that the mixture surrounding it was explosive, shots were fired from a gun at a distance of 30 yards. The barrel of the gun which was used is $\frac{13}{16}$ of an inch in diameter, and it is rifled for a length of 3 ft. with seven grooves; the breech which received the charge is smooth-bored, and $4\frac{1}{8}$ inches long. Each measure of gunpowder weighed 3·822 grammes (=59 grains), and the charges fired ranged between 1 and 9 measures; paper tamping was rammed down tightly, and the charge was fired by a cap.

The gun was tied to a prop in the middle of the mine, with its barrel at an angle of about 35° upwards, pointing towards the apparatus; the muzzle was 18 inches from the floor. At the part where the experiments were made, the sizes of the mine are:—width at top, 4 ft.; width at bottom, 6 ft.; height, 5 ft. 6 in.

The sound-wave from a shot of two measures extinguished the flame of the Davy lamp when it was placed on the outside of the apparatus; but when it was placed in the inside of *d*, the flame could not be extinguished nor passed through the meshes, even when the quantity of gunpowder was raised to nine measures. However, after the lamp had been allowed to burn in the isolated space for a few minutes (the supply of fresh air not being very good), its flame could be extinguished by the sound-wave from a shot of four measures. The whole quantity of fire-damp was so small that there was no opportunity for enlarging or varying the apparatus.

These experiments, and one which I made formerly in the sewer with the *b* tube of the apparatus, fig. 2, Plate VI., show that a very slight obstacle will interfere with the action of the sound-wave. They were concluded in March 1874.

I would add, in concluding, that the liberal grant of money which I received from the Government-Grant Committee of this Society has been of great value in enabling me to carry out these experiments.

I have also been much indebted for assistance to each of the following gentlemen:—Mr. Robert H. Scott, F.R.S.; Professor A. C. Ramsay, F.R.S.; Professor W. W. Smyth, F.R.S.; Professor Marreco, of the College of Physical Science, Newcastle-on-Tyne; Mr. John Galloway, of Barleith and Dollars Collieries; Mr. J. B. Simpson, of Newcastle-on-Tyne; Mr. Charles Shute, of Hebburn Colliery; and to Mr. William Kirkwood, of the Inkerman Mines, near Glasgow.

XX. "On the Adiabatics and Isothermals of Water." By A. W. Rücker, M.A., Fellow of Brasenose College, Oxford. Communicated by R. B. Clifton, M.A., F.R.S., Professor of Experimental Philosophy in the University of Oxford. Received June 4, 1874.

M. Verdet, in his work on Thermodynamics ('Œuvres,' vol. vii. p. 184), enunciates the proposition "Deux courbes de nulle transmission ne peu-

vent se couper," and offers a proof which rests upon the assumption that if a body could undergo a series of operations represented as to the changes of pressure and volume by PQMP (where PQ is an isothermal and PM, QM two adiabatics), no heat would be gained or lost at any part of the cycle except PQ.

It is, however, evidently impossible that the body could, at the point M, pass from one adiabatic to another without absorbing or emitting heat, *i. e.* while fulfilling the very condition that it should *not* pass from one adiabatic to another; and the question as to the possibility of the intersection of two adiabatics must therefore be submitted to a more general investigation, as it is certainly conceivable that heat might be gained or lost during the passage from the point M considered as lying on the first curve to the point M considered as belonging to the second, whether it took place, as supposed by M. Verdet, without any accompanying changes of pressure or volume, or whether, as we shall see would be generally the case, it could only be accomplished if the body were caused to assume a series of intermediate states involving such changes.

The question admits of an easy answer if we consider the case of bodies which can exist in two distinct states under the same circumstances of pressure and volume; and for the present we may confine our attention to water, which is the most conspicuous representative of the class, and which, at the ordinary atmospheric pressure and at temperatures between 0° C. and 4° C., exists in a series of states in which the volumes are the same as those which it assumes if heated at the same pressure from 4° C. to about 8° C.

Hence whereas for higher temperatures all the properties of water at atmospheric pressure are completely defined if we know the volume, such is not the case between the limits above indicated; but each point on the line of constant pressure given by $p=1$ atmosphere between its intersections with the isothermals 0° C. and 4° C. corresponds to two states of the water, or rather, since if the water-substance be converted into ice it will, if cooled sufficiently, again pass through the same range of volumes, each point corresponds to three states and is the intersection of three isothermals; and as a similar remark may be made with respect to neighbouring lines of constant pressure, it follows that there is a region in the plane of pv such that three states of the water-substance correspond to each point within it, and that therefore the values of p and v given by any such point do not define the state of the water.

