CHAPTER XV.

THERMO-DYNAMICS.

202. Connection between Heat and Work.—That heat can be made to produce work is evident when we consider that the work done by steam-engines and other heat-engines is due to this source.

Conversely, by means of work we can produce heat. Fig. 122 represents an apparatus called the fire-syringe or pneumatic tinder-box, consisting of a piston working tightly in a glass barrel. If a piece of cotton wool moistened with bisulphide of carbon be fixed in the cavity of the piston, and the air be then suddenly compressed, so much heat will be developed as to produce a visible flash of light.

A singular explanation of this effect was at one time put forward. It was maintained that heat or *caloric* was a kind of imponderable fluid, which, when introduced into a body, produced at once an increase of volume and an elevation of temperature. If, then, the body was compressed, the caloric which had served to dilate it was, so to speak, *squeezed out*,[1] and hence the development of heat. An immediate consequence of this theory is that heat cannot be increased or diminished in quantity, but that any addition to the quantity of heat in one part of a system must be compensated by a corresponding loss in another part. But we know that there are cases in which heat is produced by two bodies in contact, without our being able to observe any traces of this compensating process. An instance of this is the production of heat by friction.

Fig. 122.
Fire-syringe.

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[1] In other words, the thermal capacity of the body was supposed to be diminished, so that the amount of heat contained in it, without undergoing any increase, was able to raise it to a higher temperature.

203. Heat produced by Friction.—Friction is a well-known source of heat. Savages are said to obtain fire by rubbing two pieces of dry wood together. The friction between the wheel and axle in railway-carriages frequently produces the same effect, when they have been insufficiently greased; and the stoppage of a train by applying a brake to the wheels usually produces a shower of sparks.

The production of heat by friction may be readily exemplified by the following experiment, due to Tyndall. A glass tube containing water (Fig. 123) and closed by a cork, can be rotated rapidly about its axis. While thus rotating, it is pressed by two pieces of wood, covered with leather. The water is gradually warmed, and finally enters into ebullition, when the cork is driven out, followed by a jet of steam. Friction, then, may produce an intense heating of the bodies rubbed together, without any corresponding loss of heat elsewhere.

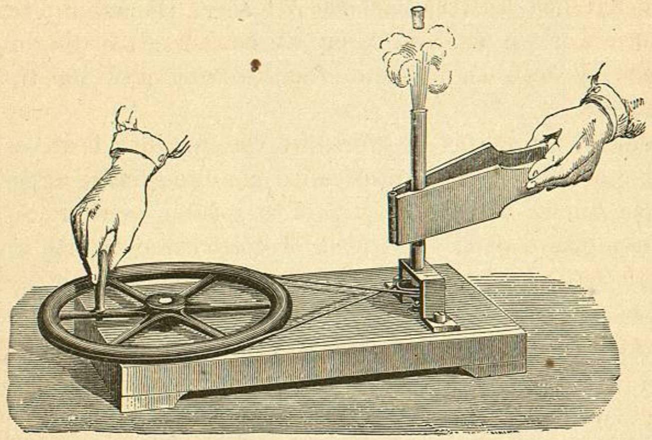

Fig. 123.—Heat produced by Friction.

At the close of last century, Count Rumford (an American in the service of the Bavarian government) called attention to the enormous amount of heat generated in the boring of cannon, and found, in a special experiment, that a cylinder of gun-metal was raised from the temperature of 60° F. to that of 130° F. by the friction of a blunt steel borer, during the abrasion of a weight of metal equal to about $\frac{1}{950}$ of the whole mass of the cylinder. In another experiment, he surrounded the gun by water (which was prevented from entering the bore), and, by continuing the operation of boring for 2½ hours, he made this water boil. In reasoning from these experiments, he strenuously maintained that heat cannot be a material substance, but must consist in motion.

The advocates of the caloric theory endeavoured to account for these effects by asserting that caloric, which was latent in the metal when united in one solid mass, had been forced out and rendered sensible by the process of disintegration under heavy pressure. This supposition was entirely gratuitous, no difference having ever been detected between the thermal properties of entire and of comminuted metal; and, to account for the observed effect, the latent heat thus supposed to be rendered sensible in the abrasion of a given weight of metal, must be sufficient to raise 950 × 70, that is 66,500 times its own weight of metal through 1°.

