

The life of a metal or of an alloy consists of the transformations, reversible or non-reversible, which such metal or alloy may undergo in the conditions, normal or experimental, of its manufacture or application.

The factors in these transformations are temperature and pressure, and, as their duration is generally measurable, time should also enter into our reckoning. We shall assume in the first place that the pressure remains equal to that of the atmosphere.

The changes which may take place in structure and, generally speaking, in all the properties of a metal, when the temperature varies with a given rapidity, are of two kinds: continuous changes and critical changes.

Critical changes are those which correspond to a sudden modification in the normal relation between a certain property and temperature. On the curves which represent this relation, they are usually indicated by the intersection of two branches.

These critical changes are evidently the most important to be considered, because they divide the whole scale of temperatures into so many intervals in which the body under consideration only undergoes slow, progressive, and, as a result, easily managed modifications. We know also that they indicate a sudden change of energy, which is at the same time the indication and the cause of their occurrence. Knowledge of the sudden changes of energy is therefore one of the first requirements in the study of a body.

Every metal undergoes at least two such changes: fusion and volatilisation. These are the changes of physical state. Certain bodies, undoubtedly much

more numerous than is generally believed, possess other points of transformation which are called allotropic or isomeric changes according to whether they involve simple bodies (iron, nickel, cobalt, carbon, sulphur, phosphorus, etc.), or compound bodies (iodide of silver, iodide of potassium, etc.).

Iron.—If, for example, pure iron be left to cool from the temperature of casting and the temperatures are recorded as functions of time, the curve will indicate three arrests, or at least three retardations, in the rate of cooling. The first, which occurs at about 1530° ,¹ corresponds to solidification; the second which occurs at about 860° and the third, between 750° and 700° , correspond to two allotropic transformations; and the whole curve presents the general aspect of the diagram shown on p. 22.

Spiegeleisen.—If, instead of bodies, simple or compound, but chemically homogeneous, we consider complex bodies, mixtures of several constituents, these mixtures will have as a rule as many points of solidification as the constituents, without speaking of the allotropic or isomeric transformations possible to each constituent.

Spiegeleisen, with 20 per cent. of manganese, has two points of solidification: the first about 1085° , the second about 1050° (fig. 12, B). The diagrams of Professor Martens have also further revealed, in a metal of the same family, two distinct constituents—a definite carbide and a solid solution of the same carbide, more or less dissociated, in an isomorphous mixture of the alloyed metals.

¹ The exact figures are not yet ascertained. Carpenter gives 1519° as the nearest approximation (*Jour. of I. and S. Inst.*, 1908, No. iii, p. 299) and Benedicks (*ibid.*, p. 304) gives 1536° .

This example carries us back to micrography and helps us to understand its use. Micrography, with the aid of chemistry if needful, will assist us to inter-

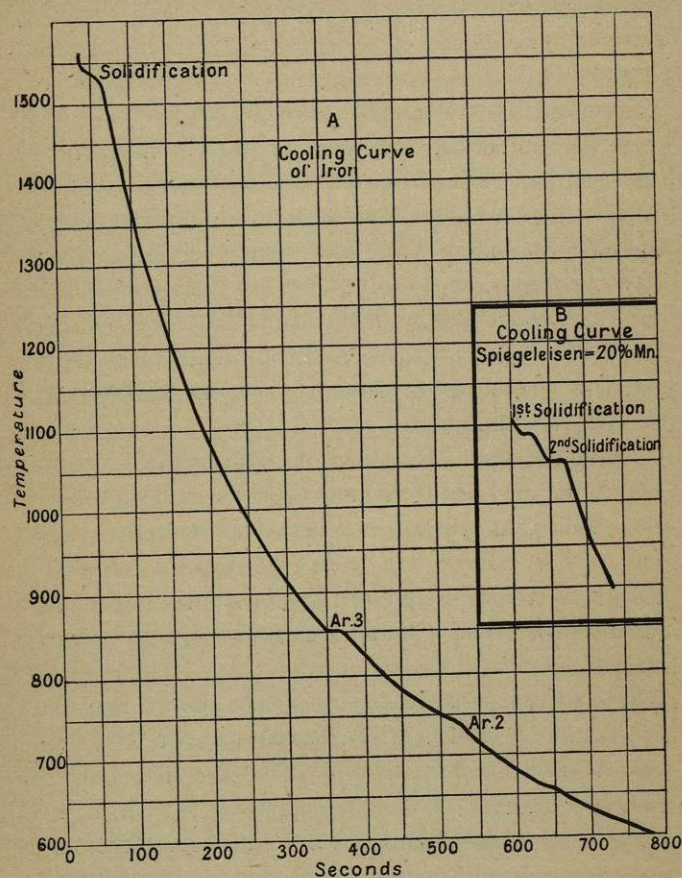


Fig. 12.—Cooling Curve of pure Iron, and 20 per cent, Spiegeleisen.

