

ENTROPY.

BY PROF. H. POINCARÉ.

The controversy about entropy, in which Messrs. Swinburne, Perry and Sir Oliver Lodge have taken part, has a lively interest for me, and if I intervene it is because it affords a chance of going more deeply into the nature and the methods of thermodynamical reasoning.

§ 1. Take any system, S, whose state is defined by a certain number of variables, or "co-ordinates." It is needless to say I will include among these variables the positions and the speeds of the different parts of the system, so that if the *vis viva* of one of these parts varies, I say that the state of the system has not remained the same.

Let A and B be two states of the system S. What is the condition under which we can pass from the state A to the state B? The first law tells us, first, that if the system S is isolated, we cannot pass from A to B, or, on the other hand, from B to A unless a certain function of the co-ordinates, which is called the energy, has the same value in A as in B.

§ 2. What does the second law tell us? It may be true that we can pass from the state A to the state B *directly*—that is to say, while the system S remains completely isolated; and it may also be true that we can pass from A to B *indirectly*, that is to say, with the help of the intervention of other auxiliary systems, S', but in such a way that at the end of the change these auxiliary systems have come back to their original states.

Then it is generally admitted that when we have two states, A and B, corresponding to the same energy value, and two changes by which the system goes from A to B, and from B to A, one of these transformations is always possible, either directly or indirectly, while the other is impossible, directly or indirectly. Theoretically, we have to consider the limiting case, where the two changes are possible, but infinitely slow; and then we say that the change is reversible. That is the second law.

§ 3. On what foundations does the second law rest? Two states, A and B, being given, can we imagine an auxiliary system, S, which will enable us to pass indirectly, either from A to B, or from B to A? This is a question which must be discussed in each particular case; so far we have always succeeded. If we had a system such that we could not imagine the auxiliary system S' enabling us to carry out one of the inverse transformations, the ordinary reasoning of thermodynamics would not be applicable to this system, and entropy could not be defined.

Then how are we to show that only one of the two transformations is possible? This is the ordinary way. We conceive an auxiliary system S, so chosen that we can change S from the state A to the state B in a reversible manner, and so that the system S' changes from the state C to the state D. In accordance with what we have already said, it would be impossible to bring S from A to B by reversible change without changing the state of S'.

If, then, S could pass directly or indirectly from B to A, S would pass indirectly from C to D; all that is needed is to make the transformation of which we have just spoken reversible, which would bring S from A to B, and S' from C to D, then to bring S back from B to A; finally S would have passed from C to D and S would not have changed. The impossibility of the change C to D is then a criterion of the impossibility of the change B to A.

If, therefore, we know already (either by experiments numerous enough for us to deduce a general law from them, or by reasoning) that the change C to D is impossible, we must conclude that the change from B to A is also impossible. It is in this way that from Clausius' axiom, which referred only to one particular change, we have been able to deduce the impossibility of a host of other changes, and finally the second law of thermodynamics in all its generality.

We can only reason in this way if we are able to conceive this auxiliary reversible change of which I have just spoken. So far we have always succeeded. Let me take but two examples: I assume that the system S is made up of two bodies, α and β , at different temperatures, and that the change

from A to B consists in passing heat from the hotter α to the colder β . We will take for our system S a body γ at the same temperature as α and a thermodynamic engine, with which we can describe a Carnot cycle, using the bodies α , β and γ as reservoirs. We can then, by means of the engine, pass a certain amount of heat from the hot body to the cold body by reversible changes, while the engine at the same time borrows an additional amount of heat from the body γ to transform it into work.

The system S will thus have passed from the state A to B, and the system S' will have also changed (and passed from the state C to the state D), since the body γ has lost heat, and the work or kinetic energy of the system is increased. These two changes taken together are reversible. It is in this way that from the impossibility of making an engine work with only one source we can prove the impossibility of a cold body giving heat to a hot one.

Another example. The system S is made up of two gases; in the state A these two gases are separate; in the state B they are mixed. I will take it that the two gases are nitrogen and carbonic anhydride; and I will add an auxiliary system S', consisting of lime and various sources of heat. To pass from A to B by a reversible path, I absorb the carbonic anhydride by the lime, at the pressure of dissociation, giving up the heat so produced (without fall of temperature) to the reservoirs of the system S'; I put the calcium carbonate into the vessel containing nitrogen, then I dissociate the carbonate by taking the necessary heat from the reservoirs of S; finally, we get the two gases mixed, and S passed from A to B; at the same time there has been an exchange of heat from the reservoirs of S', so that S' has changed from the state C to the state D. The impossibility of separating two gases once they are mixed in such a way that the auxiliary system comes back to its original state, can thus be demonstrated.

