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CHAPTER I

FIRST PRINCIPLES

1. **The Science of Thermodynamics** treats of the relation of heat to mechanical work. In its engineering aspect it is chiefly concerned with the process of getting work done through the agency of heat. Any machine for doing this is called a Heat-Engine. It is also concerned with the process of removing heat from bodies that are already colder than their surroundings. Any machine for doing this is called a Refrigerating Machine.

It is convenient to study the thermodynamic action of heat-engines and refrigerating machines together, because one is the reverse of the other, and by considering both we arrive more easily at an understanding of the whole subject.

2. **Heat-Engine and Heat-Pump.** In a Heat-Engine heat is supplied, generally by the combustion of fuel, at a high temperature, and the engine discharges heat at a lower temperature. Thus in a steam-engine heat is taken in at the temperature of the boiler and discharged at the temperature of the condenser. In any kind of heat-engine the heat is let down, within the engine, from a high level of temperature to a lower level of temperature, and it is by so letting heat down that the engine is able to do work, as a water-wheel is able to do work by letting water down from a high level to a lower level. But there is this important difference, that some of the heat disappears in the process of being let down: it is converted into the work which the engine does.

In a Refrigerating Machine work has to be spent upon the machine to enable it to take in heat at a low level of temperature, and discharge heat at a higher level of temperature, just as work would have to be spent upon a water-wheel if it were used as a means of raising water by reversing its action, in such a way that the buckets were filled at a low level and emptied at a higher level, so that it should serve as a pump. It would be quite correct to speak of a refrigerating machine as a heat-pump. But again there is an important difference between the refrigerating machine and the reversed water-wheel: the refrigerating machine is a heat-pump which discharges more heat than it takes in, for the work which is spent in driving the machine is converted into heat, which has to be discharged at the higher level of temperature in addition to the heat that is taken in at the low temperature.

3. **Efficiency of a Heat-Engine.** From the point of view of practical thermodynamics the object of a heat-engine is to get work done with the least possible expenditure of fuel. In other words the ratio of the work done to the heat taken in should be as large as is practicable. This ratio is called the Efficiency of the engine as a heat-engine. The theory of heat-engines deals with the conditions that affect efficiency, and with the limit of efficiency that can be reached when the conditions are most favourable.

4. **Coefficient of Performance of a Refrigerating Machine.** In a refrigerating machine the object is to get heat removed from the cold body and pumped up to a higher level of temperature at which it can be discharged, and what is wanted is that this should be done with the least possible expenditure of work. The ratio of the heat taken in by the machine from the cold body to the work that is spent in driving the machine is called the Coefficient of Performance. The theory of refrigeration deals with the conditions that will allow this ratio to be as large as possible.

5. **Working Substance.** In the action of a heat-engine or of a refrigerating machine there is always a working substance which forms the vehicle by which heat passes through the machine. It is because the working substance has a capacity for taking in heat that it can act as a vehicle for conveying heat from one level of temperature to another. In this process its volume changes, and it is by means of changes of volume on the part of the working substance that the machine does work, if it is a heat-engine, or has work spent upon it, if it is a refrigerating machine. Accordingly, an important part of the science of thermodynamics deals with the properties of substances in relation to heat, and the connection between such properties in any substance. The substances with which we are chiefly concerned are fluids in the gaseous or liquid states. They include air and other gases, water and water-vapour, and also some fluids more easily vaporized than water, such as ammonia and carbonic acid, which are used as the working substance in certain refrigerating machines. Each fluid has of course its own characteristics; but many of the relations between its properties are of a general kind and may be studied without limitation

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to individual fluids. It will be seen, as we go on, that much of what has to be said applies equally, whatever fluid serves for working substance, and that in any one fluid the various properties are connected with one another in a way that is true for all fluids. The study of the thermodynamic relationships between the various properties of a fluid is useful, not only because of the direct light it throws on the action of heat-engines, but also because it enables a practically complete knowledge of the properties of a fluid in detail to be inferred from a comparatively small number of experimental data. We shall see later, for example, how such relationships have been made use of in calculating modern tables of the properties of steam from the results of careful measurements, made in the laboratory, of a few fundamental quantities.