pret the curves of cooling, and to give the exact signification to these, at times mysterious, yet always so important, points of retardation or of arrest.

Alloys of Silver and Copper.—Let us now pass

on from the study of an isolated alloy to that of the group of binary alloys which two given metals may form between them. These alloys have been investigated by committees appointed by the Institution of Mechanical Engineers in England, and in France by the Société d'Encouragement. If we take as abscissæ the percentage in weight of one of the metals, and as ordinates the temperatures at which the liberations of heat occur during the course of cooling, commencing from the liquid state, we obtain, by joining the corresponding points, the so-called fusibility curves. The aspect of these curves furnishes very useful information on the chemico-physical relations of the metals considered.

Let us take, for example, a relatively simple case, that of the alloys of silver with copper. The fusibility curve of these alloys was plotted in 1875 by Roberts-Austen as exactly as was possible at that time;¹ partly corrected by the same observer in 1891 with the aid of the Le Chatelier² pyrometer, and revised later by Messrs Heycock and Neville.³ This curve (fig. 13) is therefore known exactly; it is composed of two inclined branches starting from the respective fusion points of copper and silver, and cutting at the temperature 770°, for the composition which corresponds to the formula Ag_3Cu_2 . A third branch, horizontal, passes by the point of meeting. This teaches us that copper and silver do not form a definite compound or an isomorphous mixture. If the actual theory of solutions established by H. Le Chatelier be correct, one of the branches of the curve corresponds to the

¹ *Proc. Roy. Soc.*, 1875, p. 481.

² *Proc. Inst. Mech. Eng.*, p. 555 (1891).

³ *Trans. Roy. Soc.*, t. clxxxix, p. 25 (1897).

commencing solidification of the copper, the other to the commencing solidification of the silver, and the horizontal branch to the simultaneous solidification of the two metals. In other words, according to the composition of the alloy, the metal in excess begins to separate out from the solution at a fixed temperature, and continues to be precipitated until the portion

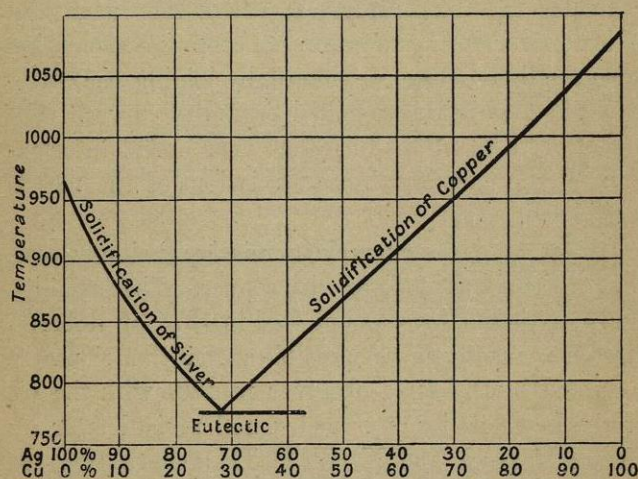


Fig. 13.—Equilibrium Curves, Silver and Copper. (Heycock and Neville.)

remaining liquid contains 72 per cent. of silver against 28 per cent. of copper; at this point the silver is saturated with copper, the copper is saturated with silver, and the two metals simultaneously solidify at a constant temperature in the form of a mechanical mixture. This is the so-called eutectic alloy, the only one the ingots of which do not liquefy, as Levol showed a long time ago.¹

However, as this alloy of Levol gives by analysis,

¹ *Ann. de Chim. et de Phys.*, 3^e série, t. xxxvi, p. 193 (1852).

as exactly as possible, an atomically simple formula (Ag_3Cu_2), and as its surface shows a very clear crystallisation, we hesitate to remove it from the list of definite compounds, and ask if it does not show the theory to be wrong.