If, however, from every point in the plane of pv we draw perpendiculars to that plane, proportional to those values of some other property of the water (say, in this case, its temperature) which correspond to the conditions of pressure and volume represented by the points from which they are drawn, the extremities of such ordinates will form a surface which will be met once, or more than once, by any particular ordinate, according as the water can exist under the circumstances of pressure

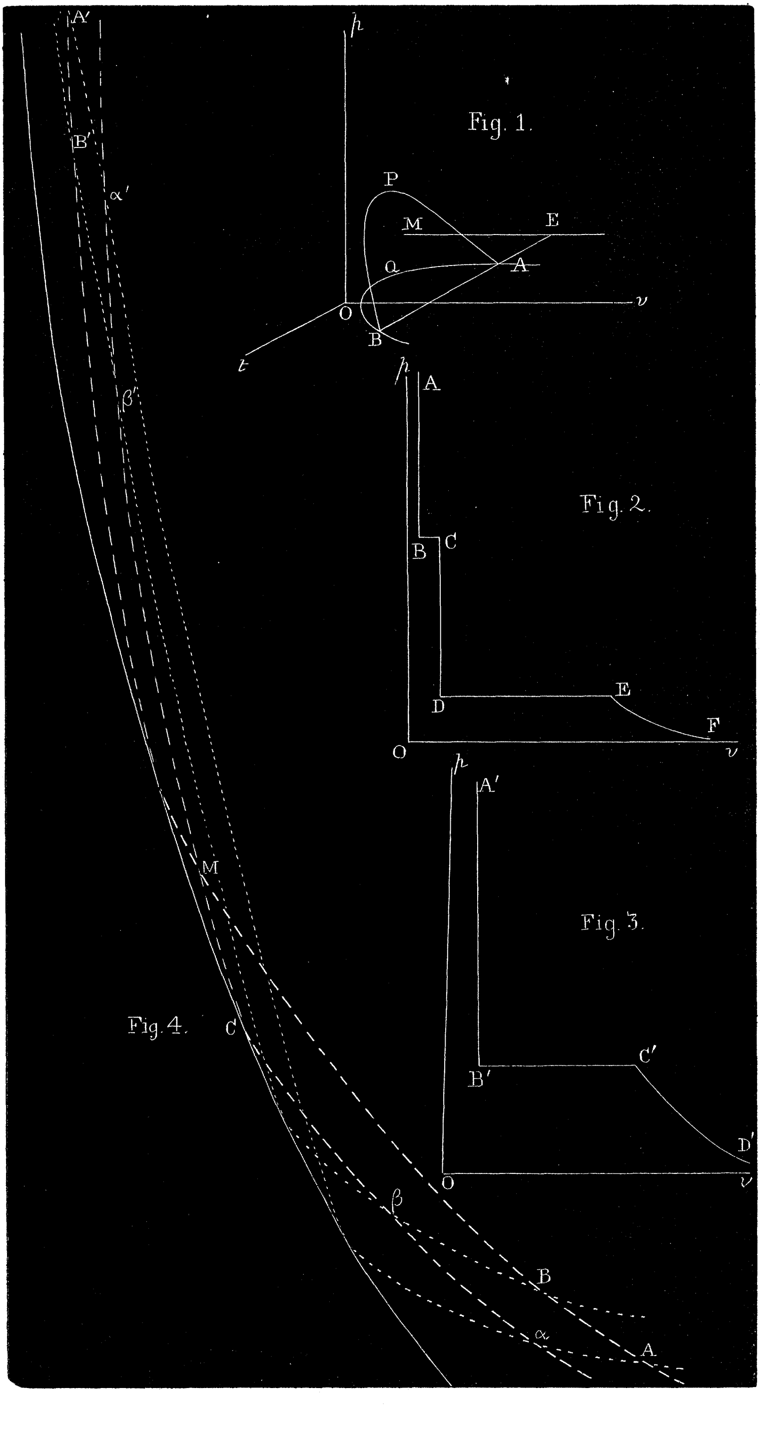
Fig. 1.
p
P
M
E
Q
A
O
v
B
t
Fig. 2.
p
A
B
C
D
E
F
O
v
Fig. 3.
p
A′
B′
C′
D′
O
v
Fig. 4.
A′
B′
α′
β′
M
C
β
B
α
A

and volume defined by the point in the plane of pv from which it is drawn in only one or in several states.

This surface will be represented by the equation

$$f(pvt)=0\ ;$$

and curves may be drawn on it showing the relations between the pressure, volume, and temperature when the state of the water is altered in any determinate manner, the projections on the plane of pv of those represented by the equation to the surface, combined with

$$\left(\frac{df}{dt}\right)=0,$$

forming the boundaries of the region from all points in which ordinates can be drawn parallel to the axis of t which intersect the surface in two or more points. The ordinary adiabatics drawn on the plane of pv are the orthogonal projections of curves on the surface, each of which is defined by the condition that the water in passing through the series of states indicated by its successive points neither gains nor loses heat, and which, to avoid confusion, will be called *complete* adiabatics.

Let now the line LM in the plane of pv (fig. 1) be the line $p=1$ atmosphere. Draw an ordinate from L meeting the surface in A and B; then, if different complete adiabatics pass through A and B, their projections on the plane of pv will intersect; and the only hypothesis on which we can avoid the assumption of the intersection of adiabatics is that the complete adiabatics are the intersections of the characteristic surface $f(pvt)=0$ with cylindrical surfaces, the director curves of which are the plane adiabatics, and the generating lines parallel to the axis of t. In this case the same complete adiabatic would pass through every such pair of points as A and B, which is evidently impossible, as in performing the cycle AQBPA the water would absorb heat along AQB without at any time emitting it, and yet would neither increase its internal energy nor perform any external work, since the cycle projects into a straight line and a discontinuous curve meeting it in only one point. As, therefore, a complete adiabatic cannot pass through A and B, and as a similar train of reasoning would hold for the third point in which AB meets the surface, three adiabatics as well as three isothermals pass through the point on the plane of pv, which is the common projection of these points.