6. **Operation of the Working Substance in a Heat-Engine.** In general the working substance is a fluid which operates by changing its volume, exerting pressure as it does so. But it is easy to imagine a heat-engine having a solid body for working substance, say a long rod of metal arranged to act as the pawl of a ratchet-wheel with closely pitched teeth. Let the rod be heated so that it lengthens sufficiently to drive the wheel forward through the space of one tooth. Then let the rod be cooled, say by applying cold water, the ratchet-wheel being meanwhile held from returning by a separate click or detent. The rod on cooling will retract so as to engage itself with the next succeeding tooth, which may then be driven forward by heating the rod again, and so on. To make it evident that such an engine would do work we have only to suppose that the ratchet-wheel carries round with it a drum by which a weight is wound up. The device forms a complete heat-engine, in which the working substance is a solid rod, doing work in this case not through changes of volume but through changes of length. While its length is increasing it is exerting force in the direction of its length. It receives heat by being brought into contact with some source of heat at a comparatively high temperature; it transforms a small part of this heat into work; and it rejects the remainder to what we may call a receiver of heat, which is kept at a comparatively low temperature. The greater part of the heat may be said simply to pass through the engine, from the source to the receiver, *becoming degraded as regards temperature in the process.* This is typical of the action of all heat-engines: they convert some heat into work only by letting down a much larger quantity of heat

from a high temperature to a relatively low temperature. The engine we have just imagined would not be at all *efficient*; the fraction of the heat supplied to it which it could convert into work would be very small. Much greater efficiency can be obtained by using a fluid for working substance and by making it act so that its own expansion of volume not only does work but also causes it to fall in temperature before it begins to reject heat to the cold receiver.

7. **Cycle of Operations of the Working Substance.** Generally in the action of a heat-engine or of a refrigerating machine the working substance returns periodically to the same state of temperature, pressure, volume and physical condition in all respects. Each time this has occurred the substance is said to have passed through a complete cycle of operations. For example, in a condensing steam-engine, water taken from the hot-well is pumped into the boiler; it then passes into the cylinder as steam, then from the cylinder into the condenser, and finally from the condenser back to the hot-well; it completes the cycle by returning to the same condition in all respects as at first, and is ready to go through the cycle again. In other less obvious cases a little consideration shows that the cycle is completed although the same portion of working substance does not go through it again: thus in a non-condensing steam-engine the steam which has passed through the engine is discharged into the atmosphere, where it cools to the temperature of the feed-water, while a fresh portion of feed-water is delivered to the engine to go through the cycle in its turn.

In the theory of heat-engines it is of the first importance to consider as a whole the cycle of operations performed by the working substance. If we stop short of the completion of the cycle matters are complicated by the fact that the substance is in a state different from its initial state. On the other hand, if the cycle is complete we know that whatever heat or other energy the substance contained within itself to begin with is there still, for the state of the substance is the same in all respects, and consequently any work that it has done must have been done at the expense of heat which it has taken in during the cycle. The total amount of energy it has parted with must be equal to the amount it has received, during the cycle, for its stock of internal energy is the same at the end as at the beginning. We can at once apply the principle of the Conservation of Energy and say that for the cyclic process as a whole the work done must be equivalent to the difference between the heat taken in and the heat rejected.

8. The First Law of Thermodynamics. The principle of the Conservation of Energy in relation to heat and work may be expressed in the following statement, which constitutes the First Law of Thermodynamics:—*When work is done by the expenditure of heat a definite quantity of heat goes out of existence for every unit of work done; and, conversely, when heat is produced by the expenditure of work the same definite quantity of heat comes into existence for every unit of work spent.*

The word "work" is to be understood here in a comprehensive sense: it includes electrical work as well as mechanical work. Electrical work may, for instance, be done by expending heat in a thermoelectric circuit, which is a true heat-engine although there are no visibly moving parts.