Fig. 14.—COPPER = 28 per cent. ; SILVER = 72 per cent. (Cast.) Heat, oxidation tinted. $\times 1000$ diameters.

Micrography solves the question in a most simple and certain manner. It is enough to prepare a well-polished section on which the two component metals are recognised by their respective colours. We can also, by annealing at a suitable temperature, give to copper a beautiful orange patina, whilst the silver

remains white. We thus see that the alloy of Level is not at all homogeneous. Its structure is identical with that of the pearlite of steel; the yellow metal is distributed, sometimes in fine points, sometimes in straight or curved layers, alternating with the white



Fig. 15.—COPPER=28 per cent. ; SILVER=72 per cent. (Cast.)
Heat, oxidation tinted. $\times 600$ diameters.

layers of silver. This alternation after annealing, which causes slight differences of level, gives the known effect of iridescence which the word pearlite recalls. The grains of first solidification can only be suitably brought out under an enlargement of 1000 diameters (fig. 14); they are enveloped in a network

of coarser structure, but quite similar (fig. 15). The alloy with 72 per cent. is therefore an eutectic, as the curve of fusibility would lead us to foresee; and the compound Ag_3Cu_2 does not exist.

In the other alloys of the group, accordingly as the

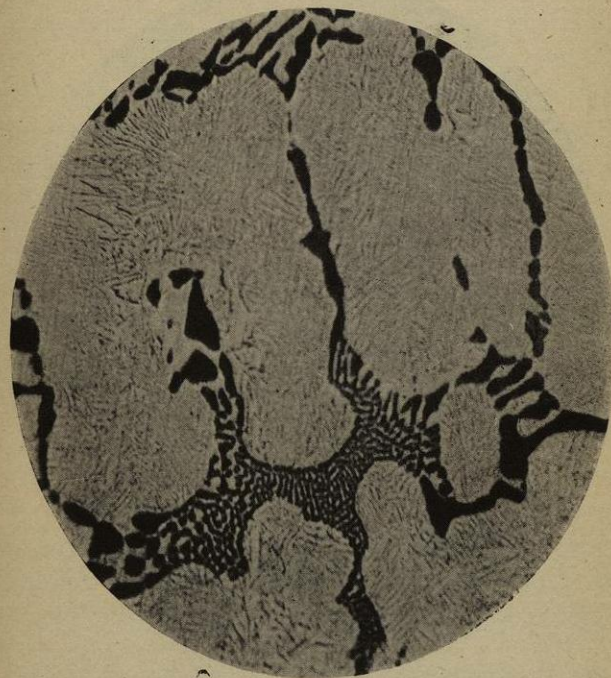


Fig. 16.—COPPER=15 per cent. ; SILVER=85 per cent. (Cast.)
Heat, oxidation tinted. $\times 600$ diameters.

amount of silver is above or below 72 per cent., there are deposited at first either crystallites of silver or crystallites of copper, which increase until the portion remaining fluid attains the desired composition; the eutectic solidifies then, at a constant temperature, and surrounds the crystallites, as figs. 16 and 17 show.

Charpy has studied several analogous cases.¹

The samples photographed were melted in the Leclerq and Forquignon furnace, and slowly cooled in the furnace itself. If the cooling is hastened by

