A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels

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VII. *A Thermomagnetic Study of the Eutectoid Transition Point of Carbon Steels.*

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1. *Introduction.*

THE manner in which the ferromagnetism of nearly pure iron varies with temperature has been the subject of many investigations; but the corresponding and even more interesting study for steel has been much less complete.   Knowledge of the constituents of iron-carbon alloys, acquired in different ways in recent years, makes it certain that, in the earlier papers upon the change of permeability with temperature, salient features of the thermomagnetic curves have escaped notice. This has happened because of the discontinuous character of the observations upon which the published curves have been based.   An example of the way in which a striking variation may remain undiscovered was given in a paper published by the Physical Society in 1912.*

The experiments described in the present paper were made upon a series of steels containing percentages of carbon varying between 0·15 and 1·53, and our discussion of them is purposely confined to phenomena observed in the neighbourhood of 700° C. It is in this region that one of the most important events in the thermal history of steel occurs.   Here steel containing about 0·9 per cent. of carbon changes during cooling from an apparently homogeneous material into a heterogeneous mixture of two different substances.   One is apparently pure iron and the other is the carbide Fe_3C.   This mixture is the eutectoid.

The same change takes place in steels containing other percentages of carbon; but it is preceded by the separation, at higher temperatures, of the carbide or of iron according as the steel contains more or less than the eutectoid percentage of carbon. In the former—the hyper-eutectoid steels—the eutectoid therefore co-exists below 700° C. with excess of carbide, whilst in the latter—the hypo-eutectoid steels—there

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* 'Proc. Phys. Soc.,' XXV., pp. 77–81.

is excess of iron. During heating the reverse changes take place. The eutectoid transforms first and then the iron or the carbide as the case may be.

Qualitative evidence of these statements is provided by the microscope, and the theory which accounts for them gives rise to the so-called equilibrium diagram based upon thermal observations during cooling. It occurred to us that the thermomagnetic method might throw some useful light upon that part of the equilibrium diagram which relates to the appearance and disappearance of the eutectoid. This opinion was based upon the fact that, for reasons which need not be dwelt upon, when the eutectoid or any portion of it disappears during heating the iron in it should lose practically all its magnetism. Conversely, when the reverse change takes place during cooling, that magnetism should be regained.

2. *Materials Used and Methods of Measurement.*

Most of the specimens of steel examined were cut from materials, described in earlier papers,* which were given to us by Mr. E. A. WRAIGHT and by Prof. J. O. ARNOLD, F.R.S., respectively. The analyses supplied, showing percentages of elements other than iron, were as below :—

No.	C.	Mn.	Si.
1	0·15	0·20	0·09
2	0·36	0·20	0·11
3	0·60	0·21	0·17
4	0·71	0·22	0·17
A	0·85	0·06	0·05
5	1·10	0·23	0·17
S	1·23	0·17	0·15
6	1·53	0·235	0·165

Traces of sulphur and of phosphorus (not exceeding 0·03 per cent. in each case) were also present. As in the paper last cited, the specimens were cut in the form of tubes, each 7 cm. long, of which the external diameter was 5·5 mm. and the internal 3 mm.

The temperature was measured by means of a platinum-rhodium platinum thermocouple, calibrated by means of a platinum thermometer, of which the junction was placed near the centre of the tube under examination. This tube was contained within a copper tube, about 11 cm. long and 1 mm. thick, of very slightly more than 5·5 mm. internal diameter, from which it was separated by very thin strips of mica.

The platinum heating coil was wound bifilarly upon a layer of asbestos paper wrapped round the copper tube. Several thicknesses of asbestos paper were then wrapped over the heating coil, and the resulting cylinder, about 15 cm. long, was

* 'Proc. Phys. Soc.,' XXIV., pp. 62–69, and pp. 342–349, 1911.

pushed into an outer copper tube of similar length, about 2 cm. in diameter. This latter tube was supported within the magnetising solenoid by means of further layers of asbestos paper wrapped round it loosely.

Experience showed that this arrangement gave a nearly uniform temperature throughout the specimen for different steady currents in the heating coil. To obtain the maximum degree of uniformity the rods might have been made shorter, but they were required for other experiments in which their length was of consequence. Moreover, our object was rather to compare the temperatures at which certain changes took place in the different steels than to find with extreme accuracy the absolute values of these temperatures.

The rods occupied successively almost exactly the same position in the furnace and the thermocouple was so mounted, in a small porcelain tube, that its junction when in use was at a fixed distance from the end of the specimen.

The magnetic measurements were made by means of a sensitive and suitably damped quartz-fibre magnetometer provided with the usual compensating arrangements.

The data necessary for the deduction of the intensity of magnetisation from the scale-readings were recorded; but the magnetisation is expressed arbitrarily in terms of these scale-readings only, in order to avoid laborious reductions which would have added little to the value of the conclusions drawn.

The coefficient of self-demagnetisation of the "rods" (roughly 0.09) was determined by comparing the magnetising solenoid fields required to produce given intensities of magnetisation in the 0.85 per cent. rod with those required to produce equal intensities in a ring of the same steel. For the present purpose, however, it is sufficient to give only the fields due to the solenoid and not the effective fields within the rods.

The procedure in the first series of experiments was as follows. Each of the alloys in turn was placed in the magnetising solenoid. It was demagnetised and a current of 1 ampere, producing a field of approximately 50 C.G.S. units, was then passed through the solenoid. This current was kept constant while the temperature of the specimen was varied. The latter was raised slowly from air temperature to about 850° C. in each case and then slowly lowered. Corresponding readings of deflection and temperature were taken over the whole range as the temperature rose and fell. The results obtained at temperatures above 660° C., which are all that are required for our present purpose, are collected in figs. 1 and 4. The former contains the observations made during heating: the latter those made during cooling. The observations for the different alloys are denoted by different signs according to the scheme shown on the figures.

The scale of the ordinates differs from one alloy to another. The distances of the different specimens from the magnetometer were unequal, being such that all of them gave approximately the same deflection at the air temperature before heating began.

The figures include, for comparison, results obtained with a rod of nearly pure iron of the same size as the others and examined in the same way. For this specimen the

heating and cooling curves very nearly coincide above 700° C.   The slight difference (exhibited in fig. 1 which contains the cooling curve above 730° C. for the iron as well as its heating curve) is no doubt due partly to a slight excess of the temperature of the thermocouple during cooling and to a slight defect during heating—not amounting to

Fig. 1.
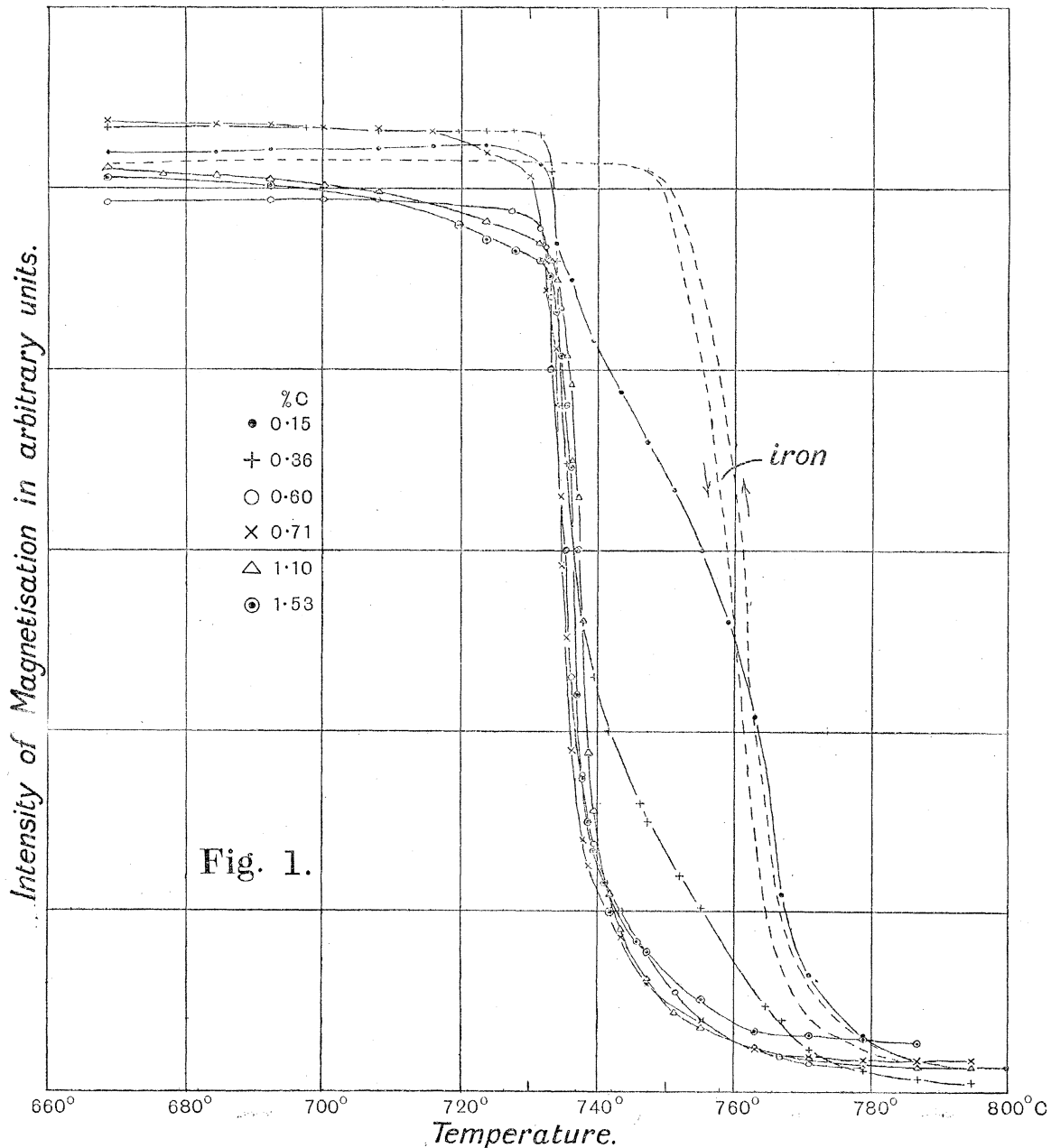
more than 1° C. in either case—compared with that of the specimen.   The temperature was not altered quite as slowly in this case as in the others ; but the observations serve to indicate the magnitude of the error which may arise owing to a temperature gradient between the thermocouple and the specimen.