§ 4. I trust I may be forgiven for the length of this explanation, as it seems a little far from the point of the controversy; but perhaps it will not be useless, and it leads up to the point I will make directly.

I now come to the main point of the discussion—the definition of entropy. If we admit the second law as I have given it, it is that there is a function of the co-ordinates which is greater in B than in A, if we can pass either directly or indirectly from A to B, but not from B to A. This function is, by definition, the entropy; but this definition of entropy is still incomplete, for two reasons: In the first place, it only allows us to compare the entropy of the system S in the two states A and B if the two states correspond to the same value of the energy, as, if it is isolated, it is in that case alone that the system S can pass from one state to the other. In the second place, the entropy so defined is not a measurable quantity, for, though we can easily see that it is greater in B than in A, we cannot see whether it is two or three times as great. If, then, ϕ is a function which answers the definition, any function of ϕ which increases would do as well.

§ 5. But we can get out of this double difficulty. Take a system, S, made up of three partial systems, S₁, S₂ and S₃, and suppose we can separate these three systems sufficiently for them to have no action on one another. Then let x_1, x_2, \dots, x_n be the variables which define the state of the system S₁, y_1, \dots those which define the state of the system S₂, z_1, \dots those which define the state of the system S₃. Let ϕ be the entropy of the whole system, and let us write

$$d\phi = \sum A_i dx_i + \sum B_j dy_j + \sum C_k dz_k.$$

We will take for ϕ any one of the functions which satisfy the preceding definition. Then we can imagine a reversible change produced as follows:—The systems S₁ and S₂ are brought together, and they act on each other, then they are separated. In these conditions the x 's and the y 's have varied, but not the z 's. Moreover, the entropy is constant, so that we have:

$$\sum A_i dx_i + \sum B_j dy_j = 0,$$

but the system S having been kept out of the way during the change, has not been acted upon, and the transformation is independent of the z 's. Whence it follows that the relations of the partial differential coefficients A and B cannot depend

on the z 's; similarly, the relations between the B and C terms cannot depend on the x 's, and those between the A and C terms cannot depend on the y 's.

Collecting these three results, we find easily

$$d\phi = W(d\phi_1 + d\phi_2 + d\phi_3),$$

W being a function of the x 's, the y 's and the z 's, ϕ a function of the x 's alone, ϕ_2 a function of the y 's alone, and ϕ_3 a function of the z 's alone. On the other hand, we see that ϕ and W can only be functions of $(\phi_1 + \phi_2 + \phi_3)$.

We can take advantage of the indeterminateness of ϕ to put

$$\phi = \phi_1 + \phi_2 + \phi_3,$$

and to say that the entropy of the whole system is the sum of the entropies of the partial systems. This new convention gets rid of the double ambiguity which I have already mentioned. It is clear, too, that we can have any number of partial systems.

§ 6. Suppose now that among the partial systems there are "sources," by which I mean systems, whose mass is so large that on that account they experience only very small changes, and further, that the state of each of the sources or reservoirs is defined by a single independent variable.

Under these conditions, if S_1 is one of the reservoirs, ϕ_1 its entropy, and U_1 its energy, U_1 will be a function of ϕ_1 , and as these two functions suffer only infinitesimal changes, the ratio $dU_1/d\phi_1$ will be constant. This constant can be regarded as the temperature of the reservoir. To entitle me to say this, it is enough for me to show that if we compare the different reservoirs this ratio varies in the same direction as the temperature. In fact, if it were otherwise, in passing heat from a cold to a hot body we should increase the entropy, and the change would be possible.

We may then put

$$\frac{dU_1}{d\phi_1} = \theta_1.$$

Let there be a complete system containing a partial system S whose entropy is ϕ , and several reservoirs S_i at temperatures θ_i and with energies U_i and entropies ϕ_i . For a change to be possible we must have

$$d\phi + \sum d\phi_i > 0,$$

or

$$d\phi > -\sum \frac{dU_i}{\theta_i}.$$

For a reversible change we have $d\phi = -\sum dU_i/\theta_i$.

§ 7. We now come to the equations of Clausius. Suppose that each part of the system S borrows its heat from a source at the same temperature as its own; or, in other words, that the properties of the system S are the same, whatever the exterior reservoirs may be from which the different parts of the system receive their heat. This is a hypothesis which it is difficult not to admit when the transmission of the heat is by conduction, but which can be certain no longer with radiated heat. Admitting this, take an infinitely little element of the system S, and suppose that its temperature is θ and that it receives from outside a quantity of heat, dH ; the corresponding reservoir, according to our hypothesis, will also be at the temperature θ , and its energy will increase by $dU = -dH$. We have, then,

$$-\sum \frac{dU}{\theta} = \int \frac{dH}{\theta},$$

and, consequently,

$$d\phi > \int \frac{dH}{\theta},$$

and for the reversible change,

$$\delta\phi = \int \frac{dH}{\theta}.$$

In the preceding integrals we have taken heat in only from the outside, but the same inequalities hold *a fortiori* if we only allow the quantities of heat dH which are exchanged between the different parts of the system S to figure in the integral $\int dH/\theta$.