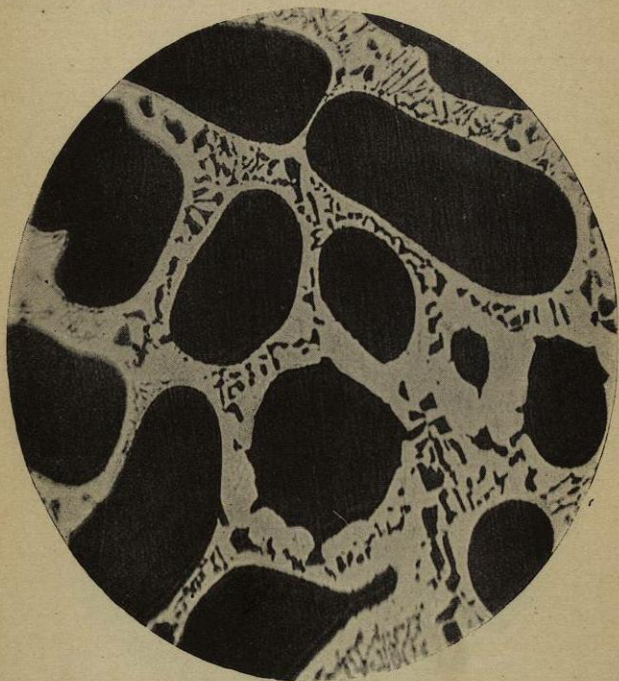


Fig. 17.—COPPER=65 per cent. ; SILVER=35 per cent. (Cast.)
Heat, oxidation tinted. $\times 600$ diameters.

casting the liquid alloy in a cold metallic ingot mould, the eutectic still shows, after annealing to orange colour, a tendency to the formation of the layers which are indicated by the effects of light; but the layers are not clearly distinguished one from the other, and the general colour of the preparation

¹ *Bull. Soc. d'Encouragement*, 5^e série, t. xi. p. 384 (1897).

remains nearly uniform with a high enlargement; the two metals have not had time to separate completely.

In fact, the two constituents of the alloys of copper and silver are not pure copper and pure silver, as might be believed from their respective colours. The copper retains a little silver, and the silver a little copper. We can be assured of this by studying the alloys which contain one of the metals in only a small proportion. The added metal does not commence to appear in independent discernible grains until the proportion of 1 per cent. is exceeded; and, for a higher amount, which is visible, estimated by the extent of the areas, remains less than the proportion added.

Steels.—This brings us to the conception of *solid solution*, of which a very conclusive example is furnished by steels.

Let us take for abscissæ the proportion of carbon from 0.0 to 1.6 per cent., and for ordinates the temperatures, as we have already done. For each proportion of carbon, let us set out on the corresponding ordinate the temperatures at which the different liberations of heat begin: we thus obtain a group of curves (fig. 18).

The branches A_3B and A_2B are those of the allotropic transformations of iron—transformations which Bergmann found out, more than a century before their definite discovery, when he said: "*Adeo ut jure dici queat polymorphum ferrum plurimum simul metallorum vices sustinere.*"¹ The two branches unite in a single one BE when the proportion of carbon exceeds 0.2 per cent., and this double branch

¹ *De analyse ferri*, p. 4 (after Roberts-Austen, *Nature*, Nov. 7, 1889).

cuts, at the point E, another one inclined in a contrary direction, of which we shall see the significance later. Finally, the horizontal A_1EA_1 , passing by the point of intersection, corresponds to the A point of Tschernoff: this is the temperature above which the steel begins to harden by quenching. The passing of the A point is accompanied by a temporary expansion interrupting the regularity of the contraction (Gore),¹ and by a

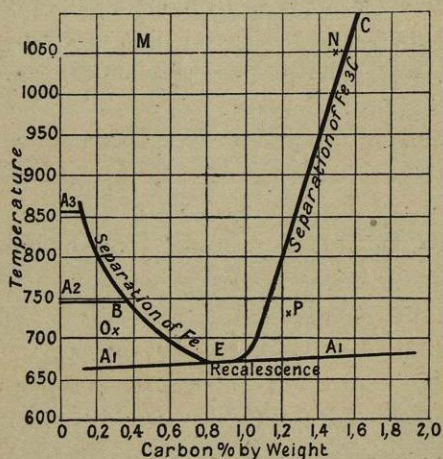


Fig. 18.—Equilibrium Curves, Iron and Carbon.

sudden liberation of heat which sometimes can be distinguished by the eye, whence the name of recalcescence (Barrett).² This phenomenon has been studied from a metallurgical standpoint by the Swedish engineer Brinell³ in a remarkable work, in which the author has been able to replace the instruments he lacked by a rare power of observation. The point E, where the three branches intersect, has for abscissa,

¹ *Phil. Mag.*, 4^e série, t. xxxviii. p. 59 (1869).

² *Loc. cit.*, t. xlvi. p. 472 (1873).

³ *Jernkontorets Ann.*, p. 9 (1885).

according to Professor Arnold,¹ the percentage of 0.9 per cent. carbon, or at least, not to be too precise, a percentage between 0.8 per cent. and 1 per cent.