9. Internal Energy. We have used in Art. 7 a phrase which requires some further explanation—the *internal energy* of a substance. No means exist by which the whole stock of energy that a substance contains can be measured. But we are concerned only with changes in that stock, changes which may arise from the substance taking in or giving out heat, or doing work, or having work spent upon it. If a substance takes in heat without doing work its stock of internal energy increases by an amount equal to the heat taken in. If it does work without taking in heat, it does the work at the expense of its stock of internal energy, and the stock is diminished by an amount equal to the work done. In general, when heat is being taken in and the substance is at the same time doing work, we have

Heat taken in = Work done + Increase of Internal Energy.

For any infinitesimally small step in the process, we may write

$$dQ = dW + dE,$$

where dQ is the heat taken in during the step, dW is the work done, and dE the increase of internal energy.

In a complete cycle there is, at the end, no change of the internal energy E, and consequently, for the cycle as a whole,

$$Q_1 - Q_2 = W,$$

where $Q_1 - Q_2$ is the net amount of heat received, namely the

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difference between the heat taken in and the heat rejected in the complete cycle, and W is the work done in the complete cycle.

In this notation we are supposing W to be expressed in units of heat, as well as Q and E. It would be more correct to speak of W as the thermal equivalent of the work done.

10. **Work done in Changes of Volume of a Fluid.** In an engine of the usual cylinder and piston type the working fluid does work by changes of volume. The amount of work done depends only on the relation of the pressure to the volume in these changes, and not on the form of the vessel or vessels in which the changes of volume take place. Let the intensity of pressure of the fluid (that is to say the pressure on unit of area) be P while the piston moves forward through a small distance δl. If the area of the piston is S the total force on it is PS and the work done is $PS\delta l$. But $S\delta l = \delta V$, the change of volume: hence the work done is $P\delta V$ for the small change of volume δV, or $\int_{V_1}^{V_2} P\,dV$ for a finite change of volume from a volume V_1 to a volume V_2 during which the pressure may vary.

In any complete cycle of operations the volume at the finish is the same as at the start, and the work done is $\int P\,dV$ taken round the cycle as a whole.

It is very useful to represent graphically the work which a fluid does in changing its volume. Let a diagram be drawn in which the relation of the pressure of any supposed working substance to its volume is shown by rectangular coordinates as in fig. 1. Beginning with the state represented by the point A, where the pressure is AM and volume OM, suppose the substance to expand to a state B, where the pressure is BN and the volume ON, and let the curve AB represent the intermediate states of pressure and volume. Then the work done by the substance in this expansion, which is $\int_{OM}^{ON} P\,dV$, is represented by the area $MABN$ under the curve AB.

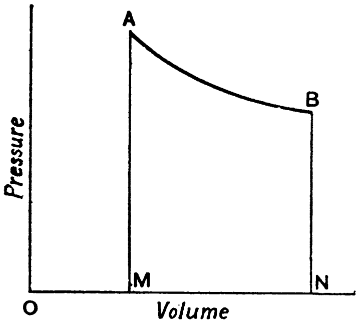

Fig. 1

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Again, if the substance undergoes any complete cycle of change (fig. 2) by expanding from *A* through *B* to *C* and by being compressed back through *D* to *A*, work is done by it while it is expanding from *A* to *C*, equal to the area *MABCN*, and work is spent upon it while it is being compressed from *C* through *D* to *A*, equal to the area *NCDAM*. The net amount of work which the substance does during the cycle is equal to the algebraic sum of those areas: in other words it is equal to the area of the closed figure *ABCDA* representing the complete cyclic operation, which area is $\int PdV$.

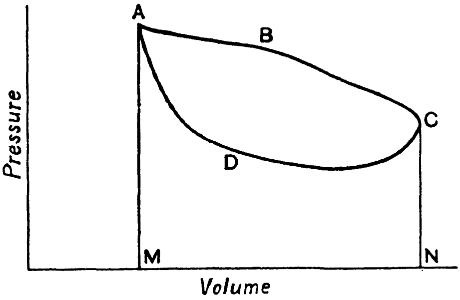

Fig. 2

If on the other hand the operation were such as to trace the figure in the opposite direction, the substance being expanded from *A* to *C* through *D* and compressed from *C* to *A* through *B*, the enclosed area would be a measure of the work expended upon the substance in the cycle.