Yet, strange to say, the caloric theory survived this exposure of its weakness, and the, if possible, still more conclusive experiment of Sir Humphry Davy, who showed that two pieces of ice, when rubbed together, were converted into water, a change which involves not the evolution but the absorption of latent heat, and which cannot be explained by diminution of thermal capacity, since the specific heat of water is much greater than that of ice.

Davy, like Rumford, maintained that heat consisted in motion, and the same view was maintained by Dr. Thos. Young; but the doctrine of caloric nevertheless continued to be generally adopted until about the year 1840, since which time, the experiments of Joule, the eloquent advocacy of Mayer, and the mathematical deductions of Thomson, Rankine, and Clausius, have completely established the mechanical theory of heat, and built up an accurate science of thermodynamics.

204. Foucault's Experiment.—The relations existing between electrical and thermal phenomena had considerable influence in leading to correct views regarding the nature of heat. An experiment devised by Foucault illustrates these relations, and at the same time furnishes a fresh example of the production of heat by the performance of mechanical work.

The apparatus consists (Fig. 124) of a copper disc which can be made to rotate with great rapidity by means of a system of toothed wheels. The motion is so free that a very slight force is sufficient to maintain it. The disc rotates between two pieces of iron, constituting the armatures of one of those temporary magnets which are obtained by the passage of an electric current (called electro-magnets). If, while the disc is turning, the current is made to pass, the armatures become strongly magnetized, and a peculiar action takes place between them and the disc, consisting in the formation of induced currents in the latter, accompanied by a resistance to motion. As long as the magnetization is continued, a considerable effort is necessary to maintain the rotation of the disc; and if the rotation be continued for two or three minutes, the disc will be found to have risen some 50° or 60° C. in temperature, the heat thus acquired by the disc being the equivalent of the work done in maintaining the motion. It is to be understood that, in this experiment, the rotating disc does not touch the armatures; the resistance which it experiences is due entirely to invisible agencies.

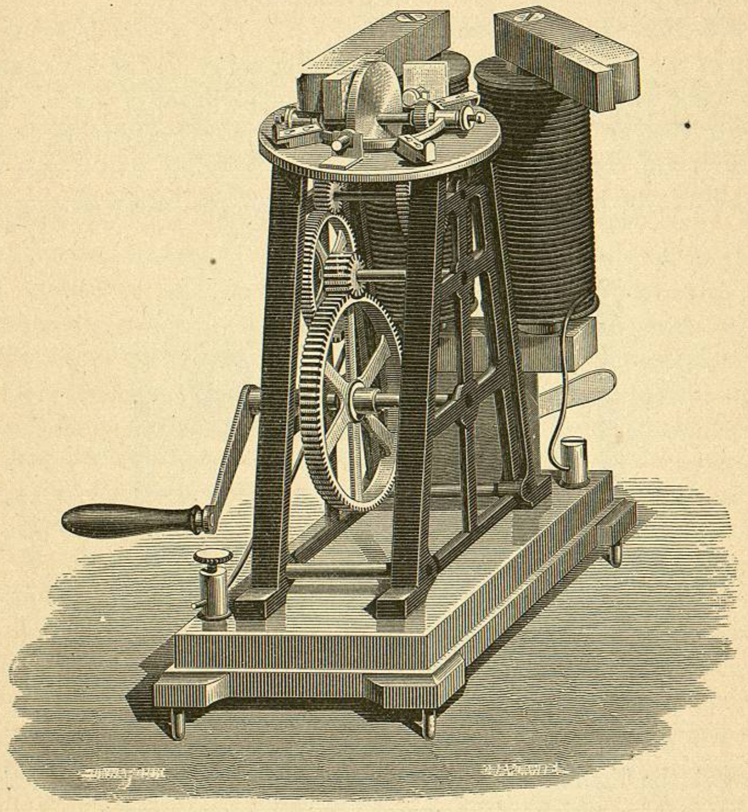

Fig. 124.—Foucault's Apparatus.