It is seen that the whole of the diagram exactly recalls the diagram of fusibility of the alloys of silver with copper. On the other hand, micrographic research has shown that the branch BE corresponds to a separation of practically pure iron (ferrite), the branch EC to a separation of carbide Fe_3C (cementite), and the horizontal branch to the simultaneous separation of the two constituents in alternating layers (pearlite). In other terms, steel above BEC is a homogeneous solid solution of the carbide Fe_3C in an allotropic form of iron: during slow cooling this solution deposits either iron or carbide when it is saturated with one or the other, and thus it reaches a definite composition, that of the eutectic; and this is always the same whatever may be the starting-point. These changes take place in just the same manner as in liquid solutions, and the allotropic transformation plays the same part as solidification. Slowly cooled steels are formed, therefore, of a mixture of ferrite and pearlite (fig. 19), of pure pearlite (fig. 20), or a mixture of pearlite and cementite (fig. 21), according as the proportion of carbon is inferior, nearly equal, or superior to the proportion in the eutectic—a proportion which may also vary in presence of other foreign bodies. Thus the microscopic observations of Dr Sorby correspond so exactly to the thermal phenomena, that the former might have led to the prediction of the latter if the theory of solution had been known sooner.

If, instead of leaving the steel to cool quietly, it is

¹ *Proc. Inst. Civ. Eng.*, t. cxxiii. p. 127 (1895-96).

quenched in a cold liquid, the transformations which would be produced during slow cooling are replaced,

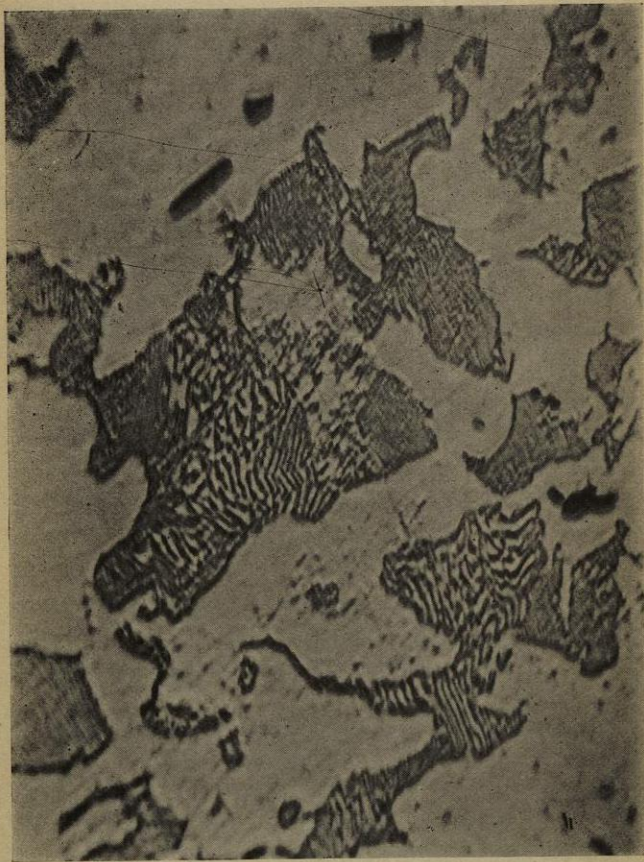


Fig. 19.—FORGED STEEL (0.45 per cent. carbon). Polish-attack.
V × 1000 diameters.

at least in part, because they have not had time to be completed in the interval of temperature in which they were possible. The carbon partially retains the

state of dissolved carbon which it possessed at higher temperatures: it is said that it remains in the state of hardening carbon; and as a dissolved body requires



Fig. 20.—FORGED STEEL (1.00 per cent. carbon). Reheated to 800°.
Polished in bas-relief. V × 1000 diameters.

a solvent, it appears necessary, although this view is energetically combated, that the iron also should be regarded as partially retaining an allotropic form. The theory of tempering, enunciated so brilliantly by

Professor Akerman,¹ still remains in existence: modern researches have extended and completed it without destroying it.



Fig. 21.—CEMENT STEEL (1.57 per cent. carbon). Polish-attack.
V × 1000 diameters.
(Typical laminated pearlite.)

These phenomena are illustrated in the structure.

