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VIII. *On the Second Law of Thermodynamics in connexion with the Kinetic Theory of Gases.* By S. H. BURBURY*.

IN a memoir by Boltzmann† is contained an analytical proof of the second law of thermodynamics, founded on results obtained in the earlier part of the same memoir. The writer's treatment of this part of the subject is not characterized by his usual lucidity, and has given much trouble to some mathematicians. It is worth while to show that the second law can be deduced by a simple process from Boltzmann's results.

A great number, λ , of material particles are moving in a closed spherical vessel. Forces of mutual attraction or repulsion act between each pair of particles and between the particles and the walls of the vessel. To simplify the case, we will suppose that these are the only forces which act on the particles.

Boltzmann has shown that the mean kinetic energy is the same for every particle. Let T be this mean kinetic energy, and let $T = \frac{3}{2h}$. The mean kinetic energy of the system is then $\frac{3\lambda}{2h}$.

Let the positions of the particles at any instant be defined by reference to three rectangular axes passing through the centre of the vessel, the coordinates of the several particles being $x_1, y_1, z_1, \dots, x_\lambda, y_\lambda, z_\lambda$.

Let v be the volume of the vessel.

The pressure exerted by the system of moving particles on any point on the surface of the sphere may vary from instant to instant according to the positions which the particles happen to have. But if the motion be stationary, this pressure must have on the average of any very long time a certain mean value P per unit area, which in the absence of impressed forces will be uniform over the whole surface.

Then P is the force per unit area which must be exerted on the surface of the sphere from without in order to maintain equilibrium.

Let χ be the ergal for any given positions of the particles of all the forces acting on the particles—that is, of all the forces which act in any manner on the system, except the external force P .

All those positions of the particles for which the coordinates of the first particle are between x_1 and $x_1 + dx_1$,

y_1 and $y_1 + dy_1$,

z_1 and $z_1 + dz_1$,

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of the second particle between x_2 and $x_2 + dx_2$,
 y_2 and $y_2 + dy_2$,
 $\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$,
 $\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$,
 of the λ th particle between x_λ and $x_\lambda + dx_\lambda$,
 y_λ and $y_\lambda + dy_\lambda$,
 z_λ and $z_\lambda + dz_\lambda$,

may, when $dx_1, dy_1, \dots dz_\lambda$ are very small, be considered as having the same value of χ for ergal, notwithstanding any variations of position within those limits.

Let all such positions be deemed to constitute one configuration, which we may call configuration M. Then, as Boltzman has shown, the time during which on the average of any very long time the system will be within configuration M is proportional to

$$\bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda$$

Its actual value is therefore

$$\frac{\bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda},$$

the integration extending over all possible configurations.. The mean value of any function, f , of the position of the particles (which we denote as usual by $\bar{f}$) is

$$\bar{f} = \frac{\iiint \dots f \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda},$$

and therefore

$$\bar{\chi} = \frac{\iiint \dots \chi \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}.$$

II. Now let the system receive a small accession of heat, δQ , and let $\delta h, \delta v$ be the consequent increments of h and v . We may suppose the alteration of volume to be effected by the vessel undergoing a uniform homogeneous strain, the centre remaining fixed. In that case the distance, r , between any two points in it becomes after the alteration θr , where θ is a ratio the same for every pair of points, and manifestly $\theta = 1 + \frac{1}{3} \frac{\delta v}{v}$.

We further assume that the external forces are so adjusted as to maintain the system in equilibrium in its altered state, and that such adjustment takes place without altering χ for any given configuration, consequently that no change takes

place in χ except as the equivalent of work done by or against the forces on change of position of the particles. Then δQ consists (1) of alteration of kinetic energy—that is,

$$\delta\left(\frac{3\lambda}{2h}\right) \text{ or } -\frac{3\lambda}{2h^2}\delta h;$$

(2) of alteration $\delta\bar{\chi}$ of $\bar{\chi}$; (3) of external work done, $P\delta v$ —that is,

$$\delta Q = -\frac{3\lambda}{2h^2}\delta h + \delta\bar{\chi} + P\delta v.$$

We may here observe that

$$\delta Q - P\delta v = -\frac{3\lambda}{2h^2}\delta h + \delta\bar{\chi},$$

which is an exact differential of a function of two variables, h and v . This proposition is proved in a different way by Rankine (see 'The Steam-Engine,' eighth edition, pp. 304–313). Again,

$$\frac{\delta Q}{T} = -\frac{\lambda}{h}\delta h + \frac{2h}{3}\delta\bar{\chi} + \frac{2h}{3}P\delta v; \quad . \quad . \quad . \quad (A)$$

and it is required to prove that this expression is an exact differential.