The differences between the final ordinates seen in fig. 1 are due merely to differences in the zero readings of the magnetometer in the different experiments, the ordinates plotted being the actual scale-readings in each case.

3. *Comparison of Heating Curves.*

The heating curves for the alloys have one feature in common. With so many curves superposed, in order to economise space, this feature is not perhaps brought out with the maximum of clearness in fig. 1. But it can be seen that a drop in the magnetism begins in all the steels at about the same temperature. Actually this temperature is the same within one or two degrees. It is usually quite sharply marked. For example, the thermocouple temperature was kept steady for several minutes at 733° C., in one case, without alteration in the magnetometer deflection which differed very little from that at 730° C. The furnace temperature was then raised very slightly, and, before the thermocouple registered 734° C., a rapid fall of magnetisation set in.

This fall is absent or imperceptibly small in the iron curve and is smallest in that for the steel weakest in carbon. Its relative magnitude increases with the percentage of carbon, as fig. 1 shows, until the specimen containing 0·7 per cent. of carbon is reached. After that, it is difficult to decide whether the ratio of the rapid fall (below 740° C.) to the subsequent fall, before the magnetisation becomes too small to be measurable, depends appreciably upon the percentage of carbon.

The first important fact, then, is that the sudden loss of magnetism begins at the same temperature in all the steels. This accords with the view that the eutectoid patches, detected by the microscope, have always the same composition. It might also suggest that this constant temperature is the true transition point between eutectoid and homogeneous solid solution.

That this inference would be wrong may be shown in two different ways. Fig. 2 shows one. The curves relate to successive interrupted heatings, of a steel containing 0·85 per cent. of carbon, described later.* At the moment it is only necessary to call attention to the descending branches of the different curves. It will be noticed that two (Nos. 4 and 5) proceed vertically downwards and one (No. 2) slopes slightly outwards from left to right. The significant one, for the present purpose, slopes inwards, *i.e.* towards the left. It (No. 3) was obtained with the most gradual rate of heating and shows that the transition continues at a lower temperature than that at which it began.

This is a case of a phenomenon which is the converse of recalescence. In the latter the material is self-warming. Here it is self-cooling. The effect is not very pronounced and might, at first sight, be attributed to irregularities of heating; but the inference that it is due to lag can be justified in another way. This is shown in fig. 3.

* See § 18. Fig. 2 is printed on p. 199.

Here the heating was interrupted (twice) before the "solution" of the eutectoid was complete.   Cooling was continued until most of the eutectoid had reappeared; but heating was begun again while some dissolved eutectoid still remained.   Now, the

Fig. 3.
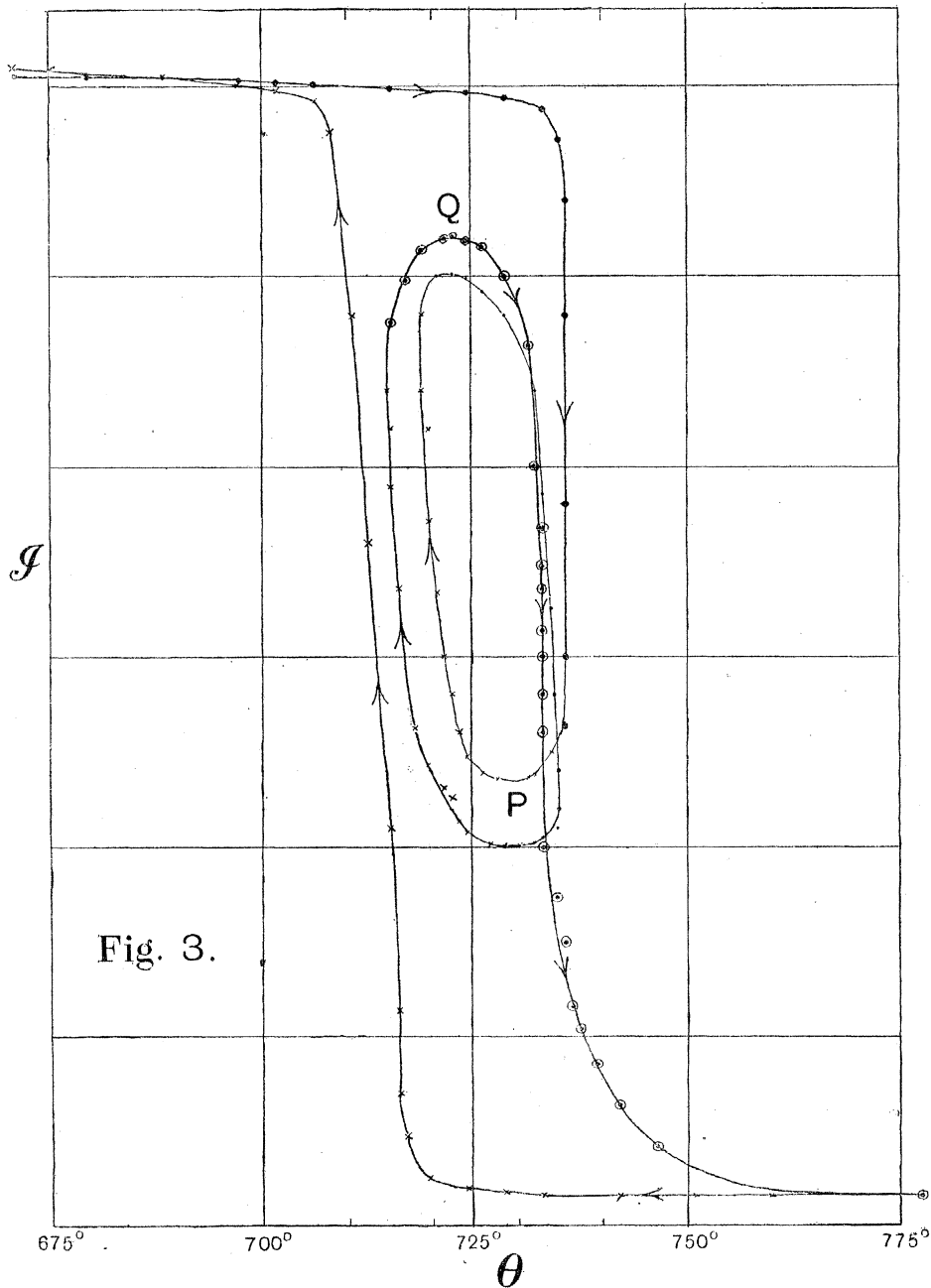
loss of magnetism took place, slowly at first and then rapidly, all at a temperature below that at which it began when none of the transformed material was present.

If the true equilibrium temperature be that at which iron, carbide of iron, and solid solution of eutectoid composition can coexist for an indefinite time in the steel without change, it follows from what precedes that this temperature is below 735° C.

Consideration of the results shown in fig. 3 makes it also reasonable to suppose that the equilibrium temperature is below 730° C., the temperature at which (point P) the magnetism reaches a minimum during cooling from 735° C. ; but that it is above

Fig. 4.
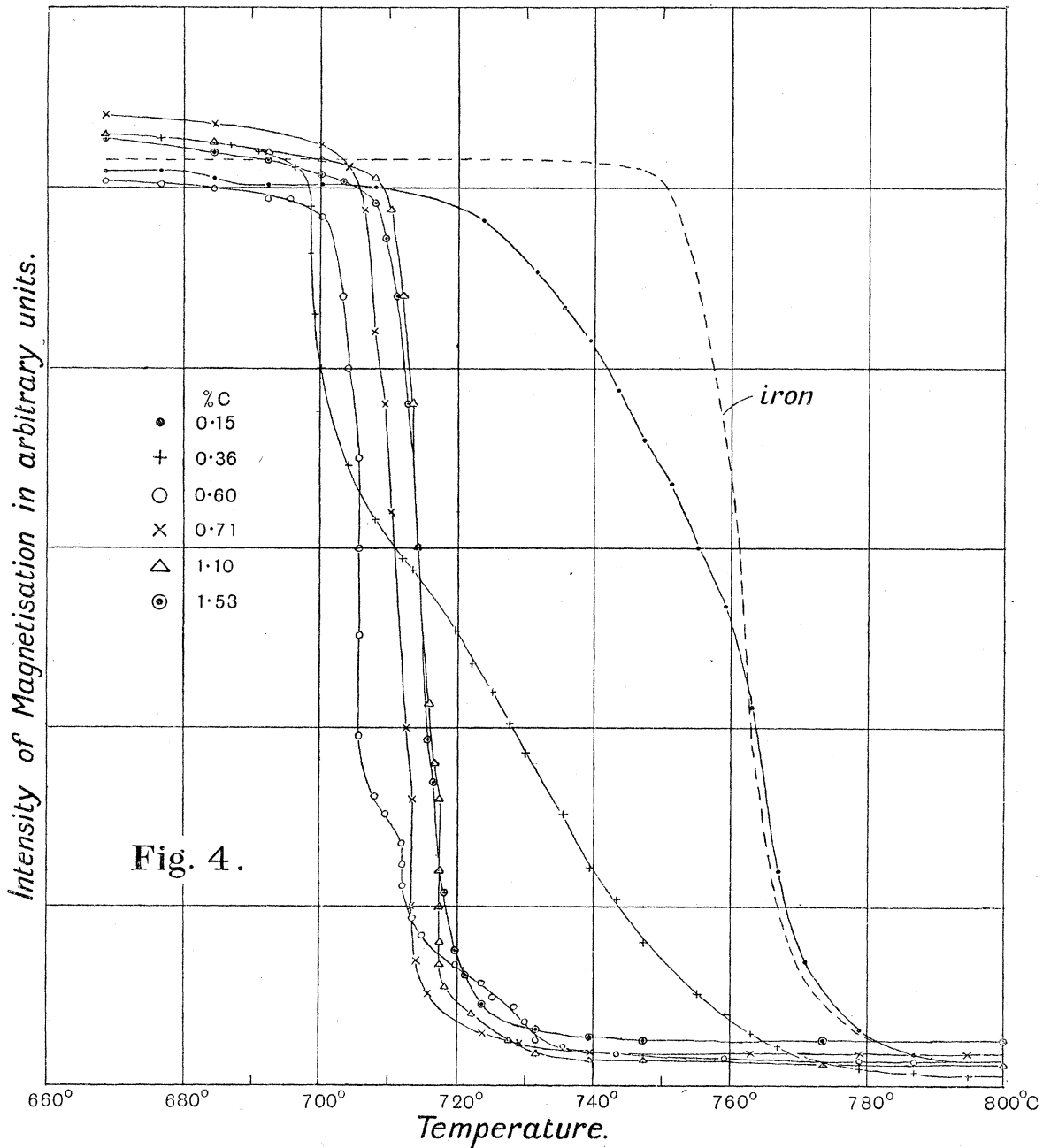
723° C., the temperature at which (point Q) the magnetisation reaches a maximum during subsequent re-heating. If so, we have a thermomagnetic method of determining the equilibrium temperature within two or three degrees as the figure shows.