11. **Indicator Diagrams.** This pressure-volume diagram is an example, and a generalization, of the method of representing work which Watt introduced by his invention of the Indicator, an instrument for automatically drawing a diagram to represent the changes of pressure in relation to changes of volume in the action of an engine. The figure *ABCDA* may be called the *Indicator Diagram* of the supposed action.

The indicator consists of a small cylinder containing a piston which can move in it without sensible friction but is controlled by a stiff spring. This is put in free communication with one end of the working cylinder of the engine, so that the working substance presses on the indicator piston and displaces it, against the spring, through distances that are proportional to the pressure at every instant. Connected with the indicator piston is a pencil which rises or falls with it, the connection being made, generally, through a lever that gives the movements of the indicator piston a convenient magnification. A sheet of paper on which the pencil marks its movements is caused to move through distances proportional to the motion of the engine piston, and at right angles to the path of the pencil. Thus a diagram is drawn like that of fig. 2, exhibiting a closed curve for each double stroke of the engine piston, and with coordinates which represent the changes of pressure and changes of volume. The enclosed area, when interpreted by reference to the appropriate scales of pressure and volume, measures the net amount of work done in the engine cylinder during the double stroke, so far as one side of the piston is concerned. If the engine is double-acting—that is to say, if the working substance acts successively on the two sides of the engine piston during successive strokes—a similar indicator diagram is taken for the other end of the cylinder as well. The mean effective pressure (M.E.P.) is that pressure which, multiplied by the volume range, gives the work done. It is obtained from the indicator diagram either by dividing the measured area by the horizontal length of the diagram, or by dividing the diagram into a number of vertical sections and finding the average length of the mid-ordinates.

12. Units of Force, Pressure, and Work. For engineering purposes, in speaking of pressure and of work, the common unit of force in British and American usage is the weight of one pound and in continental usage the weight of one kilogramme*. By the word "weight" we mean the force which gravity exerts on the mass at sea level. When scientific precision is required one must specify a locality, or rather a latitude, because gravity acts rather more strongly as we go from the equator towards the pole. The same piece of material is more strongly attracted by the earth in London than in New York to the extent of one part in 1000. If the weight of one pound of matter in mean latitude (45°) be taken as unity, its weight in any other latitude λ is

$$0{\cdot}99735\,(1 + 0{\cdot}0053\sin^2\lambda).$$

The usual units of pressure are the pound per square inch and the kilogramme per square centimetre†. Another unit is the "Atmosphere," which properly means the pressure of the atmosphere with the barometer standing at 760 mm. in latitude 45°,

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* One kilogramme is 2·20462 pounds.

† Since 1 centimetre is 0·393701 in., 1 kilogramme per sq. cm. is 14·2233 pounds per sq. in., when both are measured at the same place, so that gravity acts alike on the pound and the kilogramme. One pound per sq. in. is 0·070307 kilogramme per sq. cm.

or 759·6 mm. in London. This is equal to a pressure in London of 14·688 pounds per square inch or 1·03267 kilogrammes per square centimetre*. Continental engineers, however, often use the symbol "*At*" as a short name for one kilogramme per square centimetre: this usage will be found in Mollier's and other steam tables as well as in technical papers.

Pressures are sometimes given in inches, or in millimetres, of mercury. One inch of mercury (at 0° C.) is equivalent to 0·4912 pound per square inch; one millimetre of mercury to 1·3595 grammes per square centimetre.

The usual engineering units of work are the foot-pound and the metre-kilogramme or kilogrammetre. One kilogrammetre is 7·233 foot-pounds.