III. Consider the expression

$$\log \iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda,$$

in which the integration extends over all configurations; and let

$$\log \iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda = u.$$

Then δu denotes the whole change which takes place in u consequent on h becoming $h + \delta h$, and v becoming $v + \delta v$; that is,

$$\delta u = \frac{du}{dh}\delta h + \frac{du}{dv}\delta v.$$

Now for any given configuration the ergal χ is not altered by alteration of h , though the comparative frequency of the occurrence of such configuration is altered; therefore

$$\frac{du}{dh}\delta h = -\delta h \frac{\iiint \dots \chi \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} = -\bar{\chi}\delta h.$$

We have now to find $\frac{du}{dv}\delta v$. Both in the original and in the altered volume the integration is to be extended over all possible configurations. Now for every configuration M in the original volume there is in the altered volume a corresponding configuration, which we may call M' ; and M' is to be

formed from M by altering the distance between each pair of points in the ratio $\theta : 1$ —that is,

$$\left\{ 1 + \frac{1}{3} \frac{\delta v}{v} \right\} : 1.$$

If, then, $u, \chi, dx_1, dy_1, \dots dz_\lambda$ be denoted in the altered volume by accented letters, we shall have

$$\begin{aligned} u' &= \log \iiint \dots \bar{\epsilon}^{hx'} dx'_1 dy'_1 \dots dz'_\lambda \\ &= \log \{ \theta^{3\lambda} \bar{\epsilon}^{hx'} dx_1 dy_1 \dots dz_\lambda \}, \end{aligned}$$

since every linear element $dx_1, dy_1, \&c.$ is altered in the ratio $\theta : 1$.

In the last expression for u' , χ' is to be treated as a function of $x_1, y_1, \dots z_\lambda$. Then

$$\begin{aligned} \frac{\delta u}{\delta v} \delta v &= u' - u = \log \frac{\iiint \dots \bar{\epsilon}^{hx'} dx'_1 dy'_1 \dots dz'_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} \\ &= \log \left\{ \theta^{3\lambda} \frac{\iiint \dots \bar{\epsilon}^{hx'} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} \right\} \\ &= 3\lambda \log \theta - h \cdot \frac{\iiint \dots \delta \chi \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} \\ &= \lambda \frac{\delta v}{v} - h \delta v \cdot \frac{\iiint \dots \frac{d\chi}{dv} \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} \\ &= \lambda \frac{\delta v}{v} - h \overline{\frac{d\chi}{dv}} \delta v, \end{aligned}$$

in which expression $\overline{\frac{d\chi}{dv}}$ denotes the mean for all configurations of the alteration of χ consequent on v becoming $v + \delta v$.

Collecting our results, we obtain

$$\delta u = \frac{du}{dh} \delta h + \frac{du}{dv} \delta v = -\bar{\chi} \delta h + \lambda \frac{\delta v}{v} - h \overline{\frac{d\chi}{dv}} \delta v. \quad (B)$$

IV. The system being in stationary motion must satisfy Clausius's equation

$$\frac{3}{2} P v = \frac{3\lambda}{2h} + \frac{1}{2} \overline{\Sigma \Sigma R r},$$

in which P is the force acting from without on the surface of the vessel, and $\frac{1}{2} \overline{\Sigma \Sigma R r}$ is the mean virial of all the other forces acting on the system—that is, of all the forces of which the ergal is χ .

Also in $\Sigma\Sigma Rr$, R is the repulsive force, r the distance between any two particles, or between a particle and a point on the surface, and the summation includes every pair of points between which any force acts.

Then $\Sigma\Sigma Rr$ is a function of position of the particles, having a definite value for each configuration, and $\overline{\Sigma\Sigma Rr}$ denotes the mean value of $\Sigma\Sigma Rr$ for any long time; and we might therefore write

$$\overline{\Sigma\Sigma Rr} = \frac{\iiint \dots (\Sigma\Sigma Rr) \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}.$$

Now let

$$P = P_1 + P_2,$$

and let

$$\frac{3}{2}P_1v = \frac{3\lambda}{2h}, \quad \dots \quad (1)$$

$$\frac{3}{2}P_2v = \frac{1}{2}\overline{\Sigma\Sigma Rr}. \quad \dots \quad (2)$$

It follows from (1) that

$$hP_1 = \frac{\lambda}{v},$$

and

$$hP_1\delta v = \lambda \frac{\delta v}{v}.$$

Also from (2),

$$\begin{aligned} P_2 &= \frac{1}{3}\overline{\Sigma\Sigma Rr} \frac{r}{v}, \\ P_2\delta v &= \frac{1}{3}\overline{\Sigma\Sigma Rr} \frac{\delta v}{v} r \\ &= \overline{\Sigma\Sigma R\delta r}. \end{aligned}$$

Now for each configuration

$$\Sigma\Sigma R\delta r = -\delta\chi = -\frac{d\chi}{dv}\delta v.$$

Therefore, taking mean values,

$$\overline{\Sigma\Sigma R\delta r} = -\frac{\overline{d\chi}}{dv}\delta v;$$

therefore

$$P_2\delta v = \overline{\Sigma\Sigma R\delta r} = -\frac{\overline{d\chi}}{dv}\delta v.$$

