

ally, has been developed by the application of the laws relating to solution. It is well known that if common salt is dissolved in water the freezing point of the liquid is lowered. By adding more salt the freezing point of the resulting mixture is continually lowered until the solution contains a certain definite percentage of salt, when still further additions will gradually raise the freezing point of the brine.

It was discovered by Guthrie that the mixture of salt and water which had the lowest freezing point contained about 23.5 per cent. of common salt. A hydrate containing 10 molecules of water would contain 24.5 per cent. of Sodium Chloride, and Guthrie came to the conclusion that this mixture with the lowest freezing point was a hydrate of Sodium Chloride of the formula $\text{NaCl} + 10\text{H}_2\text{O}$. He called this and all similar bodies separating

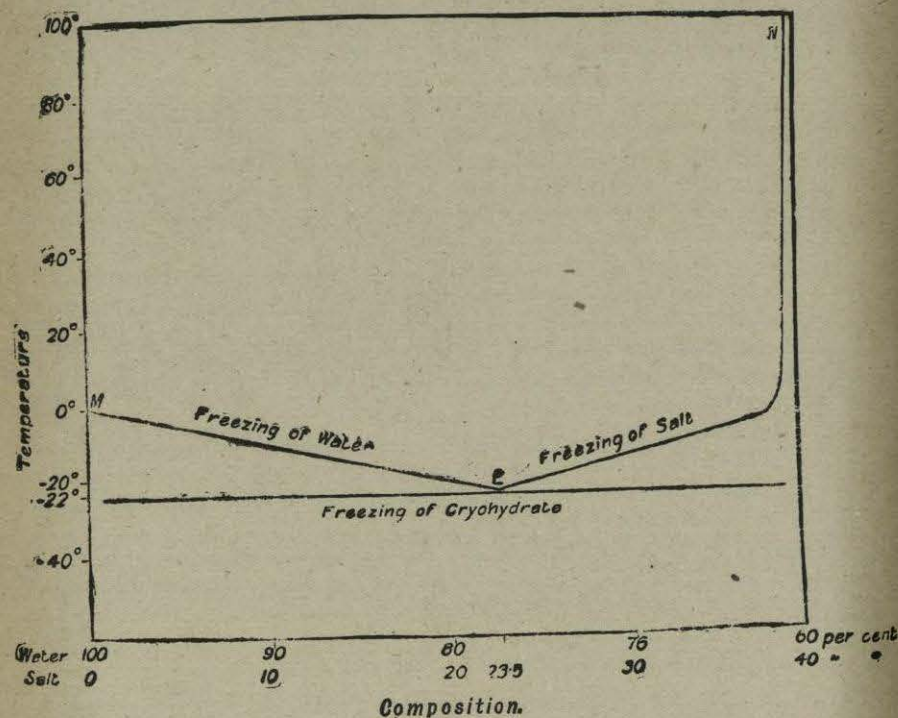


Fig. 250.—Freezing Curve of Solution of Common Salt.

from saline solutions at the lowest freezing points *Cryohydrates*, meaning literally cold hydrates or hydrates which could exist in the solid state at low temperatures only. It has since been shown that these Cryohydrates are not definite compounds, but are mechanical mixtures. If we take, therefore, a solution of salt and cool it down by means of a freezing mixture to its freezing point, then if the solution contains less salt than the Cryohydrate, ice will form as soon as its temperature is reduced below the freezing point, and if, on the other hand, it contains more salt than the Cryohydrate mixture, salt crystals will first form. In each case these crystallisations are accompanied by an "arrest" or retardation in the rate of cooling, as shown by a thermometer, and this is due to an evolution of latent heat which marks

the commencement of solidification. In the case of the weak salt solution the separation of ice gradually increases the percentage of salt in the mother liquor, while, in the case of the strong solution, the separation of salt decreases the percentage of salt in solution until finally at a temperature of -22°C . the solution reaches the composition of the Cryohydrate. At this point the remaining liquid then solidifies as a whole, the temperature, as shown by the thermometer in the mixture, remaining stationary until the mass has completely solidified, owing to the evolution of the latent heat of solidification of the Cryohydrate balancing the loss of heat by radiation and conduction.

If the cooling be continued after the whole mass is solid the fall in temperature resumes its normal rate.

A frozen saline solution containing less salt than the Cryohydrate will consist of crystals of pure ice surrounded by frozen Cryohydrate, or, if the solution contained a large excess of salt, the frozen mass will be made up of crystals of salt surrounded by solid Cryohydrate.

Fig. 250, showing the freezing curve of solutions of common salt and water, is taken from a paper by Mr. Sauveur in the *Metallographist*, July, 1898.* The abscissæ represent the composition, and the ordinates the temperatures. If we assume that a solution containing, say, 90 per cent. water and 10 per cent. salt is placed in a cooling medium, when it reaches its freezing point ice will form, and there will be a retardation in the rate of cooling denoting an evolution of latent heat, and this temperature plotted on the diagram will give us one point in the curve, M E. By the formation of ice the solution becomes richer in salt, and its freezing point is lowered, and no further separation of ice takes place until its temperature is further lowered, when fresh formations of ice take place, giving us other points in the curve. Thus the branches of the curves in fig. 250 are formed by the loci of a number of arrest points of cooling curves until finally the solution becomes richer and richer in salt, and at a temperature of -22°C . it reaches the composition of the Cryohydrate at point E, and solidifies as a whole.