This point is examined more closely later on.

4. *Comparison of Cooling Curves.*

Turning now to the results obtained during continuous cooling, collected in fig. 4, it will be seen that the temperature of rapid return of magnetism in the eutectoid is no longer constant except perhaps in the hyper-eutectoid steels. In the hypo-eutectoid steels, the temperature of rapid return appears to become continuously lower as the percentage of carbon falls. Although this is true in general, it would appear (from the present and other observations) that the behaviour of the different steels is not quite as regular during cooling as during heating.

The conditions under which the eutectoid forms during cooling are therefore apparently less simple than those under which it dissolves during heating.

Apart from surface phenomena, which probably exert an appreciable retarding influence during heating as well as during cooling, it is important to remember that whereas the transformation of the eutectoid precedes that of the excess iron during heating the opposite is true during cooling.

Since the solution expands when it changes into the eutectoid (with evolution of heat) it is easy to see that, especially in the alloys weak in carbon, the pressure exerted during the transformation, by the enveloping excess iron, may be a cause of retardation which is present during cooling but is absent during heating.

Experimental evidence concerning the retarding forces operating during cooling is given below.

5. *Comparison of Results Obtained in Different Fields with the 0·15 per cent. Carbon Steel.*

In the experiments which have been described the specimens were submitted continuously to a constant field of 50 C.G.S. units.

Fig. 5* shows the behaviour of the 0·15 per cent. carbon steel in similarly applied, but weaker and stronger, fields of about 25 C.G.S. and 200 C.G.S. respectively.

The ordinates represent intensities of magnetisation, in arbitrary units, as before. The scales for the two fields are, however, very different. Thus the intensity of magnetisation in C.G.S. units at 680° C. was actually about 13 times greater in the stronger field than in the weaker.

Observations taken during cooling are represented by crosses in each case.

The effects, upon the magnetisation-temperature curve, of loss and gain of magnetisability of the eutectoid component of the steel are much less pronounced in the field of 25 units than they were in the field of 50 units. For example, the return of magnetisation near 700° C. is now only just perceptible.

* In order to exhibit the parallelism between the time-temperature ("inverse rate") method of determining the eutectoid point and the thermomagnetic method, fig. 5 includes curves showing how the rate of variation of the intensity of magnetisation $\mathscr{J}$ with respect to the temperature θ depends upon the value of θ. The ordinates represent differences between values of $\mathscr{J}$ (in arbitrary units) measured at intervals of 4°·5 C.

In the stronger field however, the effect of the return of magnetisability, at the same temperature, is much more pronounced than in the earlier experiments.

Fig. 5.
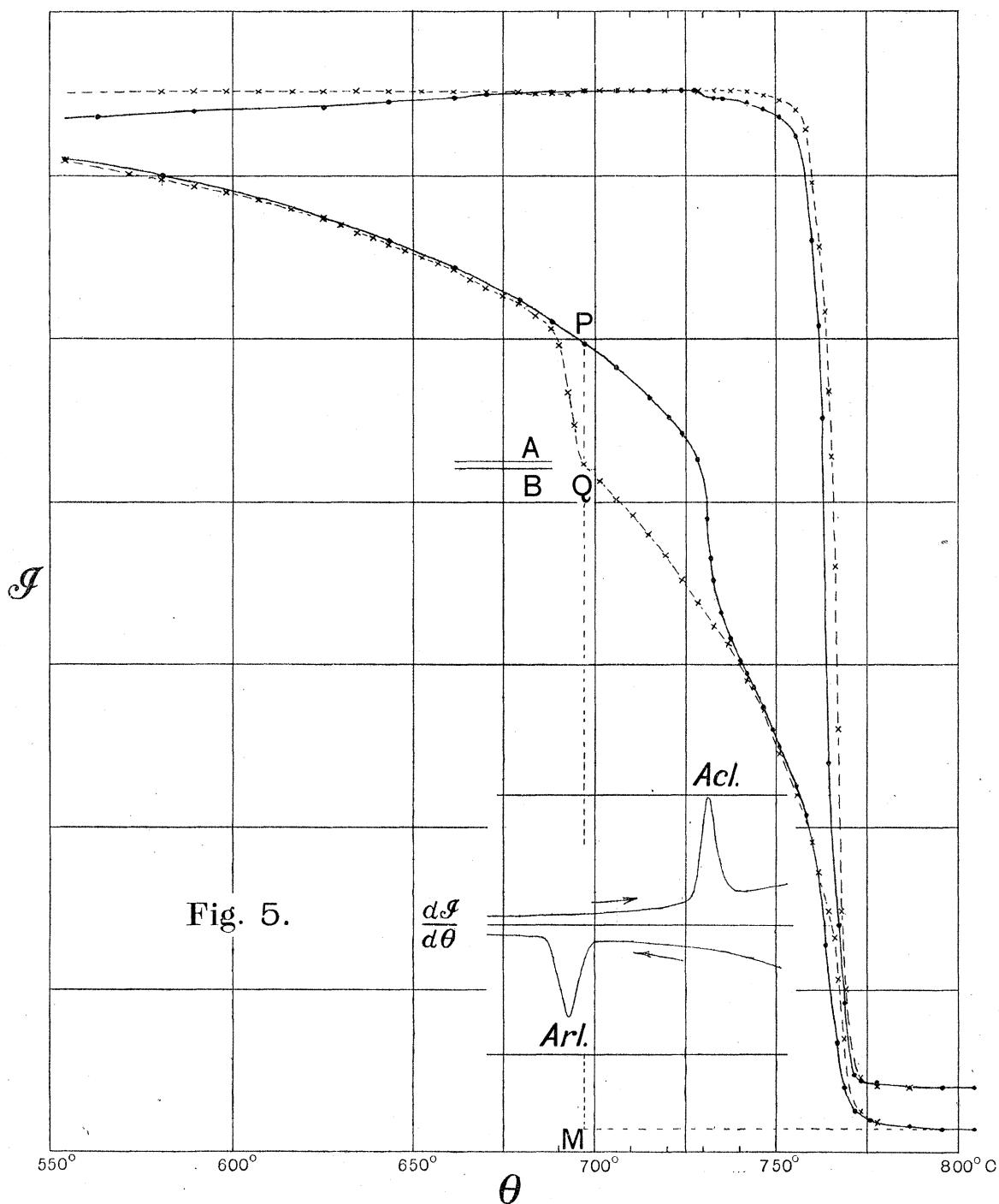
These differences are no doubt due to the fact that in weak fields the susceptibility of the iron in the eutectoid is much smaller compared with that of the excess iron than it is in strong fields.

The contribution of the carbide to the magnetisability of the material need not be considered at high temperatures because it is known that it is relatively very feeble above 250° C.*

6. *Elimination of Hysteresis in Strong Fields.*

Another significant difference between the curves in weak and strong fields is observable, particularly below 690° C.

In the former, the falling temperature observations lie increasingly above those for rising temperatures as the temperature is reduced; in the latter, the corresponding observations practically coincide. This difference is no doubt an effect of the same cause as that to which ordinary magnetic hysteresis is due, namely, the existence of various molecular groupings which make alignment difficult in weak fields but which are broken up when intense fields are applied.

Weak fields, although increasingly aided by thermal agitation as the temperature rises, are unable during heating to break up all of these molecular groupings. But the magnetism reappears during cooling in a medium in which, after heating to a high temperature, the molecular groupings are less extensive than before. Hence a greater intensity of magnetisation will now tend to arise under the same field as before, because the force required to maintain a given degree of alignment is less than that required to induce it against already existing groupings.†

In strong fields, on the other hand, the resistance to alignment is determined mainly by the thermal agitation. This is the same at a given temperature whether that is approached from above or below. Consequently the coincidence of the heating and cooling curves in the field of 200 C.G.S. units, except over the region where the lag in the transformation of the eutectoid occurs, is an indication that the observations taken continuously in this field are practically free from the effects of hysteresis. This means that they are practically the same as they would have been if the material had been demagnetised between successive applications, at different temperatures, of the field in question.

It therefore appeared that it would be possible to make quantitative use of curves obtained in strong fields in the way indicated below.

7. *A Method of Estimating the Percentage Composition of the Eutectoid.*

Considering fig. 5, we may suppose that the contribution of the iron in the eutectoid, to the total magnetisation at 697° C. during heating, is represented by the distance between the point P on the upper curve at that temperature and the corresponding point Q on the lower curve at the same temperature. In the one case the eutectoid has not yet begun to lose its magnetism; in the other it is just about to regain it.

* *Loc. cit.* XXIV., p. 63, 1911.

† Such considerations are accentuated by the fact that, although the solenoidal field remains constant, the field within the specimen increases as its magnetisation falls.

We may assume tentatively that the intercept PQ is a measure of the amount of iron in the eutectoid and that, similarly, the intercept QM is a measure of the amount of excess iron. The ratio of these two, QM/PQ, can then be compared with the calculated ratio of the excess iron to the eutectoid iron.

If we assume that the eutectoid contains e per cent. of carbon, then in a steel containing c per cent. of carbon, the ratio of the amount of excess iron to that associated with the carbide in the eutectoid is

$$100\,(e-c)/c\,(100-15e).$$

The value of e is not very accurately known. It probably lies between 0·85 and 0·9. Accordingly in a steel containing 0·15 per cent. of carbon, the calculated ratio lies between 5·35 and 5·78.

The two horizontal lines A and B, near Q in the figure, are at distances above M such that the upper one produced would divide PM in the ratio 5·78 : 1, whilst the lower one would divide it in the ratio 5·35 : 1.

It appears, therefore, from the experimental position of Q, that, within the limits of error, the contribution of the eutectoid to the total magnetism corresponds with the amount of iron which it contains. Viewing this result from the opposite standpoint it will be seen that, if we accept it, we obtain a thermomagnetic method of determining the composition of the eutectoid.

In anticipating such a method the only question was as to how intense the field would require to be in order that the computation might be made with useful accuracy. Here we could only foresee that the steels would be relatively soft magnetically at temperatures near 700° C., and that fields of moderate strength might suffice to produce the necessary approach towards saturation.