Therefore

$$hP_2\delta v = -h\frac{\overline{d\chi}}{dv}\delta v.$$

And we have seen that

$$hP_1\delta v = \lambda \frac{\delta v}{v}.$$

Therefore

$$hP_1\delta v + hP_2\delta v = \lambda \frac{\delta v}{v} - h \frac{d\bar{\chi}}{dv} \delta v;$$

that is,

$$hP\delta v = \lambda \frac{\delta v}{v} - h \frac{d\bar{\chi}}{dv} \delta v.$$

Substituting in (B), we obtain

$$\delta u = -\bar{\chi}\delta h + hP\delta v,$$

or

$$hP\delta v = \bar{\chi}\delta h + \delta u;$$

and substituting in (A), we obtain

$$\begin{aligned} \frac{\delta Q}{T} &= -\lambda \frac{\delta h}{h} + \frac{2}{3} h \delta \bar{\chi} + \frac{2}{3} \bar{\chi} \delta h + \frac{2}{3} \delta u \\ &= \delta \left\{ -\lambda \log h + \frac{2}{3} h \bar{\chi} + \frac{2}{3} u \right\}, \end{aligned}$$

an exact differential.

The expression $-\lambda \log h + \frac{2}{3} h \bar{\chi} + \frac{2}{3} u$ is what Rankine denotes by ϕ in his equation

$$JdQ = Td\phi.$$

The value which we have obtained for ϕ is the same as that obtained by Boltzmann in the memoir above referred to. But his expression for δQ is

$$\begin{aligned} & -\frac{3\lambda}{2h^2} \delta h + \delta \left\{ \frac{\iiint \dots \chi \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda} \right\} \\ & - \frac{\iiint \dots \delta \chi \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}{\iiint \dots \bar{\epsilon}^{hx} dx_1 dy_1 \dots dz_\lambda}, \end{aligned}$$

which is not easily to be reconciled with the expression we have used.

V. We have assumed hitherto that no alteration takes place in χ except as the equivalent of work done by or against the forces. It is, however, conceivable that a change should take place in χ for one and the same configuration, especially if, in the adjustment of external pressure to maintain equilibrium, new forces be brought into play. Boltzmann appears to contemplate this case. We proceed to show that, provided χ be for each

configuration a function of h and v , the function $\frac{dQ}{T}$ is still an exact differential.

Let $\delta_2\chi$ or $\frac{d_2\chi}{dh}\delta h + \frac{d_2\chi}{dv}\delta v$ be the new alteration in χ , which is not the equivalent of work done, and let $\delta_2\bar{\chi}$ be the mean value of $\delta_2\chi$.

Then, as the alteration is supposed to take place without expense to δQ_1 , $\delta_2\bar{\chi}$ must be subtracted from the whole change of the ergal in the expression for δQ . The equation (A) then becomes

$$\frac{\delta Q}{T} = -\lambda \frac{\delta h}{h} + \frac{2}{3} h \delta \bar{\chi} - \frac{2}{3} h \delta_2 \bar{\chi} + \frac{2}{3} h P \delta v.$$

Under the circumstances (B) becomes

$$\begin{aligned} \delta u &= -\bar{\chi} \delta h + \lambda \frac{\delta v}{v} - h \frac{d\bar{\chi}}{dv} \delta v - h \frac{d_2\bar{\chi}}{dh} \delta h - h \frac{d_2\bar{\chi}}{dv} \delta v \\ &= -\bar{\chi} \delta h + \lambda \frac{\delta v}{v} - h \frac{d\bar{\chi}}{dv} \delta v - h \delta_2 \bar{\chi}; \end{aligned}$$

and by substitution we obtain, as before,

$$\frac{\delta Q}{T} = \delta \left\{ -\lambda \log h + \frac{2}{3} h \bar{\chi} + \frac{2}{3} u \right\} = \delta \phi.$$

IX. *On the Production of Spectra by the Oxyhydrogen Flame.*
By TASKER H. MARVIN, Brooklyn, N. Y.*

SIX or seven months since, in using the lime-light for spectroscopic work, I had the good fortune to discover a method by which bright-line spectra, without an accompanying continuous spectrum, could be produced at will by means of the oxyhydrogen flame.

I had been engaged in examining the spectrum of calcium superimposed upon the continuous spectrum, which is easily seen by bringing the collimator of a compound spectroscope to bear *laterally* upon the incandescent point of the line. I found that I could bring out all the bands of calcium and the sodium line doubled sharply and brightly, notwithstanding the brightness of the continuous spectrum. When, however, the proportions of hydrogen and oxygen were so adjusted that there was no excess of the latter, the bright lines of calcium and sodium disappeared and the continuous spectrum alone remained. The chemical reaction then seemed evident; the

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