As this conclusion disproves M. Verdet's theorem, we may proceed to consider a few simple propositions based on the hypothesis of the possibility of the intersection of adiabatics; and in so doing it will be advisable to use a new term to distinguish between two classes of points of intersection of the projections on the plane of pv of curves on the surface; and reserving the usual expressions (intersect, cut, meet, &c.) for the projections of points of intersection on the surface, we shall say that two curves *cross* one another when they meet in a point which does not correspond

to any such point of intersection, but is only the common projection of two separate points on the surface.

In the first place, then, we know that if water, starting from an initial state such that addition of heat at constant pressure is accompanied by diminution of volume, be allowed to expand without receiving or emitting heat, its temperature will rise; *i. e.* it will at the same time be doing work, solely at the expense of its internal energy, and rising in temperature—a process which cannot go on indefinitely, as at last all the internal energy would be due to the temperature alone, and any further performance of work would necessarily involve a fall in temperature.

Hence there must be a point of maximum temperature on the complete adiabatic drawn through the point representing the initial state; and the isothermals through all other points on the same curve which lie within the region, in which addition of heat involves contraction, must meet it twice. The projections of these curves will also necessarily intersect in two points; and since when an adiabatic and isothermal meet the tangent to the former always makes the larger acute angle with the axis of v (Maxwell, 'Theory of Heat,' p. 130), it follows that the two curves must also cross at some point between their points of intersection, and will thus form two loops.

This result holds however near the points of intersection may be together; and when they coincide the curves on the characteristic surface touch one another, and their projections on the plane of pv have contact of the second order, since three points, *i. e.* the two points of intersection and the crossing point, are coincident; and, further, the isothermal which thus touches the adiabatic is evidently that which corresponds to the maximum temperature above mentioned; and the point of contact lies on the curve which is the boundary between the regions in which elevation and depression of temperature are respectively the results of compression, for at neighbouring points on the adiabatic the temperature is lowered when the volume is either increased or diminished.

All the points of maximum temperature on the complete adiabatics lie on the curve defined by the condition

$$\left(\frac{df}{dt}\right)=0\,;$$

and since at all points on this curve the tangent planes to the surface are perpendicular to the plane of pv, therefore the projections on that plane of all curves intersecting it touch its projection, because their tangents lie in a plane perpendicular to that of pv, and are projected into one line.

Hence the projection of any curve which meets this curve must at the projection of the point of section touch an adiabatic.

But the ordinary interpretation put upon contact of an odd order with an adiabatic is that the body passing through the cycle of operations

represented by the curve, at the point of contact ceases to emit and begins to absorb heat, or *vice versâ*; and that therefore every closed cycle, if a continuous curve, must have $2n$ points of contact of an odd order with adiabatics, and if a discontinuous curve, $2n-r$ such points of contact and r points of discontinuity at which the curve does not cut the adiabatics passing through them.

This, however, evidently does not hold for a curve which meets the curve in the plane of pv, defined by

$$\left(\frac{dv}{dt}\right)=0,$$

which is the projection of the curve in space, whose equations are

$$f(pvt)=0, \left(\frac{df}{dt}\right)=0.$$

For since it does not follow that the curves in space have contact because their projections touch, we see that the curve in the plane of pv may touch an adiabatic without any change taking place in the absorption or emission of heat; and such a curve may, even if continuous, have contact of an odd order with an odd number of adiabatics. The point of contact, for instance, of a curve which touches but does not intersect the limiting curve at all points on which $\left(\frac{df}{dt}\right)=0$, projects into a point of contact of the third order at least; and therefore the projected curve must lie entirely between the adiabatic and projection of the limiting curve, which only have contact of the first order—*i. e.* it has a single point of contact of an odd order, with an adiabatic which does not correspond to a change in the absorption or emission of heat, and therefore on the whole it has an odd number of points of contact of an odd order with adiabatics.

Let us now suppose that ABB′A′ and $\alpha\beta\beta'\alpha'$ are two adiabatics (fig. 4) which meet the curve $\left(\frac{dv}{dt}\right)=0$, and let two isothermals, $A\alpha\alpha'A'$ and $B\beta\beta'B'$, meet the first in AA′ and BB′ and the second in $\alpha\alpha'$ and $\beta\beta'$ respectively. We can now make the water go through Carnot's cycle of operations between the same temperatures in *four* different ways, of which we need only consider the cycles $\alpha'A'B'\beta'$ and $\alpha'A'B\beta$. In each of these the quantities of heat received along $\alpha'A'$ are the same, therefore the quantities of work done must be the same, *i. e.*

$$\begin{aligned}\text{area } \alpha'A'B'\beta'\alpha' &= \text{area } \alpha'A'B\beta\alpha' \\ &= \text{area } \alpha'A'B'\beta'\alpha' + \text{area } \beta'B'B\beta\beta'; \\ \therefore\ \text{area } \beta'B'B\beta\beta' &= 0.\end{aligned}$$

But this area is composed of the two $B'\beta'M$ and $B\beta M$, and they are of opposite signs; for in going round the closed curve $M\beta'B'M$, the work done on the body is greater than the work done by it, while in the loop $MB\beta M$ the contrary is the case; whence we conclude that the areas $B'\beta'M$ and $B\beta M$ are equal.