If we now pass from saline solutions to fused alloys, we find the same phenomena exhibited. Let us consider the case of a copper-silver alloy (fig. 251), and observe what takes place during the gradual cooling of such an alloy from the fluid state, say, from a temperature of $1,000^\circ\text{C}$., carefully noting any "arrests" or retardations during the cooling by means of a suitable pyrometer. Any such "arrests" will indicate an evolution of latent heat, marking the beginning of solidification. Assuming the alloy contains 90 per cent. silver and 10 per cent. copper, as it cools down silver will separate out, and the fluid alloy will become poorer in silver and richer in copper, in the same way as the weak salt solution became poorer in water and richer in salt. At each separation of silver there will be an evolution of heat or retardation in the rate of cooling, the melting point of the fluid alloy will be lowered, and no further separation of silver will take place until there is a further cooling. This separation of silver will continue to give a number of loci of cooling curves for alloys of different composition, which, when plotted, give the curve in the figure, until at a temperature of 778°C ., when the alloy has a composition of 28 per cent. copper and 72 per cent. silver, instead of silver continuing to separate the whole of the alloy will solidify at a constant temperature, there being no further reduction until the whole mass is solid,

* The maximum amount of salt soluble in water between 0° and 100°C . is rather under 40 per cent., consequently the curve does not extend beyond the point corresponding to this.

when the temperature again begins to fall. This particular mixture or alloy of silver and copper has the lowest freezing point of all silver-copper alloys, and is called the eutectic alloy, a name suggested by Guthrie. It may be stated that the silver crystals which separate out in these alloys are not pure, but contain up to about 3 per cent. of copper, and in the same manner the copper crystals which separate hold in solid solution up to about 22 per cent. of silver, these proportions are indicated by the dotted lines in fig. 251. The analogy between the eutectic alloy and the Cryohydrates of saline solutions will at once be apparent from the curves.

We must now go a step further, and consider a mixture or alloy of Carbon and iron not in the molten, but in the solid state during cooling from a high temperature. Let us take the case of pure steel of medium Carbon, say, about .6 per cent., which may be regarded for our present purpose as

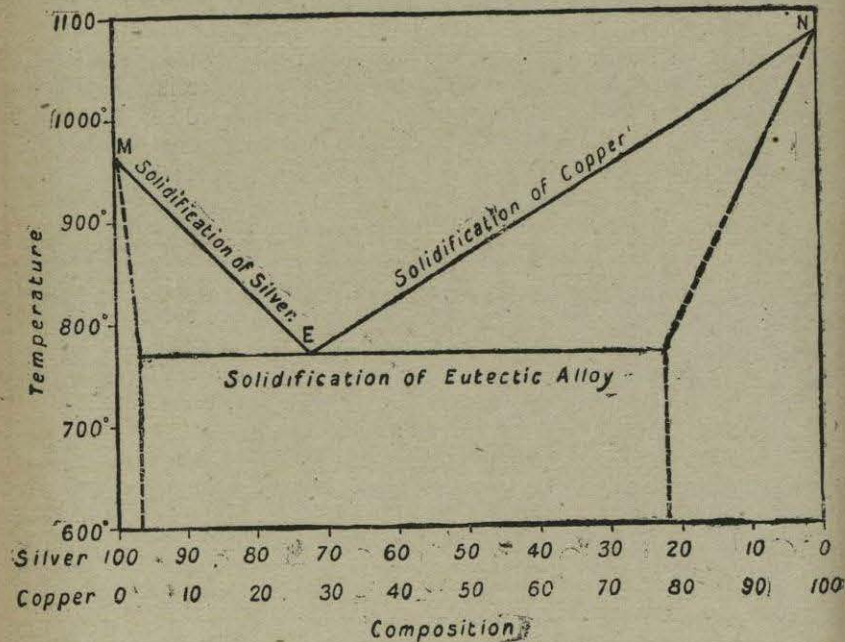


Fig. 251.—Freezing Curve of Copper-Silver Alloys.

an alloy of iron and Fe_3C . On cooling down such a steel from, say, $1,300^\circ$, and carefully observing the rate of cooling by a suitable pyrometer, there is nothing very noticeable until the temperature falls to about 740° when there is a sudden evolution of heat identical with that which occurred during the commencement of solidification of the silver-copper alloy.

This is the point at which pure iron separates from the solid solution and corresponds to the changes represented by Ar_3 and Ar_2 combined. Subsequent to this at 715° a second point occurs which is the well-known recalcence point, and is analogous to the solidification of the eutectic in the silver-copper alloy, and in passing through it the structure of the steel is entirely changed and its chemical, physical, and mechanical properties markedly altered. If we now plot these changes observed in a large number of

specimens of different Carbon contents (fig. 252) in the same way as we have done for the saline solution and the copper-silver alloy, the great similarity of the curves will be evident. We have two branches of the curve meeting at a temperature of 715° , corresponding to 13 per cent. Fe_3C and 87 per cent. iron; we have also a nearly horizontal line marking the evolution of heat at the recalcence point, clearly indicating some molecular change at a constant temperature. As we are dealing with a solid and not a fluid body, to speak of one of the bodies solidifying, as in the case of copper from the copper-silver alloy, may lead to confusion of ideas, but we may assume that during the cooling there has been a gradual separation of iron until the point E is reached, when a eutectoid alloy of iron and Fe_3C is formed—i.e., a

