

He would insist on his pupils mastering the principles of stoichiometry, and in working, as far as possible, quantitatively, even in general chemistry. Mr. C. L. Mees heartily indorsed the ideas advanced by Professor Mabery. For three hundred dollars, a good practical chemical laboratory could be established in high schools, which, if properly conducted, would result in great good. He would insist on a student repeating his work until it was exact. No careless work should be allowed. Mr. C. W. Kolbe gave an illustration of high-school instruction in chemistry, which was evidently purely bookish. The young man who had passed a brilliant examination in stoichiometry failed to do the simplest kind of a problem afterwards, because, he said, 'it was not in the book.' Miss L. J. Martin thought chemistry should be taught in high schools so as to make the pupils think, and not become mere machines. Prof. O. C. Johnson gave an amusing account of the failure to develop the sense perceptions, which he thought should be an important part of laboratory instruction. Messrs. Bennett, Sheppard, Smith, and the acting vice-president, Lupton, also took part in the discussion.

The second subject discussed was, 'To what extent is the knowledge of molecular physics necessary for one who would teach theoretical chemistry?'

Prof. J. W. Langley was invited to open the discussion on this topic. He gave a very clear and satisfactory exposition of the dependence of chemistry upon physics, and of their close relation to one another. He drew attention to the fact, that only under fixed or limited ranges of physical conditions do the ordinarily accepted reactions and chemical affinities manifest themselves. Professors Prescott and Lupton took part in the discussion, showing the advisability of delaying any attempts to teach the higher branches of physics until the student had advanced well in practical laboratory work.

### THE SECOND LAW OF THERMODYNAMICS.<sup>1</sup>

THE second law of thermodynamics has been chosen for the subject of this address: what that law is will be the main question, and the ground will be taken that Rankine's view of the subject is the correct one. After calling attention to the statements of Tait and others as to this law, and as to Rankine's way of stating it, no apology will be necessary for the choice of a question which ought already to have been fully and satisfactorily settled.

There are three different statements, each claiming to be the second law of thermodynamics. I. Rankine's law: "If the total actual heat of a homogeneous and uniformly hot substance be conceived to be divided into any number of equal parts, the effects

of those parts in causing work to be performed are equal." Rankine gives also a second form of the law, in which the expression 'absolute temperate' takes the place of 'total actual heat.' II. Clausius gives as the 'Second fundamental principle,' "Heat cannot of itself flow from a colder to a warmer body." This may be a law in the general theory of heat, but not in thermodynamics, which treats of the relations between heat and mechanical energy; and it has nothing to do with Rankine's law, except as all natural phenomena may be connected. III. The formula for the maximum efficiency of a heat-engine is given as the second law, but this is only a consequence of that law, and the form of the engine.

It would seem from this variety of statement, that a law of nature might be any thing to suit our purpose. I think, however, that a careful examination of Rankine's second law will show that it is genuine, and that it is not universally quoted only because it is not understood. Rankine's law is either copied *verbatim*, or modified in a way to make this evident; and I must confess, that, before working upon the subject myself, I had difficulty with Rankine's statements: they seem now, however, so reasonable, that I shall endeavor to lead you to the same opinion.

Let us see now what is most natural and appropriate for a second law: the first law states that heat and work are mutually convertible, and convertible in a fixed ratio; and it is appropriate that the second law should state the agency by which such conversion may be accomplished, and the rate at which it may be effected.

A quantity of heat,  $W'$ , may be employed as an instrument for the conversion of another quantity of heat,  $W$ , into work, or for the conversion of a quantity of work,  $A$ , into heat; and the converted quantity will be proportional to the converter quantity for a given change of volume or of entropy.

To realize the truth of this statement, let us imagine the simplest physical air-engine: we need no fly-wheel, valves, etc., but simply a vertical cylinder of infinite height, and unit section, with non-conducting walls, the bottom permeable to heat, and the non-conducting piston loaded with a pressure varying so as to be always equal to the gaseous pressure beneath it.

But this is no more than the shell of the engine: we will suppose the piston at such a point that the cylinder shall have a volume of one cubic unit; and we must now put in it, say, one unit of mass of the molecules of a perfect gas, resting on the bottom as dust, or distributed through the space as in any gas, but devoid of motion: we have now added the muscles, but they are dead flesh; the engine is not capable of transforming heat into work, or *vice versa*. The agent by which such a transformation may be accomplished is not present; the space through which the piston may move exists, but the molecules exert no pressure against the piston, and there can be no question of work until we have both space and pressure. To obtain this necessary pressure we must heat the gas to the absolute temperature,  $\tau$ ; i. e., we must store in the molecules an amount of kinetic energy propor-

<sup>1</sup> Abstract of an address delivered before the section of mechanical science of the American association for the advancement of science, at Ann Arbor, Aug. 26, by Prof. J. BURKITT WEBB of Ithaca, N.Y., vice-president of the section. For the complete address, see *Van Nostrand's eng. mag.*, October, 1885.

tional to  $\tau$ ; and calculation shows us that the pressure, which they will then produce by rebounding from the piston, will be proportional to this amount. It will also, for any increased volume, be inversely proportional to that volume. In the ordinary formula connecting the volume pressure and temperature of a perfect gas,  $p\tau = R\tau$ , we have only to suitably change the value of  $R$  to be able to write  $p\tau = R'W'$  where  $W'$  is the converter quantity of energy referred to in the law, which we have stored up in the molecules to act as the agent or instrument for the conversion of heat into work, or *vice versa*.