The possibility of error in moderately strong fields, owing to the shortness of the specimen, must of course be borne in mind. For, although the solenoidal field is kept constant, the field within the specimen will vary appreciably with the intensity of magnetisation. In the present case the intensity of magnetisation of the specimen, at the point P, was about 720 C.G.S. units; while, at the point Q, it was about 600 units.

Assuming a constant demagnetisation coefficient (independent of the distribution of magnetic material within the specimen) of about 0·09, the demagnetising fields in the two cases would be about 65 and 54 C.G.S. units respectively. Thus the effective fields at P and Q would differ by 11 units, being 135 and 146 C.G.S. respectively, and the comparison made above upon the assumption of their equality would require a correction for this difference.

The correction required is apparently small. It would of course become negligible if very strong fields were used. As a step in this direction, we attempted to obtain curves with a magnetising field of 400 C.G.S. We found, however, that the compensation between the magnetising solenoid and the particular balancing coil used

could not be maintained satisfactorily when large currents were passed through them
and were obliged to postpone further experiments in this direction.

8. *An Attempt to Apply the Method to Steels Richer in Carbon.*

It seemed worth while, however, to examine some of the other steels in the field of
200 C.G.S. units in the same way. Figs. 6 and 7 show the results of experiments

Fig. 6.
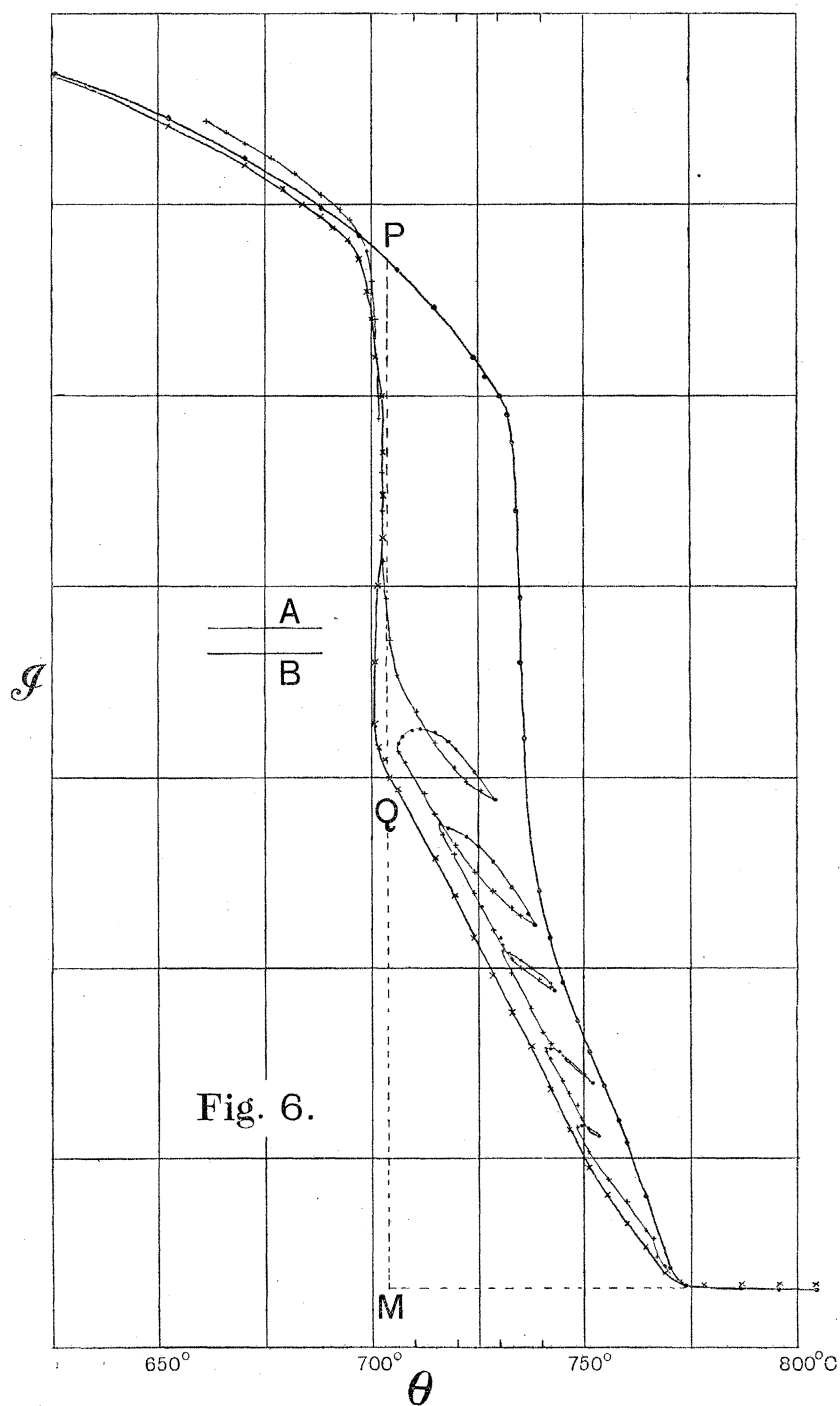
made upon the 0·36 and 0·60 per cent. steels. The thicker-lined curves were obtained during uninterrupted heating and cooling as in fig. 5. The letters P, Q, M and the lines A and B have the same significance as before.

It will be seen at once that the point Q no longer occupies the position calculated for it on the assumption that MQ should represent the contribution of the excess iron,

Fig. 7.
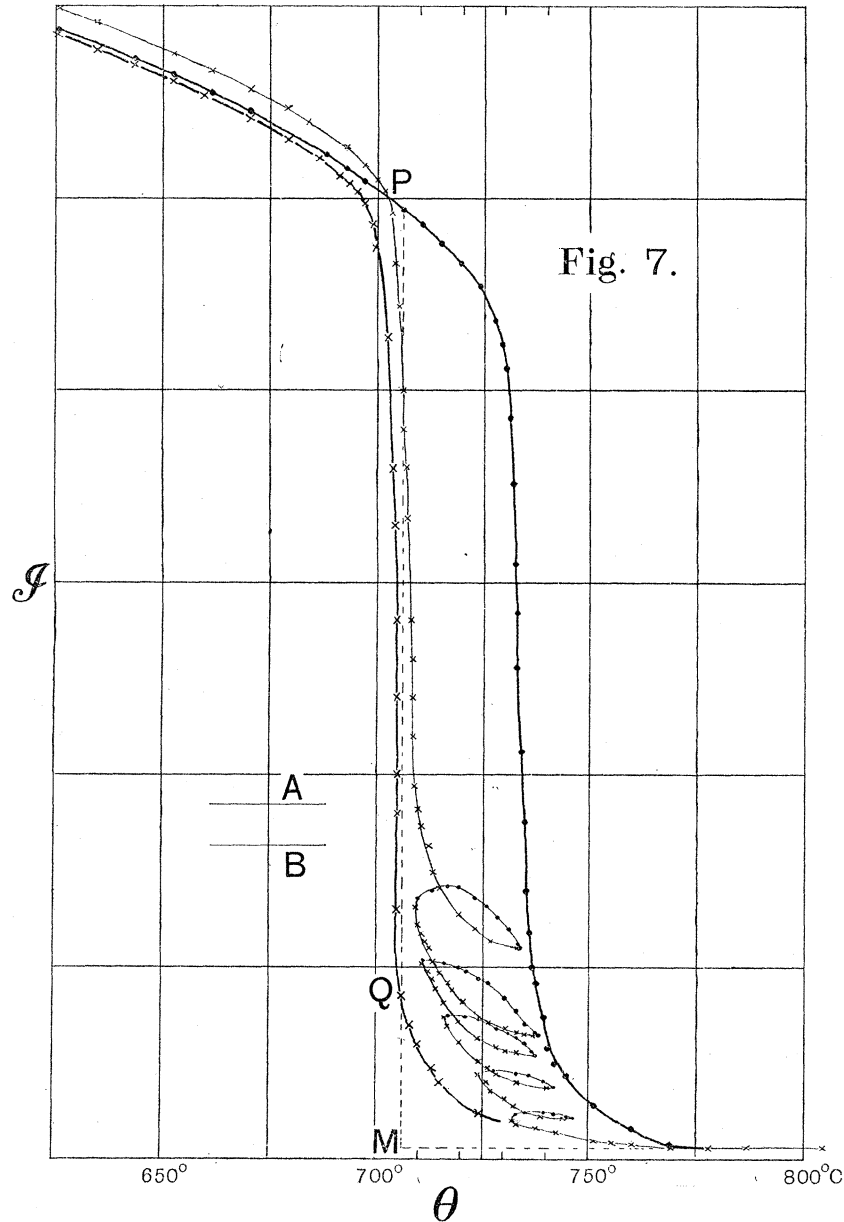
and QP that of the eutectoid iron to the total magnetisation MP. In each case the eutectoid iron appears to contribute more than its calculated share to the total magnetisation. The apparent excess is very marked in the 0·60 per cent. steel.

The error due to the shortness of the specimen, already mentioned, would increase with the percentage of carbon, and would be much more important in the 0·60

per cent. steel than in that first considered on account of the greater difference between the ordinates MP and MQ. But the discrepancy between the calculated and observed values cannot be ascribed to this cause alone if we assume a constant demagnetising coefficient as before. For, in that case, it would appear that the calculated position of Q should be below, not above, that observed.

It is not impossible, however, that the demagnetising coefficient is greater when the material is in the state corresponding with Q than when the rod is more completely magnetic. Under such circumstances the difference between the demagnetising fields would be less than a calculation like that in § 7 would give.

Apart from such uncertainties, which only observations in very strong fields could remove, there are reasons why, even in the strongest fields, the calculated position of Q should, as in figs. 6 and 7, be higher than that observed.

To make these reasons clear, it is necessary to consider the conditions under which the eutectoid forms in the different alloys.

9. *The Effects of Incomplete Equilibrium Arising out of the Slowness of Diffusion.*

Suppose that the cooling alloy contains c per cent. of carbon, where c is less than the eutectoid percentage e. We need consider only the changes which occur below 900° C. At some temperature between this and the eutectoid temperature, which is lower the greater c is, iron "crystals" (easily magnetisable below about 780° C.) begin to separate from the homogeneous "solid solution" of iron and carbide.

As the temperature falls these crystals grow, and simultaneously the remaining solution becomes richer in carbide.