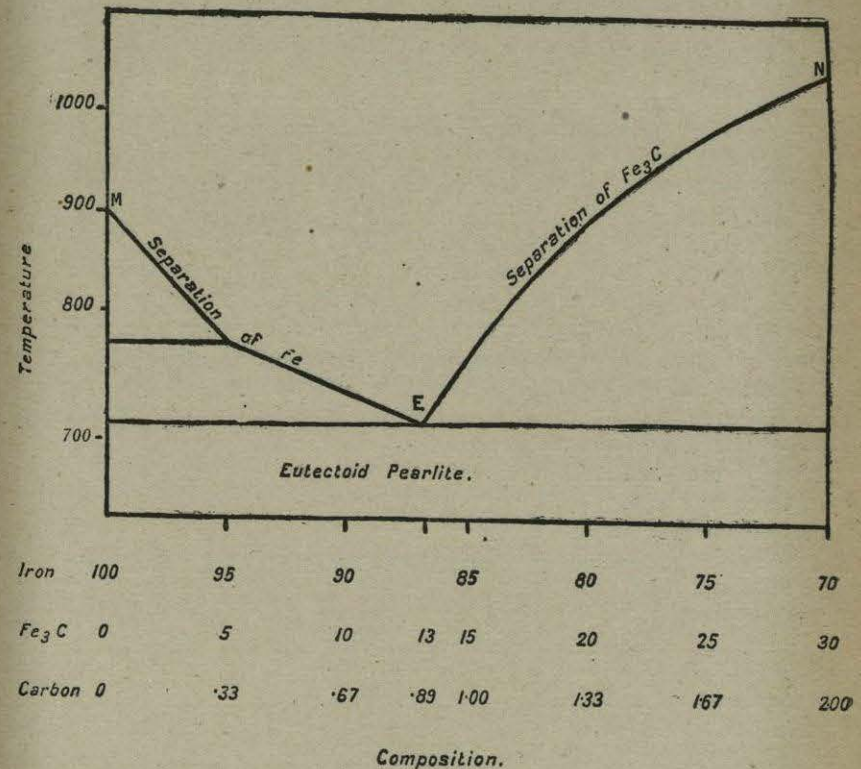


Fig. 252.—Curve showing Separation of Iron and Carbide during the Cooling of Carbon Steels.

mechanical mixture of these two in the same way as a Cryohydrate is a mechanical mixture of ice and salt, or the copper-silver eutectic, a mechanical mixture of its constituents. If the above hypothesis is right, slowly cooled steel containing less than .89 of Carbon should be made up of crystalline grains of carbonless iron, surrounded by the eutectoid alloy of Fe and Fe_3C —i.e., Pearlite; steel more highly carburised should be formed of grains of Carbide, Fe_3C (Cementite), surrounded by the eutectoid alloy Pearlite, while metal containing .89 per cent. of Carbon should consist entirely of the eutectoid alloy. Microscopic evidence shows this to be the case.

To trace the analogy more clearly between the copper-silver alloy and steel we place them in parallel columns.

Copper Silver Alloy, as shown
under Microscope.

1. Larger percentage of silver than eutectic mixture. Crystalline particles of silver in matrix of eutectic alloy (fig. 253).
2. Larger percentage of copper than eutectic. Crystalline particles of copper surrounded by, or embedded in, eutectic (fig. 254).
3. Alloy of same composition as eutectic when it solidifies as a whole at 778° C. Whole mass entirely eutectic consisting of laminae (fig. 255).

Iron Carbide Alloy, as shown
under Microscope.

1. Larger percentage of iron than eutectoid mixture. Carbonless iron (Ferrite) in matrix of eutectoid Pearlite (fig. 256).
2. Larger percentages of Carbide than in eutectoid mixture. Grains or bands of Carbide (Cementite) surrounded by, or embedded in, eutectoid Pearlite (fig. 257).
3. Same composition as eutectoid, .89 per cent. Carbon. Should consist entirely of eutectoid Pearlite (fig. 258).

On reference to the photographs referred to it will be seen that the above statements are confirmed in every case by the microstructure. We find that fig. 258, illustrating the structure of .89 Carbon steel, consists entirely of Pearlite, which has the characteristic structure of eutectic alloys, being made up of alternate thin plates of iron and Fe_3C . Fig. 257 shows the Cementite embedded in the Pearlite, and fig. 256 shows Ferrite embedded in Pearlite.

In connection with the solution theory of Carbon steels, an attempt to explain the hardening of these steels has been made by assuming that during rapid cooling through the critical range conditions which normally exist above this range are retained. In this manner by sudden cooling the Carbon may be kept in solid solution and cause hardness.

Such are some of the leading considerations which have led to the conception and enunciation of the theory of solid solution as applied to steel, and they are placed before the student that he may understand what is embraced by the term, and the general basis—both on analogy and experiments—on which the theory rests.

The following statement by Dr. Stansfield from his paper read before the Iron and Steel Institute in 1899 clearly defines the position and claims of the solution theory:—

“The solution theory of carburised iron affirms that this substance is, when fluid, a solution of Carbon in iron, and that under certain conditions the solidified mass also forms a solid solution. It further affirms that these liquid and solid solutions obey the ordinary laws of solution, which have been fully studied in the case of aqueous, saline, and organic solutions. (The Carbon may, however, be considered to be in solution as the compound Fe_3C .) The solution theory can, therefore, be invoked to explain both the mode of solidification of carburised iron and the molecular changes that take place after solidification. The experimental data which enable the theory to be applied are mainly afforded by the pyrometer and the microscope used in conjunction with chemical analysis, but all the other chemical and physical properties of carburised iron must be studied, for the sake of the contributory evidence they afford.”

The Allotropic Theory.—The molecular changes occurring in iron itself have been very carefully studied, and form the basis of what is known as the allotropic theory. Sir Wm. Roberts-Austen defined allotropy as “a change of internal energy occurring in an element at a critical temperature, not necessarily accompanied by a change of state.” Professor H. M. Howe

silver and Iron Carbide Alloys.

[To face p. 358.]