In the figure the point β' is represented as further from C than M is; if, however, β' lies between M and C, then the crossing point of the isothermal and adiabatic must be substituted for that of the two adiabatics; and in any case the areas of the two loops formed by two adiabatics and an isothermal which meets each of them twice are equal.

This result will still hold if we suppose that the two points of intersection with one of the adiabatics coincide, *i. e.* that it is that one which has contact of the second order with the isothermal; whence it follows that the areas of the loops formed by any adiabatic and an isothermal which meets it twice are equal; or, in other words, that

If a body perform a cycle of operations which can be represented by an adiabatic and an isothermal, it will on the whole do no useful work.

If we now proceed to consider the shapes of the adiabatics and isothermals of water near their points of section with the curve which is the second boundary between the regions in which addition of heat causes respectively increase and diminution of volume, and which corresponds for any given pressure to a local maximum as that already discussed does to a minimum volume, the applications of several of the above remarks are too obvious to need any special comment; but there is one isothermal the relations of which to the adiabatics which intersect it are of a very complex order, and to which therefore it may be well to draw attention. The isothermals of water may be divided into two classes, according as the pressure corresponding to the freezing-point is or is not less than the maximum tension of aqueous vapour at the given temperature.

As a type of the first we may take the isothermal corresponding to 0° C., which is represented in fig. 2. The maximum tension of steam at this temperature is 4·6 millims.; and as this is less than the pressure at the freezing-point, the vapour will be directly precipitated into ice, which will in turn be converted into water, when the pressure amounts to 760 millims., the solid being thus intermediate between the gaseous and liquid states.

An isothermal of the second class is represented in fig. 3. In this case the vapour is precipitated in the form of water; and as the possibility of the existence of water at the given temperature and pressure proves that the freezing-point for the given pressure is below the temperature proper to the isothermal, and as any further increase of pressure will tend still further to depress it, it is evident that the water-substance can never exist in the solid state at the given temperature unless at very great pressures contraction instead of expansion accompanies solidification. There must, therefore, be some isothermal which is at once the boundary and limiting form of these two classes; and if considered as belonging to the first, it will be that for which the portion CD disappears, *i. e.* for which the pressures corresponding to the freezing- and boiling-points are the same.

The form of this curve will therefore be that of an isothermal of the second class; but for the pressure corresponding to B′C′ the water-substance can exist in all three states; and as the portion of the curve in space corresponding to B′C′ is a line perpendicular to the plane of pt, its projection on that plane is the triple point of Professor James Thomson; and if we assume, with him, that ice, water, and steam can all exist together at the temperature and pressure in question, it follows that this line is both an isothermal and adiabatic; for if we suppose the water-substance to exist at the same time in all three states in a vessel impermeable to heat, we can evidently by diminishing the volume convert some of the steam into water, and employ the heat so set free in melting a portion of the ice, during which operation the state of the mixture will always correspond to a point on B′C′.

Not only, however, is a single adiabatic coincident with the isothermal, but all the adiabatics within certain limits pass through each point on B′C′, and are for a certain distance coincident with it, and therefore with each other; for as the conversion of ice into water is accompanied by contraction, and that of water into steam by expansion, we can keep the volume and pressure of a mixture of ice, water, and steam constant, while, by supplying or subtracting heat, we alter their relative proportions.

The mixture can thus be made to go through Carnot's cycle without any change either in the pressure or temperature, the result always being that no useful work is done; and as in the earlier portion of this paper it has been shown that it is possible for two adiabatics, drawn as plane curves, to intersect, so now we have an instance of the intersection of complete adiabatics, all three variables p, v, and t, to which points on these curves are referred, being insufficient to determine the state of the water-substance along the line B′C′.

It is easy to determine the points at which the adiabatic corresponding to any given mixture enters and leaves B′C′.