The conditions of equilibrium at any temperature θ require that the solid solution in immediate contact with the separated iron crystals should contain a percentage of carbon c_θ which is a definite function of θ, intermediate between c and e, increasing in magnitude as the temperature falls.

The separated iron crystals grow around nuclei distributed throughout the solid solution and their growth gradually restricts the regions within which the carbide is contained. But it will be noticed that the concentration of the carbide within these regions is not necessarily uniform. It is c_θ where contact with the separated crystals of iron occurs; but it is only by diffusion inwards from the contact layers that the concentration in carbide can rise throughout the rest of the solution. Simultaneously with this diffusion, the crystals of separated iron grow.

Thus we see that, unless we suppose a continuous separation of fresh nuclei as the temperature falls (which surface effects tend to prevent), the rate of crystallisation of the iron (and of rise in concentration of carbide in the solution remaining) depends very largely upon the rate of diffusion of the carbide within the solid solution.

Thus also, we see that the amount of iron which has separated at any given

temperature tends always to be less than the amount which would be present if the solution had the uniform concentration corresponding with complete equilibrium.

The calculated fraction of the whole mass which deposits as eutectoid being c/e, it follows that when c is small the amount of solid solution remaining when the eutectoid temperature is approached is also small.

Consequently, the effects arising out of the comparative slowness of diffusion are not likely to be considerable. But when c is larger, these effects may become important. We shall then have comparatively thick layers of solid solution just above the eutectoid point, and there may be an appreciable difference of concentration between their centres and their surfaces.

As the temperature falls, however, the surface concentrations rise and the layers become thinner. Each of these effects tends to increase the concentration gradients from the surface inwards. Hence the diffusion tends to accelerate. This acceleration will be maintained because the iron crystals will grow and maintain the surface concentration of the carbide in solution as the layers thin down. Hence the transformation of the last of the pre-eutectoid iron will be rapid and difficult to distinguish thermomagnetically from that of the eutectoid.

Such considerations enable us to see that the amount of magnetisation acquired after Q in the figures is passed may easily be greater than corresponds with the amount of iron contained in the eutectoid.

10. *Experimental Evidence of the Effects of Diffusion.*

In order to confirm the existence of incomplete equilibrium of the kind pictured above, we performed the experiments indicated by the thinner-lined curves of figs. 6 and 7.

Instead of allowing the temperature of the material to fall continuously as before, the cooling was now interrupted repeatedly. After each interruption the temperature was slowly raised some 10 or 20 degrees, and then allowed to fall slowly to a point below that at which the interruption took place. This process was repeated several times in each steel as shown in the curves.

It will be obvious at once that the general result of every interruption and re-heat is to add to the amount of magnetisation shown by the steel when the temperature of interruption is regained.

Each cycle of temperature change tends to reduce the concentration differences within the solid solution and to make the amount of iron set free correspond more nearly with that required for complete equilibrium. It thus becomes possible to distinguish more clearly between the real contribution of the excess iron and that of the eutectoid iron to the magnetism of the material as a whole.

From the positions of the lines A and B with respect to the "interrupted" curves, it will be seen that there is no reason to doubt (1) that in these steels, as in that of

fig. 5, the contribution of the eutectoid to the total magnetisation, at say 700° C., indicates the amount of iron which it contains, (2) that the eutectoid mixture has the same composition in all the steels.

It is instructive to consider in detail the forms of the thermal hysteresis loops and connecting curves shown in the figures, and to examine their significance with respect to the sequence of changes within the material; but considerations of space do not permit further reference to this here.

11. *Evidence of the Relative Unimportance of the Effects of Diffusion in Low-carbon Steel.*

We proceed to describe further experiments of which the results are shown in fig. 8. These were made upon a steel containing about 0·1 per cent. of carbon. Their object was to test the inference, from a comparison of fig. 5 with figs. 6 and 7, that the effects of the slowness of diffusion are relatively unimportant when the layers of solid solution from which the eutectoid is about to separate are relatively thin. In the present case the eutectoid patches form about one-ninth part only of the total mass of the steel.

The thicker-lined curves represent, as before, the results obtained during continuous slow heating and cooling. The heating was stopped at about 815° C. The equilibrium diagram indicates that, at this temperature, the solution in contact with the still undissolved iron contains roughly 0·3 per cent. of carbon. The patches of transformed eutectoid are therefore bordered by layers in which the concentration of carbon drops to about 0·3 per cent.

During cooling the iron in these border layers separates out again from the surface inwards, the surface concentration rising continuously from 0·3 per cent. towards the eutectoid percentage as the temperature falls. The re-crystallising iron closes in upon the layers of solid solution; but the re-precipitation of the excess iron is not quite complete at the temperature at which it begins to dissolve during heating. For it will be observed that the cooling curve RS rises slightly, but distinctly, more rapidly than the heating curve PQ falls, and therefore that, if we assume no solution of iron along PQ, we must suppose some precipitation along RS.

It is easy to see, as before, how this effect may arise; but it is also easy to show how much less pronounced it is in the present case. To do this, we repeated the experiment, but interrupted the cooling at various temperatures between R and S, as in the experiments of figs. 6 and 7.

The results are shown in the centre fig. 8. For the sake of clearness, we have displaced the observed ordinates downwards. Their true positions are to be found by raising all of them through the distance between the lower AB and the upper. It will be observed that the effects of alternation during cooling, although perceptible, are now very slight, compared with those of figs. 6 and 7, until the temperature at which the eutectoid appeared during continuous cooling is approached.
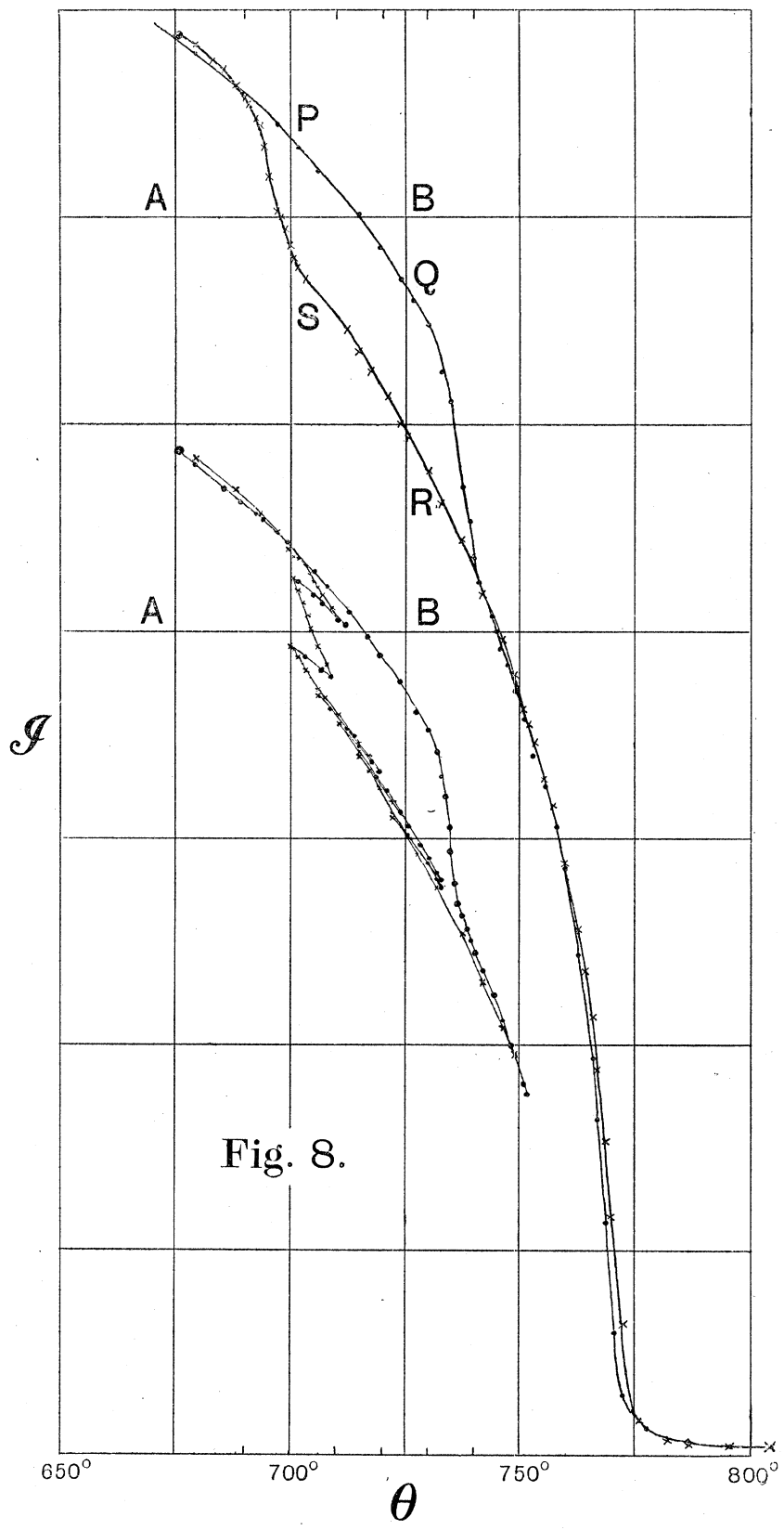
Fig. 8.

The loops significant of the pronounced effects of concentration gradients are now absent.

12. *Possible Evidence of the Effects of Pressure.*

The effects of alternation begun just above the temperature at which the eutectoid previously made its appearance are noteworthy.

It will be observed that this alternation is sufficient to induce practically the whole of the eutectoid change at a temperature higher than that at which, in its absence, the transformation appeared to begin.

It seems to us most natural to explain this phenomenon by supposing that the transformation of the eutectoid is retarded by the existence of internal pressure.

On this view the eutectoid would form at a higher temperature than that at which it ordinarily appears were it not for the expansion which accompanies the transformation and causes pressure to be exerted by the surrounding envelope of iron immediately after it begins. This pressure cannot increase without limit. The separation of the eutectoid in bulk begins when the increase in pressure, required to prevent further transformation as the temperature falls, cannot be supplied. The effective transition point will thus depend upon the elastic properties of the enveloping iron.

If, as is likely, the capacity to resist strain is reduced when the temperature is raised, the transition should simultaneously be facilitated. Fig. 8 shows that what happens is as if a very slight elevation of temperature at the critical stage induces that amount of breakdown in the envelope which is necessary before the eutectoid can appear in bulk.