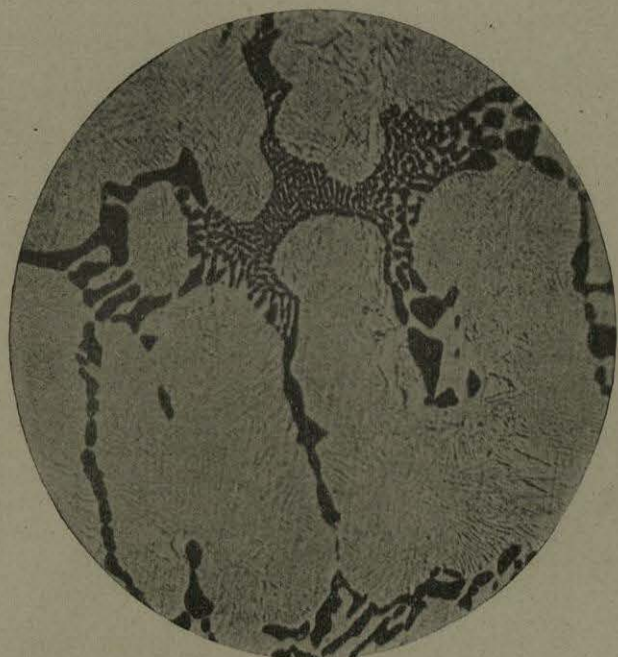


Fig. 253.—Larger percentage of silver than eutectic mixture. Crystalline particles of silver in matrix of eutectic alloy.



Fig. 256.—Larger percentage of iron than eutectoid mixture. Carbonless iron (Ferrite) in matrix of eutectoid Pearlite.

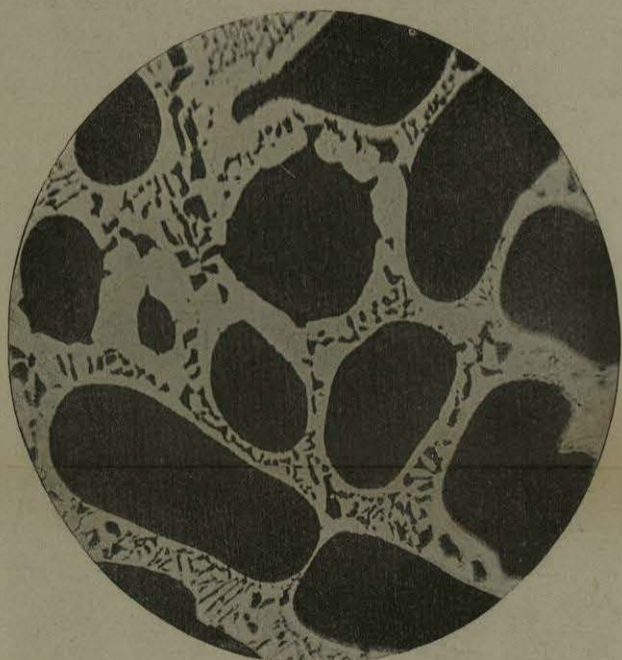


Fig. 254.—Larger percentage of copper than eutectic. Crystalline particles of copper surrounded by, or embedded in, eutectic.

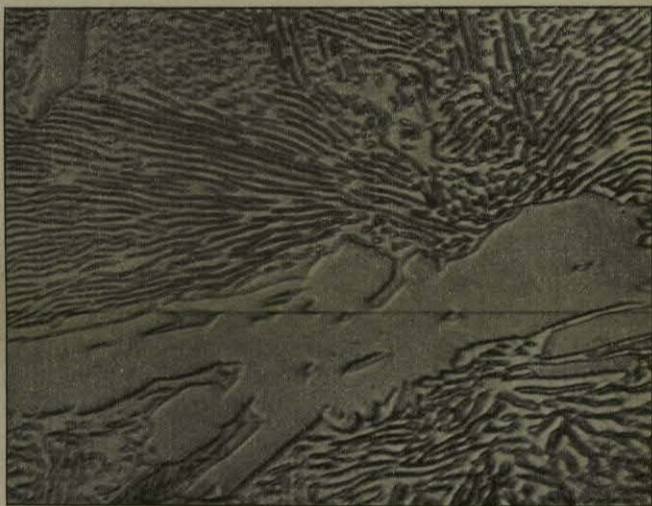


Fig. 257.—Larger percentages of Carbide than in eutectoid mixture. Grains or bands of Carbide (Cementite) surrounded by, or embedded in, eutectoid Pearlite.

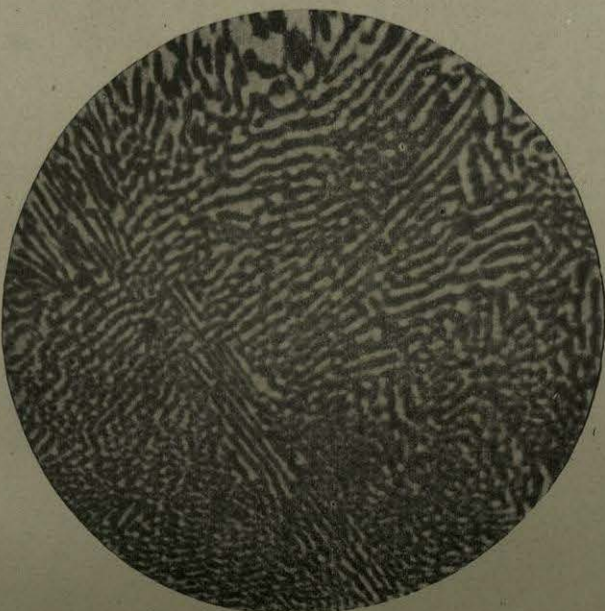


Fig. 255.—Alloy of same composition as eutectic when it solidifies as a whole at 778° C. Whole mass entirely eutectic, consisting of laminae.