§ 8.—CONCLUSIONS.

- A. The entropy is a function of the co-ordinates.
- B. Is not defined by the equation

$$d\phi = \int dH/\theta.$$

This equation, arising from another definition of entropy, can be demonstrated for reversible changes.

C. It is wrong for all irreversible changes, and not only for those where there is exchange of heat in the narrow sense of the word.

D. In an irreversible change in which there is no exchange of heat the entropy increases.

E. It increases, for instance, in the case of a mixture of gases, and the increase can be calculated by the artifice I have discussed at the end of section 3.

F. If the universe is regarded as an isolated system, it can never come back to its original state; for its entropy is always growing, and this entropy being a function of the co-ordinates, would come back to its original value if the universe came back to its original state.

§ 9. In what I have said I have been careful to state explicitly the hypotheses I have made. To what extent the reasoning is on an artificial basis is evident; and if this article were not already rather long, I would further insist on that point—it is clear that the reasoning must be continually controlled by experiment. There has been no want of such control so far; and there is really no doubt left as to the validity of the second law. But it is well, all the same, to remember what the mathematical basis is, and how far this basis is not quite satisfactory.

THE PHOTOMETRY OF ELECTRIC LAMPS.

(Concluded from page 640.)

The following is the conclusion of the discussion on Dr. Fleming's Paper on the above subject:—

Mr. F. H. VARLEY said that the variation in the candle-power of a pentane lamp was not due to any fault of the pentane nor to the lamp itself, but was entirely due to the impurities in the air. The lamp drew in air through the valve and was saturated with pentane vapour, if the air was moist, then there was a repellent action, and it did not absorb so much pentane vapour as when the air was perfectly dry. The effect of moisture in the air, as far as combustion was concerned, was well known. It chilled the flame and caused imperfect combustion of the carbon, with the result that the flame smoked. If precautions were taken so that the air was perfectly dry, and the organic matter, chiefly ammonia and carbonic dioxide, removed, it was possible to remove, by using pure air, all the variations of the pentane lamp, except those of barometric pressure and temperature. But these, surely, could be calibrated, and a constant given for each millimetre change in barometric pressure and for each degree of temperature. In the year 1889 he devised a direct-reading photometer which had the advantage of being able to be used in a very small space. He illustrated the principle of his device by a cardboard disc. It was a sector photometer. There were two openings—one small and one large. By getting a full opening on one sector the other was entirely closed. By twisting the discs the length of the opening was shortened, and the corresponding opening on the other side made larger.

Mr. LEON GASTER thought it would be interesting if the price of the pentane required for the Vernon Harcourt lamp could be given, and also the price of the lamp itself.

Mr. H. E. MOUL, who emphasised throughout his remarks that he only spoke on the commercial side of the question, said that engineers ought to take great interest in the subject; but in England, at any rate, they did very little with it. No photometric results were really comparable when taken by different observers and different instruments. It seemed to him that if comparative tests were to be made at different places—one in Germany and one in England—a standard class of photometer must be adopted for doing it, just as much as a standard source of light. Anyone who had worked with a Lummer-Brodhun photometer would never go back to anything else. It was now being superseded by the Kruss type, a modification with straight telescope and contrast field. As engineers they were not so much interested in what was to be the final standard as in getting a standard at all. It was not possible in actual commercial practice in Great Britain to refer any readings which might be taken to a standard, for the simple reason that there was none, and the net result of this state of affairs was that lamp makers supplied what they said was a good thing, but which the central station engineer said was a bad thing, and really neither party knew what it was talking about. If they differed they had no standard of reference and no place in which to refer for a legal decision on the question. While this battle of standards was going on there ought to be one class of standard to which instruments could be correlated, even if something else was adopted afterwards. If central station engineers were going to set up their own standards it was necessary to have some other than what had been seen at the meeting. Standardised lamps were the right thing, they could be obtained on the Continent from the Reichsanstalt standardised at a cost of 2s. 6d. with the position marked on them on which they had been standardised, and one knew that they were as accurate as they were wanted—technically, not scientifically. The potentiometer was a very pretty instrument in the laboratory, but how it would turn out in the ordinary course of events he did not know. When stations supplied their own lamps, which would be the case in the future, the lamps would go through the photometer rooms in thousands, and what would be the state