13. **Units of Heat.** For the purpose of reckoning quantities of heat we may compare them with the quantity required to warm a unit mass of water from the temperature of melting ice to the temperature at which water boils under a pressure of one atmosphere. These two points serve to determine two fixed states of temperature that are quite definite and are independent of the particular way in which temperature may be measured. The unit of heat which is obtained by taking a certain fraction of this quantity is described as the *mean thermal unit.* Thus we have a mean thermal unit which is one-hundredth part of the heat required to warm one pound of water from the melting point to the boiling point at a pressure of one atmosphere. This unit is called the pound-calory. The reason why one-hundredth part is taken is that on the Centigrade scale of temperature the interval between these fixed points is divided into 100 degrees: consequently the pound-calory is the *average* amount of heat required to warm a pound of water through one degree Centigrade, between the melting point and the boiling point as limits. The actual amount required per degree need not be the same for each degree of the scale, and in fact is not the same, for the specific heat of water is not quite constant.

Similarly, what is commonly called the British Thermal Unit (when the Fahrenheit scale is employed) would be defined as 1/180 of the quantity of heat required to warm one pound of water from

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* 1 atmosphere is the pressure exerted by a 76 cm. column of mercury (of density 13·5951 grams per cm.^{3} at 0° C.); the value of gravity is 980·665 cm./sec.^{2} (i.e. at sea level and latitude 45°); 1 atmosphere = 1·033228 kg./cm.^{2} = 14·6959 lb./in.^{2} = 1·013250 bar; 1 bar = 10^6 dynes per cm.^{2}.

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the melting point to the boiling point, because on the Fahrenheit scale there are 180 degrees between the two fixed points.

Again, the mean kilo-calory is one-hundredth of the amount of heat required to warm one kilogramme of water from the melting point to the boiling point, and the mean gramme-calory is one-thousandth of a kilo-calory.

It should be added that instead of the mean calory a unit is often used called the 15° calory, which means the heat required to raise unit quantity of water from 14·5° to 15·5° on the Centigrade scale.

14. **Mechanical Equivalent of Heat.** The experiments of Joule, begun in 1843 and continued for several years, demonstrated that when work is expended in producing heat a definite relation holds between the amount of heat produced and the amount of work spent. Causing the potential energy of a raised weight to be used up in turning a paddle which generated heat by stirring water in a vessel, and observing the rise of temperature so produced, Joule found that 772 foot-pounds of work served to heat one pound of water through one degree (Fahrenheit) on the thermometer he employed, at a particular part of the scale.

Later and more exact determinations made by Joule himself and other observers agree in showing that Joule's original figure was rather low. The general result is to fix 1400 as the number of foot-pounds (in the latitude of London) that are equivalent to the mean pound-calory as defined in Art. 13. The corresponding value of the mechanical equivalent of the "British Thermal Unit" is 777·8 foot-pounds, and that of the mean gramme-calory is 426·7 gramme-metres*.

* H. L. Callendar, who gave numerical values in his *Steam Tables* (published 1915), used the mean thermal unit for stating quantities of heat. He says there (p. 6) that his mean gramme-calory was equivalent to 4·1868 Joules, the Joule, or Watt-Second, being 10^7 ergs.

An International Steam-Table Conference which met in 1929, 1930 and 1934 has done most useful service, to be referred to later. Among its work has been to *define* what is now called the "International Steam-Table Unit" as a quantity of heat equivalent to 1/860 of an International Watt-Hour or 3600/860 International Watt-Seconds. It also accepted the official International Watt-Second to be larger than the true Joule in the ratio of 1·0003 to 1. Hence the value of the agreed International Steam-Table Unit as defined by the Conference is 1·0003 × 3600/860 or 4·1873 true Joules.

If Callendar's estimate of 4·1868 Joules for the mean gramme-calory used in his *Steam Tables* of 1915 was correct, it follows that his heat unit was less than the modern International Steam-Table Unit by only a very small quantity—about one part in 8000. The International Union of Physics (1931) accepted the Joule (10^7 ergs) as the Unit of Heat when measured in Units of Energy, and also defined the gramme-calory as the amount of heat required