## 13. *Evidence of the Existence of other Effects.*

It is apparent that effects of pressure of the kind just contemplated would decrease along with the amount of free iron present beforehand, and would therefore become less important as the percentage of carbon in the steel rose towards that contained by the eutectoid. They might therefore explain the observed gradual rise in the temperature of reappearance of the eutectoid as the percentage of carbon in the steel rises towards 0·9; but they would not account for the whole of the lag. In particular, they would not explain the fact that in the hyper-eutectoid steels the temperature of reappearance seems to be practically constant and higher than in any of the others.

It is, in fact, obvious that surface effects, considered in conjunction with the conditions of equilibrium, must play an important part in determining the temperature at which the eutectoid appears.

We proceed to consider important cases from this point of view.

14. *The Conditions Preceding the Separation of the Eutectoid in Hyper-Eutectoid Steels.*

Fig. 9 represents the results of experiments upon the hyper-eutectoid steel, included in the table given in § 2, containing about 1·2 per cent. of carbon. The

Fig. 9.

Fig. 9a.
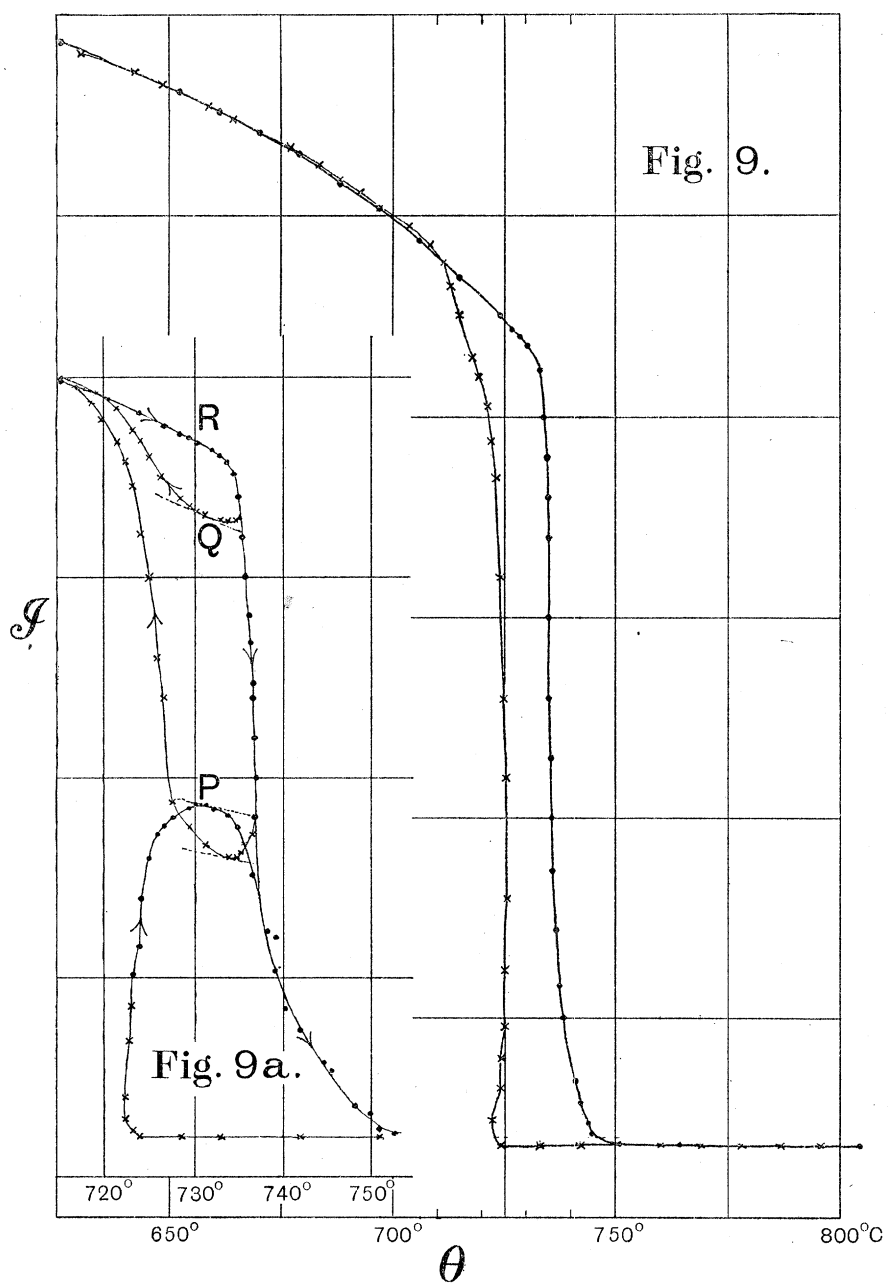
experiments were carried out, in the same way as those of figs. 5, 6, 7, and 8, in a field of about 200 C.G.S. units.

Although the eutectoid disappears at the same temperature as in the hypo-eutectoid steels of those figures, the reappearance now occurs at a much higher temperature. It is interesting to notice also that there is now no appreciable return of magnetism prior to the crystallisation of the eutectoid.

The process of crystallisation in such an alloy may be regarded as follows:— Suppose that the alloy, still at a temperature above that at which the excess carbide begins to deposit, is cooling down. Eventually it will reach the temperature at which it could exist in equilibrium with free carbide if the latter were present in bulk. Precipitation will not begin at this temperature, however, if there is appreciable surface energy between carbide crystals and solid solution.

Every re-crystallisation is characterised by the fact that, in the minute crystals first formed, the ratio of surface area to mass is relatively very great. Consequently the surface energy may be an appreciable fraction of the total energy of these crystals. This surface energy virtually increases the chemical potential of the separated material and therefore tends to make the temperature at which crystals can form, in a given solution, lower than it would be otherwise.

The disturbing effects of surface energy become less important as the crystals enlarge. Hence crystallisation, once begun, tends to proceed around the nuclei first deposited. At the same time the concentration in carbide of the solution in contact with the crystals approaches the equilibrium value.

This value decreases as the temperature falls, and is attained by deposition from the solution upon the crystals. As before, owing to the slowness of diffusion, the equilibrium will not be complete. The parts of the solution remote from the crystals will be too rich in carbide unless the rate of cooling is infinitely slow.

When the eutectoid temperature is reached the solution in contact with the crystals will have the eutectoid composition; but the eutectoid will not form without lag of a similar nature to that which delayed the appearance of the carbide.

In this case the lag will be due mainly to the iron, since carbide crystals are already present.

15. *An Effect Due to the Excess Carbide.*

Indirectly the presence of the carbide crystals will accelerate the crystallisation of the iron. For when the temperature falls below the eutectoid point the carbide continues to deposit and the solution in contact with the crystals continues to get richer in iron. The chemical potential of this iron therefore diminishes less rapidly as the temperature falls than it would do if carbide crystals were not present. Hence the amount by which this potential exceeds that of the iron crystals in bulk at any temperature below the eutectoid point is greater than it would be in the absence of the carbide. Therefore the resistance to the formation of the iron crystals and hence of the eutectoid will be overcome at a higher temperature when carbide crystals are present beforehand, as in the case of fig. 9, than in the eutectoid steel.

16. *A Working Hypothesis as to the Mode of Crystallisation of the Eutectoid.*

We may next consider the eutectoid steel itself and describe some experiments made upon it.

The surface energy between the solid solution and iron is probably less than that between it and the carbide. Accordingly, in such a steel, the lag in the precipitation of the eutectoid is probably terminated by the crystallisation of some of the iron which it contains. But the sudden precipitation of iron would increase temporarily to a very high value the concentration of the carbide in solution in its immediate neighbourhood. Hence, even if the retardations tended to be unequal, the crystallisation of the one constituent would induce the appearance of the other.

It is necessary to attempt to form a picture of the way in which crystallisation proceeds. For simplicity in description we may suppose that, as frequently happens, the eutectoid crystallises in grains, each consisting of, approximately parallel, alternating layers of iron and of carbide.*

It is unlikely that the production of these alternating layers of very different composition and finite thickness is instantaneous.

We may suppose that the first stage in the crystallisation of each grain results in the formation of parallel and excessively thin threads at approximately uniform distances apart, consisting of iron and the carbide in the eutectoid proportions, separated by layers of still untransformed solid solution in the way represented diagrammatically in fig. 10 (i.), and that the second stage is the growth of the threads to their final thicknesses, represented in fig. 10 (ii.), by the diffusion in
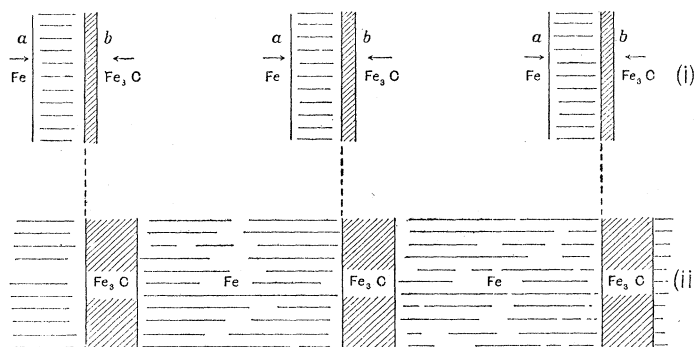

Fig. 10.

opposite directions, and deposition, of the constituents of the intervening layers of the solid solution.

Assuming the first stage, it is easy to see that the kind of diffusion postulated in the second will occur.

Owing to the lag the temperature is below the eutectoid point. Consequently the chemical potential of the carbide in solution is higher than in the separated

* *Cf. e.g.* BENEDICKS, 'Recherches sur l'acier au carbone,' Photogramme 1.

crystals. Carbide must therefore precipitate from the solution on the surfaces b in fig. 10 (i.) until the concentration of that in solution is lowered to the equilibrium value corresponding with the temperature of the material. Similarly the chemical potential of the iron in solution is higher than that in the separated crystals, and precipitation of iron must occur on the surfaces a until the concentration of the iron in solution is lowered to the equilibrium value.

The solution near the surfaces b thus at once gets weaker in carbide, and that near the surfaces a weaker in iron. The concentration gradients thus established cause the iron to diffuse in one direction and the carbide in the opposite. This diffusion in its turn causes fresh separation of iron on the one side and of carbide on the other. Hence separation and diffusion will occur continuously until crystallisation is complete.

The transformation of the eutectoid during subsequent re-heating can be treated in a similar manner by supposing solution to begin again where the crystallisation ended. It is not difficult to see how this view of what happens could be extended to meet other cases in which the structure of the eutectoid is different.