We wish to emphasize this point, — just as the animal cannot perform its functions without life, so it is this stored-up energy which is the real agent in the engine. Rankine says, "The effect of the presence in a substance of a quantity of actual energy in causing transformation of energy, is the sum of the effects of all its parts." Here he distinctly represents energy as the agent for the transformation of energy.

I believe that nothing but energy can thus act, and that the general law underlying transformations of energy may perhaps be thus stated: "Every conversion of energy from a form  $A$  into a form  $B$  can be effected only through the agency of a quantity of energy," (and I venture to add) and this agent or converter quantity must possess at once the characteristics of  $A$  and  $B$ .

In the engine the agent possesses temperature and pressure, — the characteristics of heat and work: in the dynamo the field is characterized by both electrical and mechanical tension.

Now our agent-quantity of heat must act without expense to itself, for this is the peculiarity of agents; therefore the expansion must be isothermal: a source of heat at the temperature  $\tau + d\tau$  being applied to the conducting bottom, the gas will then expand without loss of energy from the volume unity to the volume  $v$ , thereby converting a quantity of heat into work, which will be infinite for an infinite volume. For any given change of volume, the amount of work will be proportional to the pressure; that is, to the amount of agent-energy: so that for such a change the truth of the law is seen.

Let us look now at the behavior of the molecules: as each rebounds from the hot bottom, its stock of agent-energy receives into itself a portion of the heat  $W$  which is to be converted into work; i.e., the molecule is driven away with an increased velocity by the hotter molecules of the bottom; it carries this portion to the piston, to which it gives it up in the form of work, because if the piston be moving with a velocity  $V$ , the molecule will rebound from it with its velocity reduced by  $2V$ . As the volume increases, the pressure must fall, on account of the rebounds becoming less frequent, and the heat will be converted into work more slowly; but for any and all particular changes of volume, the rate of conversion will be in proportion to the amount of agent-energy, and, therefore, to the temperature of the gas. It is interesting, also, to notice that the distance (from the bottom to the piston), over which the heat-energy  $W$

must be carried, increases directly with the volume; and therefore the time required to carry a certain amount will be proportionately increased, the only way to obtain a more rapid conversion being evidently to increase the velocity of the molecules; i.e. the amount of agent-energy.

Let us turn now to Rankine: he is most easily understood if we commence with his 'general law for the transformation of energy,' already quoted, and proceed backward; and we come first to a graphical representation of the second law. After explaining the quantities in his diagram, and the known relations between them, he asks us to suppose the temperature  $\tau$  to be divided into  $n$  equal parts. Should this supposition be difficult to make, we have only to remember that  $\tau$  is the temperature of the agent, and, therefore, the amount of agent-energy in terms of a suitable unit; in fact, the statement that a unit mass of gas possesses a temperature  $\tau$ , is equivalent to saying that it possesses  $\tau$  units of energy, the unit being the energy required to raise this amount of gas one degree in temperature. We are to suppose, then, the agent-energy divided into  $n$  equal parts; and we are afterward told that these parts are 'similar and similarly circumstanced.' Now let us suppose a molecule, at the temperature  $\tau = 0$ , to be heated to the temperature  $\tau$  by the addition of  $n$  equal increments of energy; once added, all distinction between these parts vanishes, and there remains only the conception of the whole amount of energy as consisting necessarily of  $n$  smaller amounts; and the effects of all these amounts will be the same, and the sum of their effects the effect of the whole. It is only upon the thermometer-scale that degrees of temperature have special places, and that the last one added, and the first subtracted, must be the top one: we cannot, however, see any way in which the energy last added must be the same as the first subtracted.

In Rankine's graphical treatment he shows isothermal expansion; and it should be emphasized that it is the only expansion suitable for the conversion of heat into work, or *vice versa*. With adiabatic expansion we have nothing to do: its only use is to alter the amount of agent-energy, and it need not be used until we come to engines working in a cycle.

Rankine's next statement of his law is the second one criticised by Maxwell, and it supposes nothing more than the division of the absolute temperature already discussed. The first formula should, however, read

$$\tau \frac{d}{d\tau} = Q \frac{d}{dQ}.$$

Proceeding backward, we come to a seemingly more general and comprehensible statement of the law, which speaks of 'the total actual heat.' Now, Rankine has, I think, sufficiently defined this; and it is simply the kinetic energy of the molecules, or that portion of the heat furnished which remains as heat.