The experiment may be varied by setting the disc in very rapid rotation, while no current is passing, then leaving it to itself, and immediately afterwards causing the current to pass. The result will be, that the disc will be brought to rest almost instantaneously, and will undergo a very slight elevation of temperature, the heat gained being the equivalent of the motion which is destroyed.

205. Mechanical Equivalent of Heat.—The first precise determination of the numerical relation subsisting between heat and mechanical work was obtained by the following experiment of Joule. He constructed an agitator which is somewhat imperfectly represented in Fig. 125, consisting of a vertical shaft carrying several sets of paddles revolving between stationary vanes, these latter serving to prevent the liquid in the vessel from being bodily whirled in the direction of rotation. The vessel was filled with water, and the agitator was made to revolve by means of a cord, wound round the upper part of the shaft, carried over a pulley, and attached to a weight, which by its descent drove the agitator, and furnished a measure of the work done. The pulley was mounted on friction-wheels, and the weight could be wound up without moving the paddles. When all corrections had been applied, it was found that the heat communicated to the water by the agitation amounted to one pound-degree Fahrenheit for every 772 foot-pounds of work spent in producing it. This result was verified by various other forms of experiment, and is certainly very near the truth.

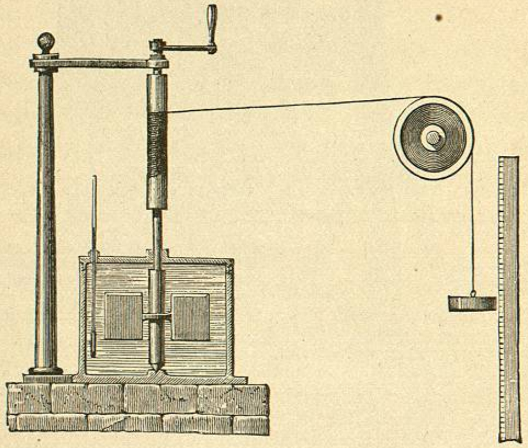

Fig. 125.—Determination of the Mechanical Equivalent of Heat.

For an elevation of 1° Centigrade, the corresponding number will be $772 \times 9/5$, that is, 1390.

For an elevation of 1° C. in a kilogramme of water, the number of kilogrammetres of work required will be the number of metres in 1390 feet, that is, 424. Any one of these numbers is called a value of *Joule's equivalent*, and is usually denoted by the symbol J. It is sometimes called the *mechanical equivalent of heat*, or more fully, the *mechanical equivalent of the unit of heat*.

206. Rowland's Determination.—Among subsequent verifications of Joule's result, the experiments of Professor Rowland[1] at Baltimore are specially important. He drove, by means of a steam-engine, a revolving stirrer, having numerous blades pierced with holes and passing between similar blades fixed to the water-vessel. The revolutions were counted by means of an endless screw on the shaft of the stirrer; and the mutual couple between the stirrer and the vessel was determined by measuring the counterbalancing couple which prevented the vessel from turning; this counterbalancing couple consisting of (1) a pair of equal weights acting (by means of pulleys) on the circumference of a horizontal wheel and composing a couple of any constant magnitude; (2) the torsion of a suspending wire, which, by increasing or diminishing with the couple to be equilibrated, made the arrangement stable. The average elevation of temperature in each trial was about 20°, whereas in Joule's classical experiment it was only a fraction of a degree.

Rowland's result, for water at 10° C., was 428·5, when expressed in kilogrammetres at Baltimore, which is equivalent to 428·0 kilogrammetres at Manchester, where Joule's determination was made. Eliminating the local element of gravitation by reducing to absolute measure, his result for water at 10° C. was *42 millions of ergs for 1° C. of change of temperature in a gramme of water*, temperature being reckoned on the absolute thermo-dynamic scale which will be explained further on in this chapter. At 5° C. the number (instead of 42) was 42·12; at 15° C., 41·89; at 20° C., 41·79; at 30° C., 41·71; and at 35° C., 41·73; showing that the specific heat of water passes through a minimum at about 30° C.