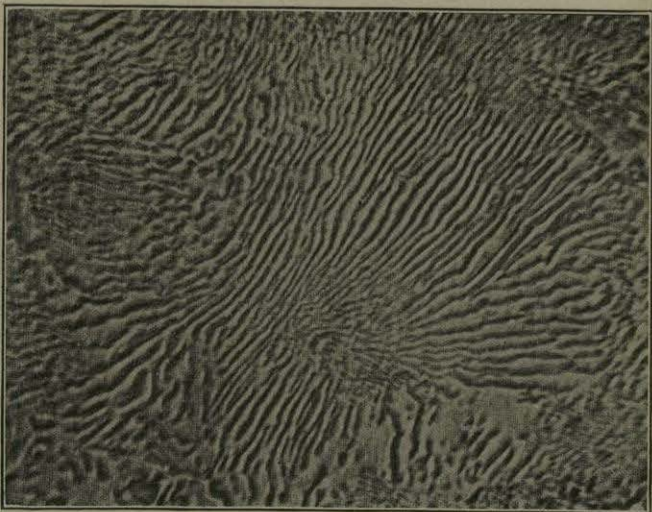


Fig. 258.—Same composition as eutectoid, .89 per cent. Carbon. Should consist entirely of eutectoid Pearlite. Laminated structure.

has proposed the following definition:—"Allotropy is a change in the properties of an element without change of state. It is habitually accompanied by a change of internal energy. It is due in some, perhaps in all, cases to a change in the number or in the arrangements of the atoms in the molecule."* Taking either of the above definitions, it is clear that the evolution of heat on cooling, and the absorption of heat on heating, taken in conjunction with the altered physical properties of hardened steel, would be undoubted evidence of allotropy, once granting that Carbon or some other element plays no part in the observed phenomena; and, in the case of electrolytic iron (such as that used in some of Sir Wm. Roberts-Austen's experiments, with only 0.007 per cent. Carbon), the presence of the critical points Ar_3 and Ar_2 has been considered as undoubted evidence of allotropy, but not, of course, in itself, of a *hard* allotropic form.

In 1890, at the spring meeting of the Iron and Steel Institute, M. Osmond read a very notable paper, in which he brought forward the theory that there are two allotropic modifications of iron, one the ordinary soft iron as we know it in ingot iron or steel, which he called "alpha" iron, and the other a hard variety as we know it in hardened steel, which he called "beta" iron.

Hardened steel, he asserted, owed its properties principally to the presence of β iron, which is hard and brittle by itself at the ordinary temperature. According to him, iron below the point Ar_2 possesses the molecular form "alpha"—that is, the soft form—but above the critical point Ac_2 the allotropic hard form, or "beta," iron exists. Carbon, in the state of hardening Carbon, maintains iron in the β condition, during slow cooling, to a temperature which is in inverse proportion to the amount of Carbon contained in the metal. When the rate of cooling is fairly rapid, the changes occurring during slow cooling do not take place, at least not in their entirety. Hardened steel is a steel in which the iron and Carbon have more or less completely preserved in the cold the condition which they possessed at high temperatures. It should be carefully noted that M. Osmond did not assume that hard "beta" iron is of itself sufficient to account for all the observed facts; Carbon undoubtedly plays an important rôle. On the other hand, although the presence of Carbon is essential to the hardening of steel, the changes of the Carbon condition do not enable all the facts to be explained. The influence of Carbon, according to him, is of the same character as that of the rate of cooling, and both combine to produce the final result. The rate of cooling alone is not sufficient, under the ordinary conditions in which hardening is effected, to maintain an appreciable fraction of the iron in the β condition. But as, under the same conditions, it is easy to maintain the Carbon in the state of hardening Carbon, and as the hardening Carbon imparts stability to β iron, β iron may be successfully preserved at the ordinary temperature by the aid of Carbon.

Later on, M. Osmond recognised the existence of three distinct modifications of iron, his reasons being based chiefly on the distinction between the points Ar_2 and Ar_3 , which in his early paper he did not think were independent and definitely separated. His later view was that iron existed in the α state below Ar_2 , in the β state between Ar_2 and Ar_3 , and in the γ state above Ar_3 .

Considerable doubt has recently been raised as to the existence of the β variety of iron, and there is certainly insufficient evidence to support the existence of a β iron which is in itself harder than α or γ iron.

* "Nomenclature of Metallography," *Iron and Steel Inst. Journ.*, 1902, vol. i

More recent views as to the condition of the iron in hardened steels include those of Edwards, Le Chatelier, and Guillet.

Edwards puts forward the view that during rapid cooling through the transformation range the iron is retained in the γ condition, whilst Le Chatelier and Guillet suggest that the A_2 change is not allotropic, and that in hardened steels the iron exists in the α condition, but retains Carbon or Fe_3C in solid solution.

The Carbon and Sub-Carbide Theories.—The allotropic theory has been strongly opposed by Professor Arnold and others. The supporters of the Carbon theories, as opposed to the allotropic theory, maintain that all the phenomena observed in the hardening of steel are explained by changes in the condition of the Carbon, and that hardening is not in any way due to allotropic modifications of the iron.

What may be termed the Carbon theory assumes that Carbon can exist in two states in steel; that the Carbon exists as "hardening Carbon" at a temperature above the critical points, and on rapid cooling, as by quenching in water, this Carbon is retained in the same state. On slow cooling from above the critical points, the hardening Carbon passes into the form known as cement Carbon, and combines with the iron to form the Carbide, Fe_3C . Even if this theory is accepted as a satisfactory explanation of hardening, it certainly does not explain the critical points in carbonless iron and other observed facts, such as the disappearance of magnetism at Ar_2 . In May, 1894, Prof. Arnold* thus accounted for the critical points in steel:— Ar_1 is due to the combination of iron and Carbon to form the normal Carbide, Fe_3C ; its intensity is proportional to the amount of Fe_3C present, and to the area of pearlite in the microsection. A_2 marks the exceedingly faint evolution or absorption of heat due respectively to the passage of iron from a plastic to a crystalline condition or *vice versa*. Ar_2 is explained on the hypothesis that it marks the formation of a sub-Carbide of iron. In the case of low Carbon steels, a prolonged exposure to a white heat converts the normal into the sub-Carbide.