Inasmuch as the first statement of the law seems more general, insomuch as it led, as I believe, to a false comprehension of its meaning. It may seem more general in this way: —

Let  $x$ , in a system of rectangular coördinates, represent mass, and  $y$  absolute temperature, then the area,  $xy$ , will be proportional to the energy, or, with a suitable unit of temperature, will equal it. Now, we may cut this area into  $n$  equal parts by vertical lines, which will also cut the mass into  $n$  equal parts. In such case it requires no scientific imagination to see that these parts are similar and 'similarly circumstanced;' but this is altogether too simple for the use to be made of it, and no such statement can pass for a law of thermodynamics; it is simply the law of homogeneity.

Rankine leads up to his statement in an unfortunate way, perhaps, emphasizing the fact that every particle is equally hot. Well, so it must be, or the upper line of the figure would not exist, or would be curved, which would interfere with the argument, because there would then be no one temperature for all the molecules. But Rankine intended no such vertical subdivision: in fact, he says, 'Let unity of weight,' etc.; and we may take a differential unit, and so put such a division out of the question. The division intended by Rankine was by horizontal lines, which makes the statement of the law identical with the other: only he says here, 'heat;' and there, 'temperature;' and he commences with heat, because heat is energy, and changes to temperature, because temperature is the practical way of estimating this energy, and is proportional to it.

We believe, then, that this is the one and only second law; and as our agent is a quantity of energy, and as energy resides in mass, whereas different substances do not differ in their mass, therefore the particular working substance used has no effect.

We will now look again at the formula for efficiency, which flows directly from Rankine's law, in a simple and evident manner.

If we could make an infinite-cylinder engine, this formula would not be needed. This engine works at a temperature, not *between* two temperatures, and it transforms all the heat into work. But mechanical considerations require us to build engines that run in cycles, and we then need it. Every engine running in a cycle is a double engine, consisting of an engine proper and a condenser; i.e., while the piston rises in the cylinder, which we cannot make infinitely high, we transform heat into work completely: then we must use our engine as a condenser for recompressing the gas; and, while doing so, we transform work completely into heat; and if we lower the temperature of the gas before compressing it, there remains a margin of work, according to the efficiency formula.

It should be remarked, that we have made no special reference in this address to any thing but a perfect-gas engine; and we believe the theory of this should be made clear before introducing the necessary modifications to include liquids and solids: Rankine has, however, framed his formula to cover both. Many other points have been left untouched; but if I have made plainer how heat, and therefore temperature, may be supposed to consist of any number of equal parts, and convinced you that Rankine's is the real

and only second law, my main object will have been accomplished.

#### PROCEEDINGS OF THE SECTION OF MECHANICAL SCIENCE.

THE valuable work done by a few in this section deserves the special recognition and support of all its members. The four divisions under which this work may be classified, embrace wide and interesting fields of thought and study. These divisions are, Technical education, Accurate standards of measurement, General, scientific and practical engineering work, and Original investigation. These are proper lines of work for the advancement of 'mechanical science and engineering,' because they include the education of men for the work; the production of instruments and appliances suited to the work; excite enthusiasm, and diffuse knowledge, among the workers; and enlarge the realm subjected to the exact knowledge and control of the intellect and will of man.

The first paper read before this section was on the strength of stay-bolts in boilers, and gave an account of experiments by the writer, Mr. L. S. Randolph. These experiments were designed to furnish data for the explanation of the peculiar manner in which the stay-bolts between the fire-box and boiler-shell had been found to break. The theory was, that the extreme difference of temperature liable to occur between the parallel plates — being at times 200° F., — caused a shifting of these plates, parallel to one another, sufficient to bend the stay-bolts considerably; and that this bending, occurring near the surface of the plate into which the bolt is screwed, caused the bolts to break at this point. The amount of such bending having been calculated from the known difference of temperature and the length of the plates, the experiments showed that if similar stay-bolts were subjected to this amount of bending, they would ultimately break, thus, apparently, confirming the theory. In the discussion, different forms of bolts or stays were suggested as likely to remedy the difficulty. The adoption of a link in place of a bolt was thought to be impracticable in this case on account of the small distance between the plates. Proportioning the stays so as to enable them to bend under the stress to which they are subjected without reaching the elastic limit of the material, was suggested as a remedy for the difficulty. It was shown that stays are sometimes worn away by being vibrated or bent. This bending causes the scale which has been formed to be thrown off; and oxidation occurring again under the action of the water, this new scale is thrown off, and this process continued wears away or 'channels' the iron.

A short abstract of a paper on a universal form of pressure-motor by Prof. D. P. Todd was presented by