Let σ, s, and Σ be the specific volumes of the ice, water, and steam, r and ρ the latent heats of conversion of ice into water and steam respectively, and v the volume of a kilogramme of the water-substance, when the proportions by weight of steam, water, and ice are

$$\xi : x : 1-x-\xi.$$

We have then, as the temperature is constant,

$$dQ = r dx + \rho d\xi,$$

and

$$v = \Sigma\xi + sx + \sigma(1-x-\xi).$$

If no heat is supplied or abstracted,

$$dQ = 0 \text{ and } r(x-x_0) + \rho(\xi-\xi_0) = 0.$$

If we consider x_0 and ξ_0 to belong to the initial state, two cases arise according as

$$\xi_0 \text{ is or is not } > (1-x_0)\frac{r}{\rho},$$

i. e. according as there is or is not enough steam to supply by its condensation a sufficient quantity of heat to melt all the ice; and as

$$\frac{dv}{d\xi}=\Sigma-\sigma-(s-\sigma)\frac{\rho}{r},$$

which is always positive, as $s-\sigma$ is negative, we have the largest and smallest volumes given by the limits

$$x=0 \text{ and } 1-x-\xi=0,$$

or

$$x=0 \text{ and } \xi=0.$$

The maximum volume is therefore in any case given by

$$(\Sigma-\sigma)\frac{rx_0+\rho\xi_0}{\rho}+\sigma,$$

and the minimum volume is

$$(\Sigma-s)\frac{r(1-x_0)-\rho\xi_0}{r-\rho}+s \text{ in the first}$$

and

$$(s-\sigma)\frac{rx_0+\rho\xi_0}{r}+\sigma \text{ in the second case;}$$

and the differences between these quantities give the range of volumes for which the adiabatic belonging to the initial values x_0, ξ_0 coincides with the isothermal.

In conclusion it is only necessary to point out that some of the results in the earlier part of the paper follow immediately from the ordinary formulæ of thermodynamics.

If C_p and C_v are the specific heats at constant pressure and constant volume respectively, and if, to avoid confusion, we write the quantity which is supposed to remain constant as a subscript to a partial differential coefficient, we have the well-known expressions

$$C_v=C_p-AT\left(\frac{dv}{dt}\right)_p\left(\frac{dp}{dt}\right)_v$$

and

$$\left(\frac{dv}{dp}\right)_Q=\frac{C_v}{C_p}\left(\frac{dv}{dp}\right)_t,$$

where Q is constant for any adiabatic. From the first it follows that when $\left(\frac{dv}{dt}\right)=0$,

$$C_v=C_p,$$

and

$$\therefore\left(\frac{dv}{dp}\right)_Q=\left(\frac{dv}{dp}\right)_t,$$

i. e. the adiabatics and isothermals touch one another at points of maximum or minimum volume.

Also by differentiation,

$$\left(\frac{d^2v}{dp^2}\right)_Q=\frac{C_v}{C_p}\left(\frac{d^2v}{dp^2}\right)_t+\frac{d}{dp}\left(\frac{C_v}{C_p}\right)\left(\frac{dv}{dp}\right)_t;$$

whence for all points on the curve $\frac{dv}{dt}=0$, we have

$$\left(\frac{d^2v}{dp^2}\right)_Q=\left(\frac{d^2v}{dp^2}\right)_t,$$

and therefore the contact is of the second order.

P.S. Since the above was written, a paper has been published in the 'Annales de Chimie et de Physique' for March 1874, in which the author, M. J. Moutier, is led, from thermodynamical considerations, to the conclusion that it is impossible for aqueous vapour in contact with ice to have the same tension as when it is in contact with water at the same temperature; and as some conclusions have been pointed out in the preceding pages which follow on the assumption that at the triple point the tension of the vapour is the same in each case, it may be well to show that his arguments do not really touch the question as to which of the two hypotheses is the true one.

M. Moutier discusses the case of a body which can exist in two different states, M and M′, such as the solid and liquid; and supposing that the tension of the vapour is different according as it is in contact with the first or second, he obtains a general formula for the heat of transformation from M to M′, from a consideration of the quantities of heat gained or lost if the body is compelled to undergo a definite series of changes constituting a closed cycle (p. 348).

The second operation in this cycle is that the body M′ passes from the pressure ϖ to the pressure p'; and in the application of the general formula to the case of water, M is taken to represent ice at 0° C., M′ liquid water at the same temperature, ϖ the atmospheric pressure, and p' the tension of aqueous vapour over liquid water at 0° C. (p. 362).

If, however, the symbols have these meanings, the prescribed operation is, in the case of water, impossible; for as water cannot exist at 0° C. in the liquid state at less than the atmospheric pressure, the body M′ would be converted into M as soon as the pressure ϖ was diminished, and no conclusions can be drawn from the cycle in question in the case of water.

M. Moutier employs a second argument which can be shown to have no greater weight than that already discussed, and which may be stated as follows:—

If Q is the latent heat of conversion of ice into water, and L and L′ the latent heats of conversion of ice and water respectively into steam, then at the triple point we must have

$$Q=L-L'.$$

L and L′ are given by the well-known formulæ

$$L=AT(v-u)\frac{dp}{dt},$$

$$L'=AT(v'-u')\frac{dp'}{dt},$$

where u and u' are the specific volumes of ice and water, and $p, p', v,$ and v' the pressures and specific volumes of steam over ice and water respectively.

At the triple point $v=v'$ and $p=p'$; and M. Moutier further assumes that $\frac{dp}{dt}=\frac{dp'}{dt}$, and therefore obtains by substitution

$$Q=AT(u'-u)\frac{dp}{dt};$$

and as $\frac{dp}{dt}$ is positive, being derived from formulæ which have reference to the maximum tension of the vapour, and $u'-u$ is negative, it follows that Q, or the latent heat of water, is negative, a result which shows that some of the premises must be false.