In 1896 Prof. Arnold† developed his sub-Carbide theory in an able paper, which may be thus briefly summarised:—

From a series of strictly comparative experiments on normal (heated to $1,000^\circ C.$ and cooled in air), annealed, and hardened bars, he finds that in all the hardened steels only a small proportion, about 5 per cent., of the total Carbon is obtained on analysis as Fe_3C , the main portion, he argues, existing as an unstable sub-Carbide of iron. With steels of .89 per cent. Carbon, it would appear from the analyses that, practically the whole of the metal consists of this intensely hard sub-Carbide of iron. Steel of this percentage of Carbon he calls saturated steel; steels with other percentages are either unsaturated or super-saturated. The critical point Ar_1 is due to the dissociation of this Carbide, $Fe_{24}C$, and the formation Fe_3C . In the normal samples some 90 per cent. of the total Carbon is obtained in the form of the definite Carbide, Fe_3C . He sums up thus:—

"The constituents of steel may be:—(a) Crystals of pure iron which remain bright on etching. (b) Crystals of slightly impure iron which become pale brown on etching, probably owing to the presence of a small quantity of unsegregated Carbide. (c) Normal Carbide of iron, Fe_3C , which exists in four distinct modifications, each one conferring upon the iron in which it is found particular mechanical properties:—(1) Emulsified Carbide present in an excessively fine state of division in tempered steels. (2) Diffused Carbide

* *Iron and Steel Inst. Journ.*, 1894, vol. i. † *Min. Proc. Inst. C.E.*, vol. cxxiii., 1896.

of iron occurring in normal steels in the forms of small ill-defined striæ and granules. (3) Crystallised Carbide of iron occurring as well-defined laminæ in annealed and in some normal steels. (4) Segregated Carbide occurring in very slowly cooled steels, and consisting of irregular masses. (d) Sub-Carbide of iron, a compound of great hardness existing in hardened and tempered steels, and possessing the formula $Fe_{24}C$. This substance is decomposed by the most dilute acids, and at $400^\circ C.$ it is decomposed into Fe_3C and free iron, with evolution of heat. One of the most remarkable properties of this compound is its capacity for permanent magnetism. (e) Graphite or 'temper Carbon.'

"The existence of $Fe_{24}C$ is proved by the fact that iron containing 0.89 per cent. Carbon presents several correlative critical points when examined by different methods of observation:—(1) Well-marked saturation points in the microstructure of normal and annealed steels. (2) A sharp maximum in a curve the co-ordinates of which are heat evolved or absorbed at A_1 , and Carbon percentage. (3) A sharp maximum in a curve the co-ordinates of which are Carbon percentage, and permanent magnetism in hardened steels."

Prof. Arnold has kindly sent me the following paragraph briefly embodying his present views:—

"Since reading the paper in 1896, he has seen no reason to appreciably modify his views with reference to the critical point Ar_1 , but considers, as Ar_2 is undoubtedly the magnetic change point, it does mark a kind of physical allotropy. With regard to Ar_3 , the fact that this point has been shown by himself and others to be present in carbonless electrolytic iron precludes its being due to any Carbon change; it is also associated with dilatation phenomena, but he does not consider that this is necessarily evidence of an allotropic change, and, in the present state of our knowledge, has no satisfactory explanation to suggest except that it seems certain that neither Ar_2 nor Ar_3 is associated with crystalline polymorphism, and careful quenching experiments had proved that neither had any practical mechanical significance at ordinary temperatures. It is also certain that the view held by most well-known steel investigators (specifically excepting, of course, Prof. Le Chatelier) that Carbide of iron is insoluble in iron in the alpha range of temperature is curiously inaccurate. He (Prof. Arnold) had himself proved by scores of experiments that the Carbide of Pearlite completely diffused or dissolved into its iron in the alpha range."

In the autumn of 1895 Professor H. M. Howe presented a paper to the Iron and Steel Institute, the object of which was to investigate how closely the change in the Carbon condition, in passing through the critical range, coincides with the loss of the hardening power. Bars containing .21 per cent. Carbon, .31 per cent. Silicon, and 1.19 per cent. Manganese, were very carefully heated to $970^\circ C.$, slowly cooled, and quenched at different temperatures, varying from $880^\circ C.$ to $263^\circ C.$ in cold brine, untreated bars being tested for comparison. These bars were then tested for tenacity, ductility, and hardness as a measure of the intensity of hardening, and for colour Carbon as a measure of the Carbon condition.

Professor Howe found that the change in Carbon condition (from cement to hardening Carbon) lagged far behind the change in tenacity. As the temperature of quenching descended from 880° to 713° the changes in the properties of the metal and the missing Carbon were slight, but at 633° the tenacity of the metal fell off most abruptly, at least 52 per cent. of the total loss occurring in this narrow range of 55° , though only some 12 per cent. of the Carbon change occurs here. Between 620° and 600° the Carbon changes

very abruptly, with a very considerable increase in elongation, the recovery of the ductility, as measured by the elongation, seeming to be unduly concentrated into the latter part of the change in Carbon condition. Sauveur* made a very complete microscopic examination of the above steels, and his results in relation to the recalcence points are briefly these:—(1) Above Ar_2 no marked change occurred. (2) The upper part of Ar_2 showed a great change of Martensite to Ferrite, and no other change clearly marked. (3) The lower part of Ar_2 showed a further great change from Martensite to Ferrite, with great loss of tenacity. (4) Between Ar_2 and Ar_1 the only marked change was a considerable loss of tenacity and hardness. (5) Ar_1 showed a great change from Martensite to Pearlite, a great loss of tenacity, a slight loss of hardness, a moderate gain in ductility, and a marked change in Carbon condition. (6) Below Ar_1 there was no further change in structure but a considerable loss in tenacity, a great gain in ductility, a great loss in hardness, and a marked change in Carbon condition.