42 million ergs may conveniently be adopted as the value of Joule's equivalent in the C.G.S. system.

207. First Law of Thermo-dynamics.—Whenever work is per-

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[1] Rowland on *the Mechanical Equivalent of Heat*. Cambridge (U.S.) University Press, 1880.

formed by the agency of heat, an amount of heat disappears equivalent to the work performed; and whenever mechanical work is spent in generating heat, the heat generated is equivalent to the work thus spent; that is to say, we have in both cases

$$W = JH;$$

W denoting the work, H the heat, and J Joule's equivalent. This is called the *first law of thermo-dynamics*, and it is a particular case of the great natural law which asserts that energy may be transmuted, but is never created or destroyed.

It may be well to remark here that work is not energy, but is rather the process by which energy is transmuted, amount of work being measured by the amount of energy transmuted. Whenever work is done, it leaves an effect behind it in the shape of energy of some kind or other, equal in amount to the energy consumed in performing the work, or, in other words, equal to the work itself.

As regards the nature of heat, there can be little doubt that heat properly so called, that is, sensible as distinguished from latent heat, consists in some kind of motion, and that quantity of heat is quantity of energy of motion, or kinetic energy, whereas latent heat consists in energy of position or potential energy.

We have already had in the experiments of Rumford, Davy, Foucault, and Joule, some examples of transmutation of energy; but it will be instructive to consider some additional instances.

When a steam-engine is employed in hauling up coals from a pit, an amount of heat is destroyed in the engine equivalent to the energy of position which is gained by the coal.

In the propulsion of a steam-boat with uniform velocity, or in the drawing of a railway train with uniform velocity on a level, there is no gain of potential energy, neither is there, as far as the vessel or train is concerned, any gain of kinetic energy. In the case of the steamer, the immediate effect consists chiefly in the agitation of the water, which involves the generation of kinetic energy; and the ultimate effect of this is a warming of the water, as in Joule's experiment. In the case of the train, the work done in maintaining the motion is spent in friction and concussions, both of which operations give heat as the ultimate effect. Here, then, we have two instances in which heat, after going through various transformations, reappears as heat at a lower temperature.

In starting a train on a level the heat destroyed in the engine

finds its equivalent mainly in the energy of motion gained by the train; and this energy can again be transformed into heat by turning off the steam and applying brakes to the wheels.

When a cannon-ball is fired against an armour plate, it is heated red-hot if it fails to penetrate the plate, the energy of the moving ball being in this case obviously converted into heat. If the plate is penetrated, and the ball lodges in the wooden backing, or in a bank of earth, the ball will not be so much heated, although the total amount of heat generated must still be equivalent to the energy of motion destroyed. The ruptured materials, in fact, receive a large portion of the heat. The heat produced in the rupture of iron is well illustrated by punching and planing machines, the pieces of iron punched out of a plate, or the shavings planed off it, being so hot that they can scarcely be touched, although the movements of the punch and plane are exceedingly slow. The heat gained by the iron is, in fact, the equivalent of the work performed, and this work is considerable on account of the great force required.

208. Heat of Compression and Cold of Expansion.—The heating of a gas by compression or its cooling by expansion is nearly the same in amount as if a quantity of heat equivalent to the work of compression or expansion were given to or taken from the gas at constant volume. This approximate equality was established by an experiment of Joule's. He immersed two equal vessels in water, one of them containing highly-compressed air, and the other being vacuous; and when they were both at the temperature of the water he opened a stop-cock which placed the vessels in communication. The compressed air thus expanded to double its volume, but no change could be detected in the temperature of the surrounding water. The work of expansion produced its equivalent, first in kinetic energy *plus* friction, and finally in heat; and this heat sensibly compensated the cooling effect of the expansion.

Subsequent experiments by Thomson and Joule showed that the cooling effect slightly predominates; hence, conversely, the heating effect of compression slightly exceeds the equivalent of the work done in compressing the gas. The excess of the cooling effect amounted to ·26 of a degree Centigrade in the case of air, when the difference between the initial and final pressures was 1 atmosphere, and to ·26n when the difference was n atmospheres.