The erroneous assumption, however, is not the possibility of the existence of the triple point, but is contained in the equation

$$\frac{dp}{dt}=\frac{dp'}{dt};$$

for Professor James Thomson has recently shown (Proc. Royal Society, Dec. 11, 1873) that M. Regnault's experiments, on the whole, favour the conclusion, which he draws from theoretical considerations, that

$$\frac{dp}{dt}=1\cdot13\frac{dp'}{dt};$$

and if this equation be true,

$$\begin{aligned} Q &= AT\left\{(v-u)\,1\cdot13-(v-u')\right\}\frac{dp'}{dt} \\ &= AT\left\{0\cdot13v-1\cdot13u+u'\right\}\frac{dp'}{dt}; \end{aligned}$$

whence, as at 0° C., $v=210\cdot66$, while u and u' differ little from 0·001, it is evident that for a temperature so near zero as that of the triple point, the expression within the brackets must be positive, and Q is, as it should be, positive also.

XXI. "Contributions to Terrestrial Magnetism."—No. XIV. By General Sir Edward Sabine, R.A., K.C.B., F.R.S. Received June 18, 1874.

(Abstract.)

This paper is presented by the author as No. XIV. of his "Contributions to Terrestrial Magnetism," completing the magnetic survey of the northern hemisphere (of which No. XIII. comprised the higher latitudes). It consists of a very brief explanatory introduction, followed by Tables, in which (as in No. XIII.) the three magnetic elements are arranged in zones of latitude. These Tables, which form the body of the work, are accompanied by three maps, presenting the results *graphically*, in isogonic, isoclinal, and isodynamic lines.

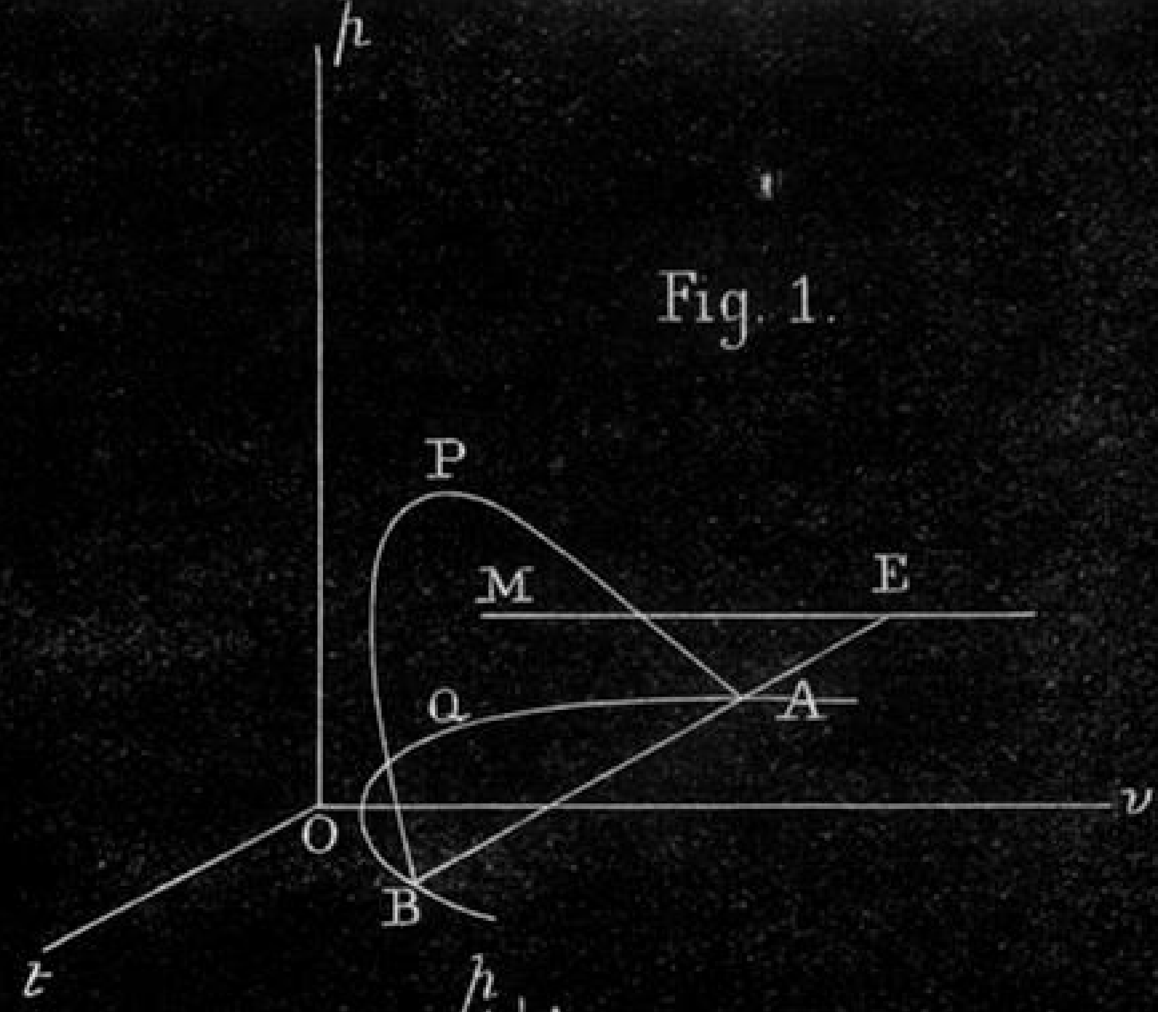

Fig. 1.