17. *Application to the Case in which the Crystallising of the Eutectoid is Interrupted.*

The utility of the above picture of the process of crystallisation can be tested by considering what, according to it, should happen if the process were interrupted before completion, and by examining, thermomagnetically, what actually occurs.

Imagine, therefore, that the temperature of the furnace, in which the steel lies, is raised slowly before crystallisation is complete.

The first effect is to lower the rate of escape of heat from the steel to the furnace, and therefore to reduce the rate of crystallisation. The diffusion within the solid solution will continue, however, and will cause the boundary films at a and b (fig. 10) to become respectively richer in iron and in carbide than they were. This will make it possible for crystallisation to continue from them at a higher temperature.

Crystallisation need not cease at once, therefore, and may go on for some time after the temperature of the material has begun to rise. But, unless the diffusion after interrupted cooling is sufficient to remove the differences of concentration within the still-untransformed material, solution must begin again before the true eutectoid temperature is reached.

Fig. 11 is an example of results obtained during interrupted cooling. In the first case the cooling was not interrupted until the return of magnetisation was nearly complete. In the third it was interrupted soon after the return had begun.

The curves show that the gain of magnetisation continues until the temperature has risen appreciably above its value when the cooling was arrested.

They show also that the subsequent loss of magnetisation begins earlier, but

more gradually, than during continuous heating from the atmospheric temperature. The same effect is shown more strikingly in figs. 12 and 13 below.

It will be noticed that, according to the views already outlined, rapid solution should not be possible until the temperature of the specimen has risen sufficiently far above the eutectoid point to make the differences between the equilibrium concentrations at the boundary films considerable.
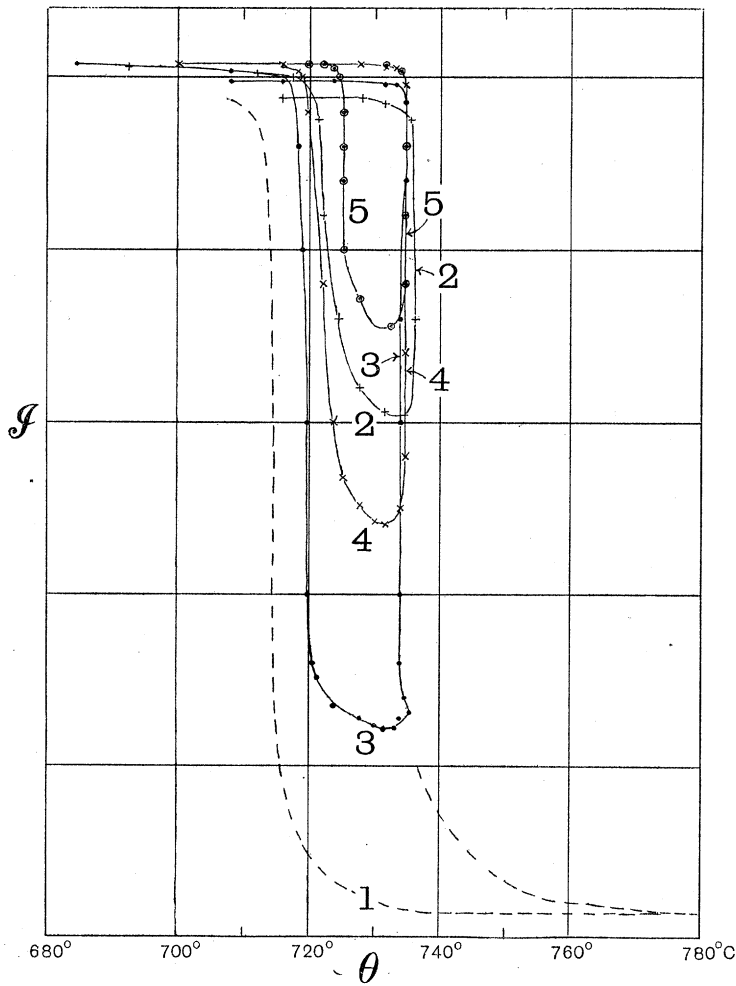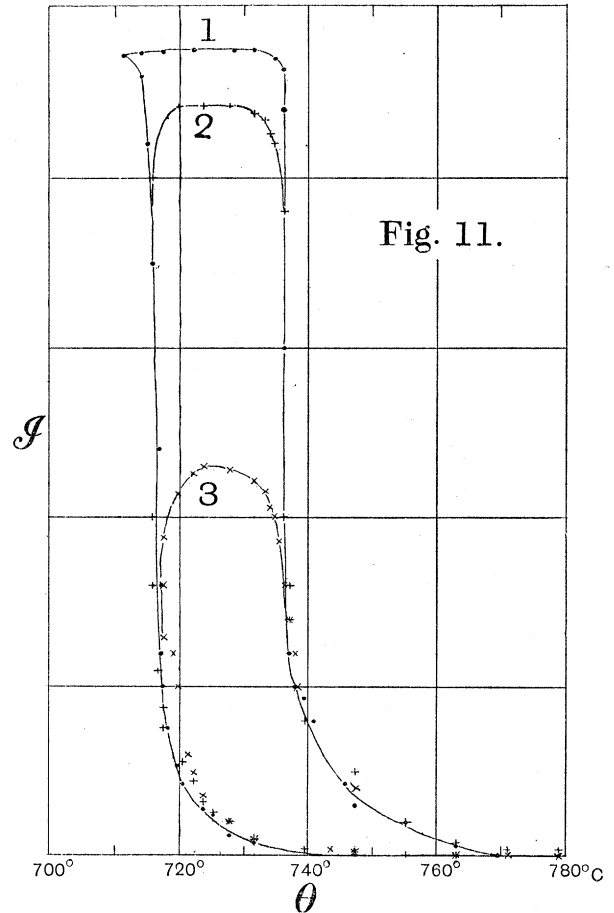

Fig. 2.

Fig. 11.

Fig. 11, together with figs. 12 and 13, shows that what happens is in agreement with this deduction.

The fact that during heating from the air temperature the solution proceeds rapidly immediately after it begins is additional evidence of the existence of the lag already considered in § 3.

18. *Application to the Case of Interrupted Solution of the Eutectoid.*

Fig. 2 (see this page) serves to show the behaviour of the material after interrupted heating. To interpret the results we have to consider what will happen when the

temperature of the furnace is lowered after solution has begun.   The immediate effect is to lower the rate of supply of heat to the material, and therefore to lower the rates of solution of the carbide and the iron at the respective surface films.

Before the lowering, the rates of diffusion of these were sufficiently rapid to keep their concentrations from rising in the regions where they were dissolving.   After it, they will be more than sufficient, and these concentrations will fall, with the result that, even when the temperature of the material is lowered, solution may still go on.

In practice, as will be seen from the figure, the rate of solution soon becomes very slow, and the temperature has not fallen very far before the magnetisation begins to rise.

The temperature at which solution ceases will be above the true eutectoid point, unless the diffusion has sufficed to make differences of concentration negligible within the solution which remains.   It will thus tend to be nearest the true value (and, incidentally, lowest) when the layers of solid solution are never very broad, i.e., when the heating is interrupted very soon after solution has begun.

It will be seen that this inference is corroborated by the experimental results.

It remains to explain why, as in the figure, the temperature at which the lost magnetism begins to be recovered rapidly is lower the higher the temperature at which the heating is interrupted.

Suppose that re-crystallisation has begun.   At one stage, marking the point where concentration differences produced during solution have been approximately obliterated by the reverse changes during re-crystallisation, the layers of solution will be nearly of eutectoid composition.   Their thickness will depend upon the amount of solution that took place before the furnace temperature was reduced.

At this stage the specimen will be at the eutectoid temperature.   When it is passed the difference in composition between one surface film and the other will change in sign and will become greater as the temperature falls.   At the same time the thickness of the whole layer will decrease.   Ultimately, a temperature will be reached at which the ratio of concentration difference to layer thickness is sufficient to permit the rapid rate of diffusion which rapid re-crystallisation requires.

If the layers of solid solution are very narrow when, during cooling, the eutectoid temperature is passed, the concentration difference required for rapid diffusion will be relatively small, i.e., the temperature of rapid re-crystallisation will be relatively high. If they are very wide, as happens when the solution is nearly complete before heating is interrupted, that temperature will be relatively low.

The temperature of rapid increase of magnetisation should thus decrease progressively from its highest value—when solution is arrested almost as soon as it has begun—to its lowest value when solution is not arrested at all.

This is exactly what happens experimentally as the curves of fig. 2 show.

19. *Confirmatory Experiments in Weak Fields.*

Some points of interest are shown in further experiments upon the eutectoid steel represented in figs. 12 and 13 and already referred to in § 17.