The mode of experimenting consisted in steadily forcing air through a plug of cotton wool, and comparing the temperatures of the entering and the issuing air. The friction of the air in passing through the plug generates heat, which in the long run is imparted to the air as it flows through; and this warming effect is combined with the cooling effect of expansion. The cooling effect preponderated, not only in the case of air but in the case of every gas that was tried except hydrogen, which showed a slight rise of temperature. For carbonic acid at about 10° C. the fall of temperature was about $4\frac{1}{2}$ times as great as for air.

209. Work in Expansion.—The work done by a gas in expanding against uniform hydrostatic or pneumatic pressure may be computed by *multiplying the increase of volume by the pressure per unit area*. For, if we suppose the expanding body to be immersed in an incompressible fluid without weight, confined in a cylinder by means of a movable piston under constant pressure, the work done by the expanding body will be spent in driving back the piston. Let A be the area of the piston, x the distance it is pushed back, and p the pressure per unit area. Then the increment of volume is Ax, and the work done is the product of the force pA by the distance x, which is the same as the product of p by Ax.

210. Difference of the two Specific Heats.—Let a gramme of air, occupying a volume V cub. cm. at the absolute temperature T°, be raised at the constant pressure of P grammes per sq. cm. to the temperature $T+1°$. It will expand by the amount $\frac{V}{T}$, and will do work to the amount $\frac{VP}{T}$ in pushing back the surrounding resistances. Now the value of $\frac{VP}{T}$ is (§ 50) the same for all pressures and temperatures. But at 0° C. and 760 mm. we have $T=273$, $P=1033$, and since the volume of 1·293 grammes is 1 litre or 1000 cub. cm., we have

$$V=\frac{1000}{1{\cdot}293},$$

and

$$\frac{VP}{T}=\frac{1000}{1{\cdot}293}\times\frac{1033}{273}=2926 \text{ gramme-centimetres.}$$

This is the work done in the expansion of 1 gramme of air at any constant pressure when raised 1° C. in temperature, and its thermal equivalent

$$\frac{2926}{42400}={\cdot}0690$$

is the excess of the specific heat at constant pressure above the specific heat at constant volume.

Since the difference of the two thermal capacities of volume V is VP/T, the *difference of the two thermal capacities of unit volume* is P/T and *is the same for all gases at the same pressure and temperature*. We neglect here the small departures of actual gases from the simple theoretical laws.

Assuming Regnault's value of the specific heat of air at constant pressure, ·2375, the specific heat at constant volume will be

$${\cdot}2375-{\cdot}0690={\cdot}1685.$$

The heat required to produce a given change of temperature in a gas, when its volume changes in any specified way, may be computed to a very close approximation by calculating the work done by the gas against external resistances during its change of volume, and adding the heat-equivalent of this work to the heat which would have produced the same change of temperature at constant volume.

The above calculation of the difference of the two specific heats rests upon the previously known value of Joule's equivalent. Conversely, from the work done in the expansion of air at constant pressure, combined with the ratio of the two specific heats and the observed value of one of them, the value of Joule's equivalent can be computed. A calculation of this kind, but with an erroneous value of the specific heat of air, was made by Mayer, before Joule's equivalent had been determined.

211. Thermic Engines.—In every form of thermic engine, work is obtained by means of expansion produced by heat, the force of expansion being usually applied by admitting a hot elastic fluid to press alternately on opposite sides of a piston travelling in a cylinder. Of the heat received by the elastic fluid from the furnace, a part leaks out by conduction through the sides of the containing vessels, another part is carried out by the fluid when it escapes into the air or into the condenser, the fluid thus escaping being always at a temperature lower than that at which it entered the cylinder, but higher than that of the air or condenser into which it escapes; but a third part has disappeared altogether, and ceased to exist as heat, having been spent in the performance of work. This third part is the exact equivalent of the work performed by the elastic fluid in driving the piston,[1] and may therefore be called the *heat utilized*, or the *heat converted*.

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[1] If negative work is done by the fluid in any part of the stroke (that is, if the piston presses back the fluid), the algebraic sum of work is to be taken.