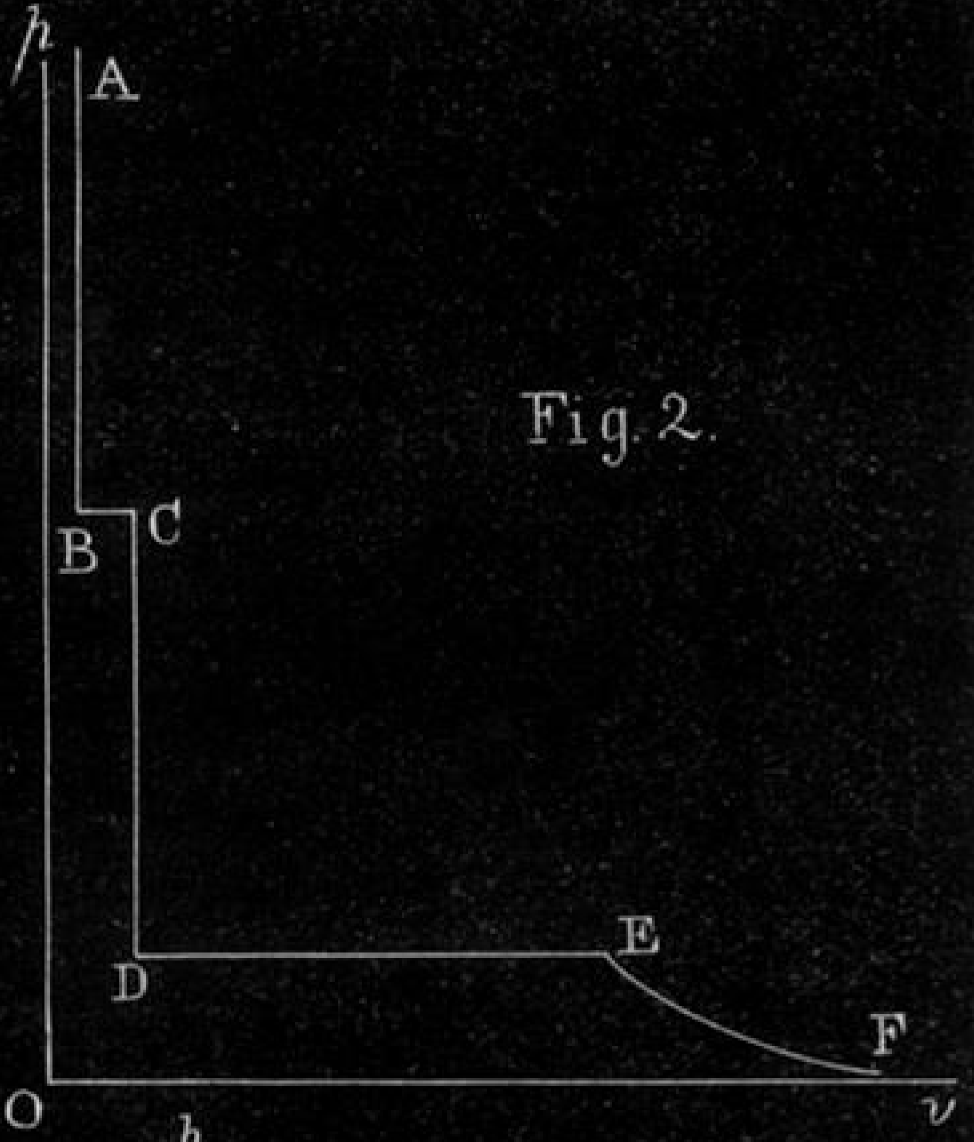

Fig. 2.