Fig. 12.
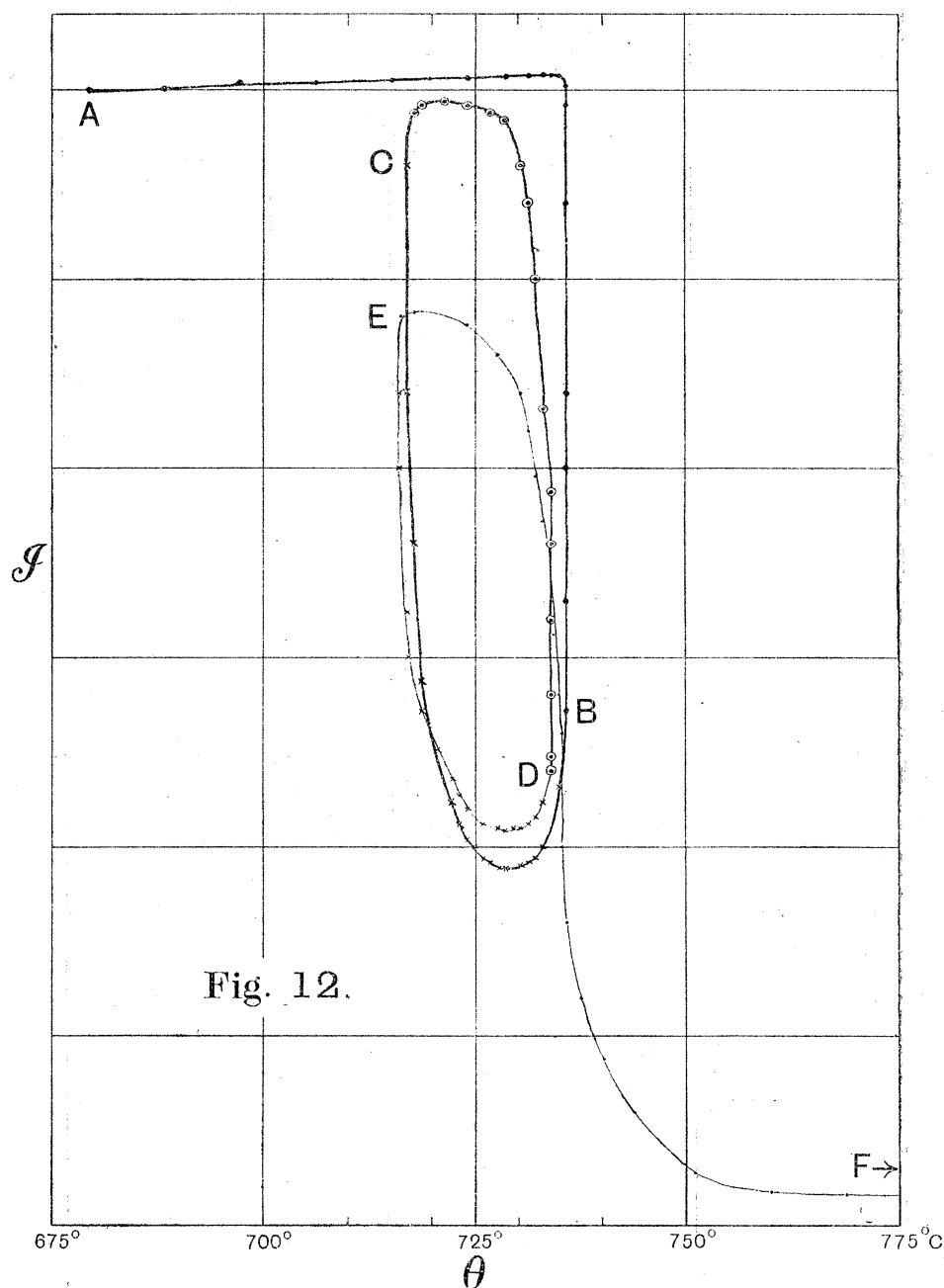
The field intensity was now only 25 C.G.S. units. The first figure shows the effects of two interruptions during heating from about 680° to about 800° C. The sequence will be obvious from the lettering. Thus heating was first interrupted at B, then cooling was interrupted at C, and so on, alphabetically, to F (about 800° C.).

These observations may be compared with those of fig. 3, described in § 3, which were obtained with the same steel in a field of 50 C.G.S. units.   The temperature

Fig. 13.
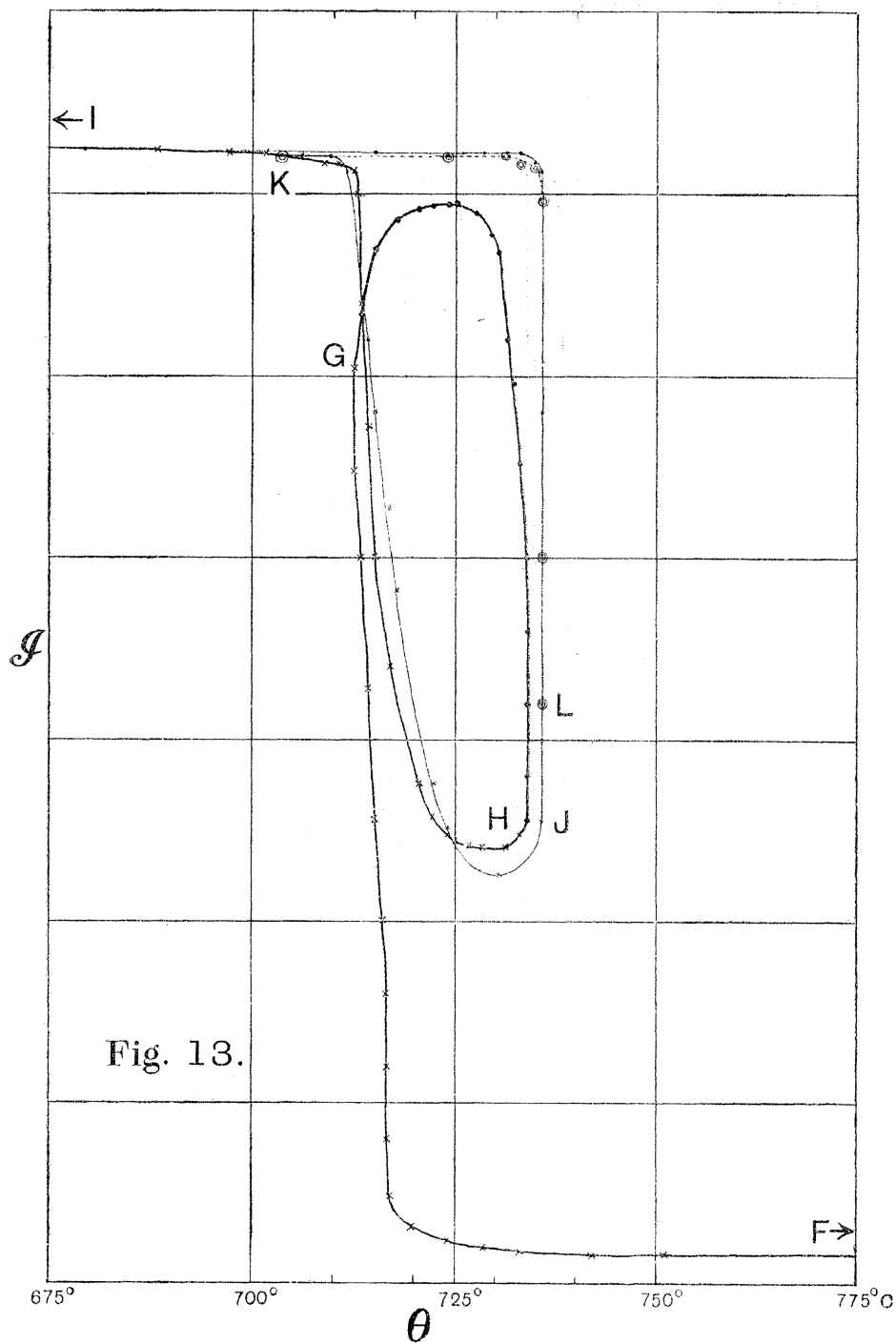
of rapid loss of magnetisation is exactly the same as before, but the beginning of the transformation is much more clearly seen in this weaker field.   The temperature

coefficient of the magnetisation now remains positive until the structural change point is reached.

It would seem, therefore, that by suitable adjustment of the field in any particular case, the thermomagnetic method can be used to indicate the change point, known to metallurgists as Ac_1, with an accuracy that can scarcely be exceeded in measurements by any other method.

The experiments of fig. 13 followed immediately after those of fig. 12. The material was cooled from F to G, then heated again to H, cooled to I (about 640° C.), then heated to J, cooled to K, and finally heated to L.

The observations from I to J show that the lag during heating (the existence of which is again clearly shown) returns to its full value when the material is allowed to cool to about 640° C. before it is re-heated. The series JKL goes a stage further and shows that the same is also true when the cooling is stopped at about 705° C.

Such observations indicate another thermomagnetic method of determining the temperature at which, during cooling under given conditions, the eutectoid change is complete. They also corroborate the hypothesis that the lag during heating is due to surface effects.

20. *The Equilibrium Temperature.*

If the interpretation of our results which has been given is correct, they show that (subject to limitations due to variations of pressure) iron crystals, carbide crystals, and a solid solution of the two of *uniform* (eutectoid) composition cannot coexist without change except at a definite temperature.

According to the results obtained with the 0·85 per cent. steel, shown in figs. 3, 12, and 13, this temperature lies between 725° and 730° C.

Fig. 9A* contains the results of an attempt to find the equilibrium temperature by means of the steel containing 1·2 per cent. of carbon. The method was the same as before, except that we used a field of 200 C.G.S. instead of the previous fields of 25 and 50 C.G.S. respectively. The thermocouple had been calibrated more recently and was probably rather more trustworthy than that used in the earlier experiments.

The point Q on the "interrupted heating" curve is that at which the temperature coefficient of $\mathscr{I}$ with respect to θ is the same as at the corresponding temperature R on the (uppermost) curve of continuous heating. It is presumably, therefore, to a first approximation, the temperature at which the change from solution to re-crystallisation began during cooling.

The point P on the "interrupted cooling" curve is similarly that at which the temperature coefficient of $\mathscr{I}$ with respect to θ became the same as at the corresponding temperature on the uppermost curve. It is, therefore, to be regarded as the point at which change from re-crystallisation to solution began during heating.

It happens that the temperatures corresponding with the points P and Q are

* See p. 195.

practically the same, viz., 731° C. This is, therefore, according to these measurements, the equilibrium temperature.

The greatest accuracy cannot be claimed for our measurements of temperature, although they were made as carefully as the conditions of experiment seemed to warrant. Sometimes the thermocouple may have been used rather too often for safety, between renewals and re-calibrations, but it is unlikely that the experimental error in the measurement of temperature ever exceeded 5° C.

Our general conclusion is that the equilibrium temperature can be measured, and that it is, so far as our measurements can decide, substantially the same whatever the percentage of carbon contained by the steel.

21. *Possible Effects of the Presence of a Magnetic Field during Crystallisation.*

It is not inconceivable that the temperature at which the eutectoid separates out, or disappears, should be influenced by the field. There is no evidence of this in the curves which we have given, nor in others in which we have varied the field from $H = 10$ to $H = 400$ C.G.S.

To apply a severer test, we took " recalescence " (time-temperature) curves, using a chronograph and a very open scale thermometer, with a specimen of the steel containing 0·7 per cent. of carbon, placed between the poles of a large Du Bois electromagnet. We could not detect any material difference between the temperature of recalescence when the magnet was fully excited, giving a very intense field, and that when the field was practically zero.

Further, we attempted to determine whether the presence of an intense field made any appreciable difference in the method of crystallisation of the eutectoid. Using the rod containing 0·85 per cent. of carbon, we cooled it from above the eutectoid point, between the poles of the electromagnet, first with its axis parallel to the field and afterwards with its axis perpendicular to the field. In each case we examined the subsequent magnetic behaviour of the rod at temperatures below 250° C.; but could not detect any difference between the changes accompanying the appearance and disappearance of magnetism in the carbide in the two cases.* It is, therefore, unlikely that the field produces any appreciable effect, during crystallisation at the eutectoid point, upon the orientation of the carbide with respect to the iron.

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* *Cf. loc. cit.* §§ 1 and 2.