45.—Bunsen's Calorimeter.

To prevent the formation of air bubbles in the reservoir B, it is filled with boiling water, which is afterwards frozen. The mercury should also be boiled to expel air, and before its introduction the tubes should be thoroughly dried.

The graduation of the tube S on which the indications are read may be arbitrary, and the value of the divisions is determined by observing the effect of a known mass of water at a known temperature when introduced into A. By means of the sliding plug D, the end of the column can be brought to a convenient part of the tube before each experiment.

69. Specific Heats of Gases.—Regnault made very careful determinations of the specific heats of air and other gases, by means of an apparatus in which a measured quantity of gas at a known temperature was passed through a series of spiral tubes surrounded by cold water, and finally escaped at a temperature sensibly the same as that of the water. The elevation produced in the temperature of the water by this process, furnished a measure of the quantity of heat given out by the gas in falling through a known range of temperature. The gas had sensibly the same pressure on entering as on leaving the calorimeter; the specific heat determined by the experiments was therefore the specific heat *at constant pressure*. This element must be carefully distinguished from the specific heat of a gas *at constant volume*. The connection between the two will be discussed in a later chapter.

Regnault's experiments established the following conclusions.

(1) The specific heat of a gas is the same at all pressures; in other words, the thermal capacity per unit volume is directly as the density.

(2) The specific heats of different simple gases are approximately in the inverse ratio of their relative densities.

Let s denote the specific heat and d the absolute density of a gas at a given pressure and temperature; then this law asserts that the product sd is the same (approximately) for all simple gases. But since d is the mass of unit volume, sd is the capacity of unit volume. The law may therefore be thus expressed:—

All simple gases have approximately the same thermal capacity per unit volume, when compared at the same pressure and temperature.

(3) The specific heat of a gas is the same at all temperatures, temperature being measured by the air-thermometer, or by the expansion

of the gas itself at constant pressure. This is equivalent to the assertion that *if equal quantities of heat be successively added to a gas at constant pressure, the volume of the gas will increase in arithmetical progression*. We here neglect the slight differences which exist between the expansions of different gases, and also their slight departures from Boyle's law.

The specific heat of dry air (at constant pressure) according to Regnault is .2375.

The three laws above stated are also true for the specific heat of gases *at constant volume*. The third law may then be stated in the following form:—

If equal quantities of heat be successively added to a gas at constant volume, the pressure will increase in arithmetical progression.

70. Dulong and Petit's Law.—According to the modern molecular theory of gases, all simple gases at the same pressure and temperature have the same number of atoms per unit volume. The mass of an atom of any gas will therefore be proportional to the relative density of the gas, and law (2) of last section will reduce to the following:—The specific heats of different simple gases are inversely as the masses of their atoms.

The second statement of the same law assumes the following still more simple form:—

An atom of one gas has the same thermal capacity as an atom of any other gas.

What is called in chemistry the *atomic weight* of an elementary substance is proportional to the supposed mass of an atom of the substance, and is believed to be proportional to the relative density of the substance when reduced to a state of vapour at high temperature and low pressure.

It was remarked by Dulong and Petit that the specific heats of elementary substances are for the most part in the inverse ratio (approximately) of their atomic weights; or the *product of specific heat and atomic weight is (approximately) constant*. The constancy is very rough when the specific heats are taken at ordinary temperatures; but it is probable that at very high temperatures the law would be nearly exact.

71. Method of Cooling.—Attempts have sometimes been made to compare the specific heats of different substances by means of the times which they occupy in cooling through the same range. If

two exactly similar thin metallic vessels are filled with two different substances, and after being heated to a common temperature are allowed to cool in air under the same conditions, the times which they occupy in falling to any other common temperature will be proportional to the quantities of heat which they emit, if we can assume that the contents of the vessels are at sensibly the same temperatures as their surfaces. We have thus a comparison of the thermal capacities of the two substances per unit volume.

In the case of solid substances, their differences in conducting power render the method worthless; but Regnault has found that it gives tolerably correct results in the case of liquids. In fact the extreme mobility of liquids, combined with their expansion when heated, prevents any considerable difference of temperature from existing in the same horizontal layer; so that the centre is sensibly at the same temperature as the circumference.

CHAPTER VII.

FUSION AND SOLIDIFICATION.

72. Fusion.—Many solid bodies, when raised to a sufficiently high temperature, become liquid. This change of state is called *melting* or *fusion*, and the temperature at which it occurs (called the melting-point, or temperature of fusion) is constant for each substance, with the exception of the variations—which in ordinary circumstances are insignificant—due to differences of pressure (§ 86). The melting-points of several substances are given in the following table:—

TABLE OF MELTING-POINTS, IN DEGREES CENTIGRADE.

| | | | |
|-------------------------|-----|-------------------------|--------------|
| Mercury, | -39 | Tin, | 230 |
| Ice, | 0 | Bismuth, | 262 |
| Butter, | 33 | Lead, | 326 |
| Lard, | 33 | Zinc, | 412 |
| Spermaceti, | 49 | Antimony, | 432 |
| Stearine, | 55 | Aluminium, | 600 |
| Yellow Wax, | 62 | Bronze, | 900 |
| White Wax, | 68 | Pure Silver, | 954 |
| Stearic Acid, | 70 | Gold, | 1045 |
| Phosphorus, | 44 | Copper, | 1054 |
| Potassium, | 63 | Cast Iron, | 1050 to 1250 |
| Sodium, | 95 | Steel, | 1300 to 1400 |
| Iodine, | 107 | Wrought Iron, | 1500 to 1600 |
| Sulphur, | 110 | Platinum, | 1775 |

Some bodies, such as charcoal, have hitherto resisted all attempts to reduce them to the liquid state; but this is to be attributed only to the insufficiency of the means which we are able to employ.

It is probable that, by proper variations of temperature and pressure, all simple substances, and all compound substances which would not be decomposed, could be compelled to assume the three forms, solid, liquid, and gaseous.

The passage from the solid to the liquid state is generally abrupt;