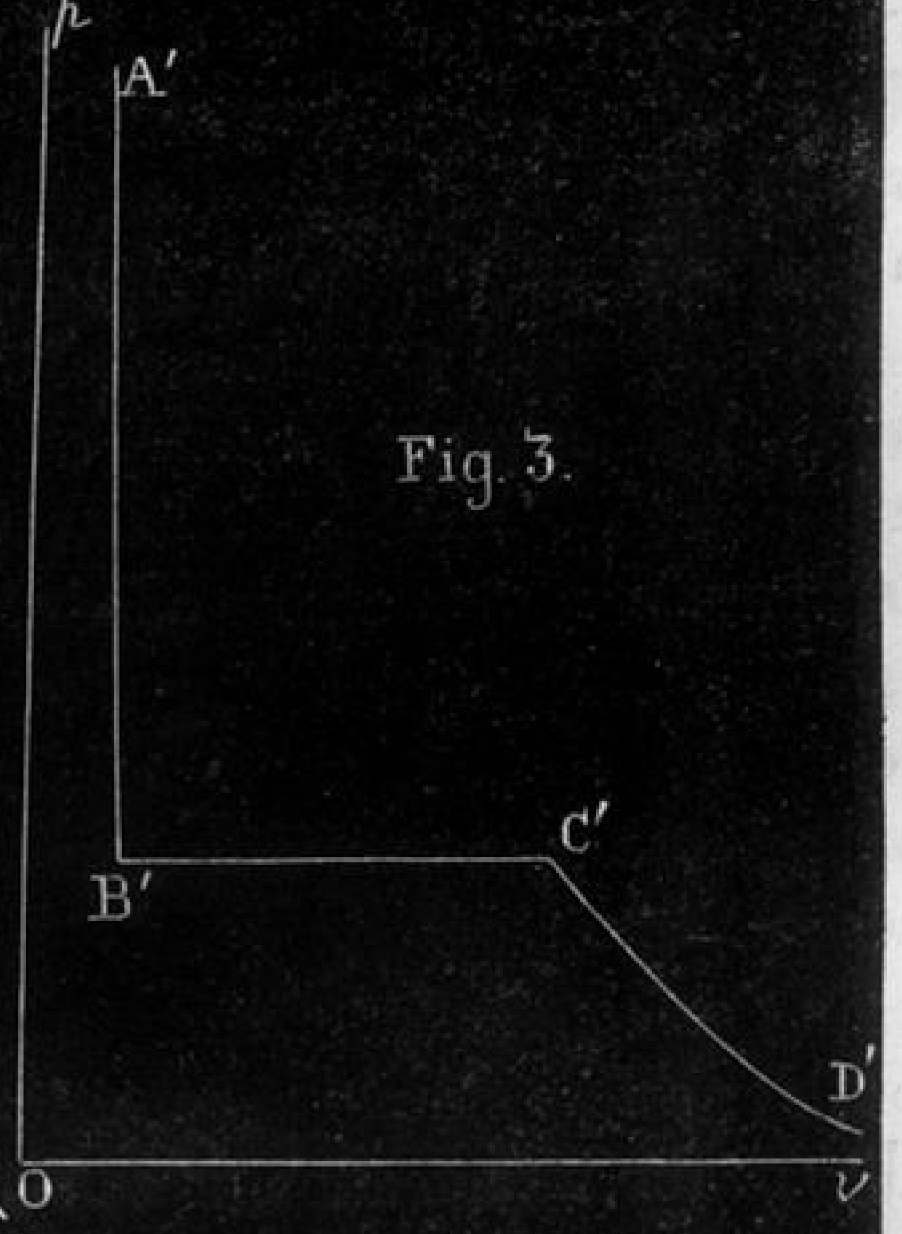

Fig. 3.

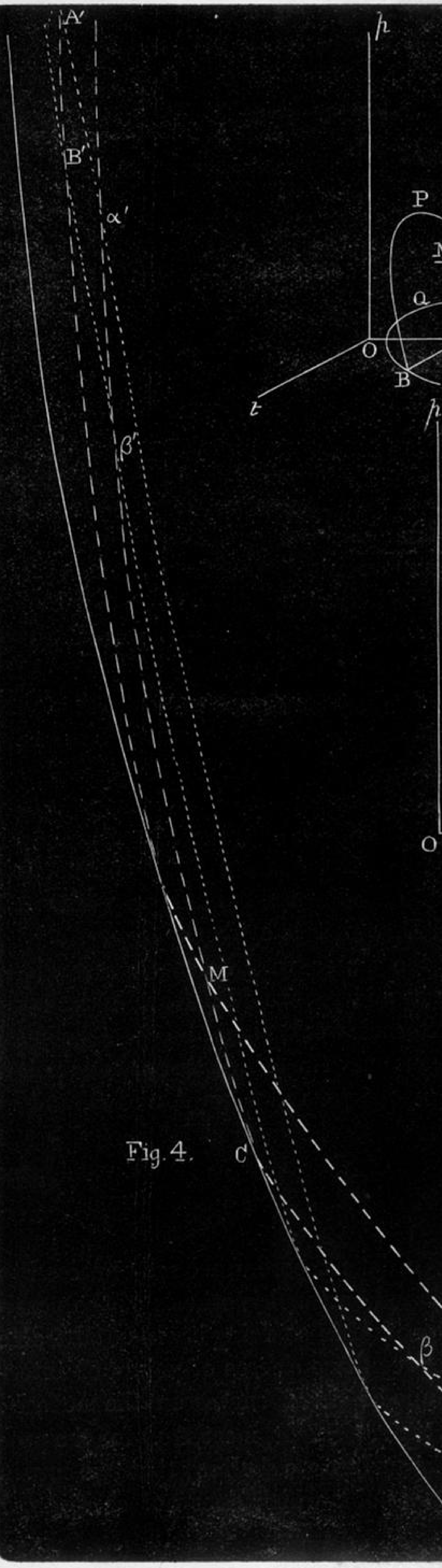

Fig. 4.