The general results obtained, together with the extraordinary increase in tensile strength on quenching—from 33 tons to nearly 100 tons per square inch—Professor Howe considered could not be explained by the direct influence of the Carbon and other impurities present, notwithstanding the high percentage of Manganese and Silicon, and he tentatively suggested that the hardening of steel is due, not to the allotropic β iron alone, nor to the Carbon alone, but to a compound of β iron with hardening Carbon, or what may be called a Carbide of β iron: this has been termed the carbo-allotropic theory.

The hardening of practically Carbonless iron by quenching has been a much debated point, but it must now be taken as proved that even the purest iron, with as little as .02 per cent. of Carbon and only traces of other metalloids, does undergo appreciable hardening on quenching, although nothing in comparison to that shown by the high Manganese steel used in Professor Howe's experiments. A sample of this pure steel, with .02 Carbon increased from 19.5 to 29 tons on quenching, and another sample containing .06 Carbon and less than .2 per cent. of Manganese, other impurities being very low, gave a maximum stress of 23.3 tons in the normal and 32.2 tons in the quenched state. Whether such hardening bears any distinct relation to the critical points, or whether it is simply a function of the quenching temperature, is still a matter of dispute, and space does not permit of dealing fairly with the controversy, although it has undoubtedly a most important bearing on the allotropic theory.

Stress Theories.—During the last few years interest has been revived in questions relating to the theories of hardening from the point of view of the effect of a severely strained condition set up as a result of stresses during quenching. These stresses may be due to the shrinkage of the outer layer of metal or to the increase of volume resulting from the change from γ to β or α iron—i.e., molecular stresses.

Work has been published in which these stresses have been considered by Le Chatelier, Charpy, Grenet, Carpenter and Edwards, McCance and Humfrey.

Prof. Carpenter has kindly sent me the following, embodying his present views on the theory of the hardening of steels:—

“Any modern theory of the hardening of steels must take into account, not only the hardening of iron-carbon steels by water quenching, but also that of the so-called special or alloy steels, where a much slower rate of cooling—e.g., that produced by air cooling—brings about the desired result. The

* *Iron and Steel Inst. Journ.*, 1896, vol. i., p. 170.

theory recently put forward by Professor C. A. Edwards and the writer,* which attempts to include all steels that can be hardened, may be summarised as follows:—

“In quenching such alloys as iron-Carbon steels severe stresses are set up, which cause very pronounced crystal twinning. This twinning appears to be directly connected with the intensity of the thermal changes that occur when such steels are slowly cooled, and in particular with the change from hardening carbon to pearlite carbon at Ar_1 (725° C.), a change which is completely suppressed by effective quenching. The increased hardness which is produced by quenching steels from temperatures above their highest critical point is directly related to the velocity and thermal magnitude of this suppressed inversion, and the connection between these factors, crystal twinning, and carbon percentage is very evident. At all the surfaces of slip upon which twinning occurs, amorphous layers are formed—and under the conditions of hardening persist—which are similar to those which Beilby has shown are produced when metals are deformed and hardened by cold-working. We consider that the ultimate cause of hardening by quenching steels is the presence of these amorphous layers. If such is the case it would follow that the final cause of hardening by quenching is exactly the same as that of hardening by cold-working—viz., the internal deformation of the crystals. The means by which this is brought about are, however, different in the two cases. The degree of hardness which is produced by quenching does not depend by any means wholly on the amount of twinning that occurs, unless the comparison is made between specimens of the same chemical composition. The chemical composition certainly has a marked effect upon the quantity of twinning produced in the quenching operation, but the hardness of the mass is also influenced by the molecular constitution of the amorphous layers that are formed. This is rendered evident by the fact that mild steel containing, say, 0.20 per cent. of carbon, when effectively quenched from temperatures above 900° C., is a mass of twinned crystals, but is nevertheless very soft as compared with quenched specimens of steel containing 0.90 per cent. of Carbon. Beilby has shown that the amorphous layers produced by cold-working possess different properties in different metals, and it is permissible to conclude that the hardness of similar layers in alloys will depend to a large extent upon their molecular constitution.

“Data with regard to the chemical and molecular constitution of quenched steels are very scanty and incomplete. Professor E. D. Campbell has shown† that with a given steel the mean molecular weight of the hydrocarbon evolved from the hardened steel is lower than that from the same steel annealed—i.e., the molecular weight of the Carbide decreases when the metal is hardened. More recently ‡ he has shown by a study of the di-nitro derivatives derived from the Carbides in steel that Carbides of low molecular weight are more readily soluble in iron than those of high molecular weight, and have greater hardening effect, and that they tend to dissociate with rising temperature. According to him, the Carbides in steel are to be regarded as ‘metallic substitution products of the hydrocarbons whose molecular weights and molecular constitutions will depend upon the Carbon concentration and heat treatment.’ § As he has pointed out, ‘no hypothesis which assumes a single Carbon atom molecule Fe_3C will satisfactorily explain the products of solution in hydrochloric, sulphuric, or nitric acid. If the increase in

* *Iron and Steel Inst. Journ.*, No. 1, 1914, pp. 138-177.

† *Ibid.*, 1899, No. 2, p. 223.

‡ *Ibid.*, 1913, No. 2, p. 367.