The *efficiency of an engine* may be measured by *the ratio of the heat thus converted to the whole amount of heat which enters the engine;* and we shall use the word *efficiency* in this sense.

212. Carnot's Investigations.—The first approach to an exact science of thermo-dynamics was made by Carnot in 1824. By reasoning based on the theory which regards heat as a substance, but which can be modified so as to remain conclusive when heat is regarded as a form of energy, he established the following principles:—

I. *The thermal agency by which mechanical effect may be obtained is the transference of heat from one body to another at a lower temperature.* These two bodies he calls the *source* and the *refrigerator.* Adopting the view generally received at that time regarding the nature of heat, he supposed that all the heat received by an engine was given out by it again as heat; so that, if all lateral escape was prevented, all the heat drawn by the engine from the source was given by the engine to the refrigerator, just as the water which by its descent turns a mill-wheel, runs off in undiminished quantity at a lower level. We now know that, when heat is let down through an engine from a higher to a lower temperature, it is diminished in amount by the equivalent of the work done by the engine against external resistances.

He further shows that the amount of work which can be obtained by letting down a given quantity of heat—or, as we should say with our present knowledge, by partly letting it down and partly consuming it in work, is increased by raising the temperature of the source, or by lowering the temperature of the refrigerator; and establishes the following important principle:—

II. *A perfect thermo-dynamic engine is such that, whatever amount of mechanical effect it can derive from a certain thermal agency; if an equal amount be spent in working it backwards, an equal reverse thermal effect will be produced.* This is often expressed by saying that a *completely reversible engine* is a *perfect engine.*

By a *perfect engine* is here meant an engine which possesses the maximum of efficiency compatible with the given temperatures of its source and refrigerator; and Carnot here asserts that all completely reversible engines attain this maximum of efficiency. The proof of this important principle, when adapted to the present state of our knowledge, is as follows:—

Let there be two thermo-dynamic engines, A and B, working between the same source and refrigerator; and let A be completely reversible.—Let the efficiency of A be m, so that, of the quantity Q of heat which it draws from the source, it converts $m\,Q$ into mechanical effect, and gives $Q-m\,Q$ to the refrigerator, when worked forwards. Accordingly, when worked backwards, with the help of work $m\,Q$ applied to it from without, it takes $Q-m\,Q$ from the refrigerator, and gives Q to the source.

In like manner, let the efficiency of B be m', so that, of heat Q' which it draws from the source, it converts $m'Q'$ into mechanical effect, and gives $Q'-m'Q'$ to the refrigerator.

Let this engine be worked forwards, and A backwards. Then, upon the whole, heat to the amount $Q'-Q$ is drawn from the source, heat $m'Q'-m\,Q$ is converted into mechanical effect, and heat $Q'-Q-(m'Q'-m\,Q)$ is given to the refrigerator.

If we make $m'Q'=m\,Q$, that is, if we suppose the external effect to be nothing, heat to the amount $Q'-Q$ or $\left(\frac{m}{m'}-1\right)Q$ is carried from the source to the refrigerator, if m be greater than m', that is, if the reversed engine be the more efficient of the two. If the other engine be the more efficient, heat to the amount $\left(1-\frac{m}{m'}\right)Q$ is transferred from the refrigerator to the source, or heat pumps itself up from a colder to a warmer body, and *that* by means of a machine which is self-acting, for B does work which is just sufficient to drive A. Such a result we are entitled to assume impossible, therefore B cannot be more efficient than A.

Another proof is obtained by making $Q'=Q$. The source then neither gains nor loses heat, and the refrigerator gains $(m-m')\,Q$, which is derived from work performed upon the combined engine from without, if A be more efficient than B. If B were the more efficient of the two, the refrigerator would lose heat to the amount $(m'-m)\,Q$, which would yield its full equivalent of external work, and thus a machine would be kept going and doing external work by means of heat drawn from the coldest body in its neighbourhood, a result which cannot be admitted to be possible.

213. Examples of Reversibility.—The following may be mentioned as examples of reversible operations.

When a gas expands at constant temperature, it must be supplied from without with a definite amount of heat; and when it returns, at the same temperature, to its original volume, it gives out the same amount of heat.