§ *Ibid.*, 1914, No. 2, p. 8.

specific volume of hardened steel compared with that of annealed metal be largely due to the osmotic pressure of the dissolved Carbides, then it would seem, if a single Carbide, Fe_3C , only were present, that the increase in specific volume should be directly proportional to the increase in percentage of Carbon. The very accurate determinations reported by M'Cance clearly show that the specific volume increases in a greater ratio than the percentage of Carbon. This is reasonably accounted for if the molecular weight of the Carbide is recognised, for, as the percentage of Carbon increases, the molecular weight of the Carbides decreases, hence the number of Carbide molecules per unit volume, and consequently the osmotic pressure at a given temperature would increase more rapidly than the percentage of Carbon. Speaking broadly, it may be said that the chemical constitution of hardened iron Carbon steels requires much more investigation than it has as yet received, and which will be needed before a reasonably complete theory of the hardening of such steels can be put forward.

"Coming now to the 'alloy' or 'special' steels, which include all the high-speed tool steels, the theory of their hardening as put forward by Professor Edwards and the writer, is that the special elements present—*e.g.*, tungsten, chromium, vanadium, molybdenum, etc., give rise to the formation of new compounds, which doubtless, owing to their molecular constitution, exert a greater osmotic pressure when in the γ iron solid solution, and lower the temperature at which the Carbon separates from it. They also decrease the velocity of the Carbide change. Their action is such that rapid quenching is not necessary in order to preserve the mass in the same physico-chemical constitution as in the case of properly quenched Carbon steels. *In both cases the Carbide change is inhibited by pressure*, but when this is brought about by external means, such as quenching, twinning of the crystals is produced, whereas when the whole of the osmotic pressure is already inherent in the mass as osmotic pressure, no internal crystalline disturbance occurs. The amount of twinning which is produced by quenching is proportional to the amount of the inversion which has to be suppressed by external means, or inversely proportional to the retarding influence of the special elements present. Hence twinning is entirely absent when the necessary internal pressure is already inherent in the mass—*e.g.*, when the required amounts of tungsten and chromium are contained in the steel.

"For the completion of this theory of the hardening of alloy steels chemical investigations are as necessary as for that of iron Carbon steels, and are even more complicated. It will be essential to determine the molecular constitution of such steels, to ascertain how far a given element enters into the constitution of the solvent, and how far into that of the solute. As Arnold has shown,* some elements—*e.g.*, nickel—seem to enter almost wholly into the solvent, others—*e.g.*, vanadium—combine with the solute, and others again—*e.g.*, chromium—enter into the constitution of both. The modern high-speed tool steel is a very complex alloy, containing not infrequently upwards of 25 per cent. of elements other than iron. Much systematic research on such alloys will be needed before their molecular constitution is adequately understood.

"Mention should be made of two other theories of the hardening of steels which have recently been put forward.

"The first, which was enunciated simultaneously with that of Professor Edwards and the writer, is due to M'Cance,† and is termed the 'Interstrain

* *Proceedings of the Institution of Mechanical Engineers*, March, 1914.

† *Iron and Steel Inst. Journ.*, No. 1, 1914, pp. 192-239.

theory of hardness.' According to this 'during the quenching of steel two transformations can take place, (a) the transformation of γ to α iron, (b) the transformation of Carbon in solution to the state of Carbon out of solution. The first of these can take place independently of the second, but the Carbon cannot change its condition without necessitating the transformation to α iron of the γ iron in which it is dissolved. . . . In a quenched and uniformly hardened steel the Carbon is in the state of solution, and it retains a portion of the iron in the γ condition—the proportion increases very rapidly with the Carbon content. The majority of the iron is, however, in the α condition, but owing to the restricted mobility during the period of quenching, the crystalline units are not homogeneously oriented, and the hardness of quenched steels is due to this condition, which is similar to that of interstrain. The hardness is interstrain hardness.' In a more recent paper M'Cance has extended this theory so as to include the hardening of alloy steels.*

"The second theory is due to Humfrey,† who summarises his position as follows:—'The hard structure which can be produced in Carbon steels by quenching, and in certain alloy steels by normal cooling, is due to the presence of a hard amorphous solution of α iron and iron Carbide, which solution may be compared with Beilby's amorphous phase formed by overstrain. To explain the formation of this amorphous phase the author advances a theory that the passage of a substance from one allotropic modification to another of different crystalline form, involves the temporary formation of an amorphous state corresponding to the liquid phase of the modification about to be formed. In steels, such a change occurs at A_{r3} , and if owing to sudden cooling or to the presence of certain alloyed elements the change point is lowered to a temperature at which crystallisation in the viscous mass becomes difficult, then the amorphous form will be retained in the metastable form in the cold.'

"If these theories be compared with each other, and that put forward by Professor Edwards and the writer, it will be seen that they have one very important point in common. Each theory postulates the complete suppression of the Carbide change. Where they differ is in regard to the condition of the iron. The presence of a hard amorphous phase is common to two of the theories—*viz.*, those of Humfrey and Edwards and Carpenter. On this point M'Cance lays apparently but little stress. According to Humfrey, the iron is completely in the α condition; according to M'Cance it is chiefly in the α but partly in the γ condition; and according to Professor Edwards and the writer it is in the decrystallised γ condition under pressure. These differences of view arise from differences in the interpretation of the magnetic properties of quenched steels, and will not be settled until it has been decided whether iron can or cannot be magnetic in other than the α condition."

It will be seen from the above that recent investigations have tended to harmonise the differences in the older theories of hardening. In view of the much more extended series of phenomena which are now receiving attention, the modern theory of hardening has to be much broader in its scope than previously enunciated theories. Although a vast amount of work has yet to be done, it seems that, as a result of further investigations on the molecular constitution of hardened steels and alloy steels, and on the relation between the condition of the iron and magnetic and other physical properties, we may expect a reasonably complete theory will finally be enunciated.

* *Transactions of the Faraday Society*, vol. x., 1915.

† *Ibid.*