If the quenching is done above the curve BEC, and as energetically as possible—in iced water, for ex-

¹ *Jour. of I. and S. Inst.*, p. 504 (1879).

ample, — ferrite, pearlite, and cementite disappear. Two cases are possible according as the proportion of carbon is inferior or superior to that of the eutectic. As an example of the first, let us quench a sample of steel with 0.45 per cent. carbon at the temperature 1050°. The commencement of the quenching is then represented by the point M of fig. 18. We obtain a constituent probably homogeneous, formed of needles parallel in the same region, which frequently cut each other parallel to three principal directions (fig. 22). This is martensite. Other things equal, the needles of martensite become smaller and less distinct according as the eutectic is approached; the hardness simultaneously augments up to its maximum. After that the mass does not remain homogeneous. A steel with 1.5 per cent. carbon, quenched at 1050° (point N of fig. 18) in iced water, separates into two constituents (fig. 23). One of the two, designated by the name austenite (this is the clear part of the figure), possesses the unexpected property of being scratched by a sewing-needle: the hardness diminishes then with the amount of carbon, when this proportion exceeds a certain limit.

If we retard the quenching until the temperature has fallen below BEC but is still above A_1E , there will naturally be found in the chilled metal the constituents which have already been isolated during the slow cooling before the commencement of the quenching. Thus, steel with 0.30 per cent. carbon, quenched at 720° C. (point O of fig. 18), will show white ferrite side by side with striated martensite (fig. 23); the steel with 1.24 per cent. carbon, quenched at 735° (point P of fig. 18), will contain cementite, in relief, which appears black under the conditions of illumina-

tion adopted, as compared with the martensite which surrounds it (fig. 24).

Below A_1E the structure is fixed, chilling com-

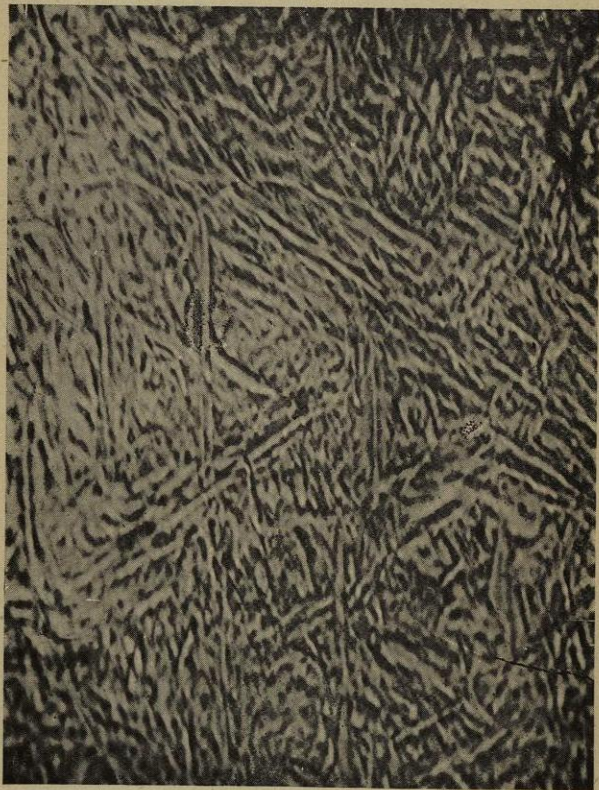


Fig. 22.—FORGED STEEL (0.45 per cent. carbon). Heated to 825°, and quenched at 720°. Polish-attack. $V \times 1000$ diameters.
(*Typical martensite.*)

menced from a point in this region remaining without effect.

Bronzes.—Knowledge of the bronzes is in a much less advanced state than that of steels. The complete

curve has been determined by Dr Stansfield¹ (fig. 26). On page 40 are shown curves which represent



Fig. 23.—CEMENT STEEL (1.57 per cent. carbon). Heated to nearly 1050°, and quenched in ice-cold water. Polish-attack. $V \times 1000$ diameters.

(*Typical austenite.*)

the variations, as functions of the chemical composi-

¹ *Proc. Inst. Mech. Eng.*, p. 269, plates 41 to 43 (1895).

tion, of several of the physical properties:—the electro-motive force (after Laurie), the electric con-



Fig. 24.—FORGED STEEL (0.30 per cent. carbon). Heated to 900°, and quenched at 720°. Polish-attack. $V \times 1000$ diameters.

ductivity (after Lodge), the calorific conductivity (after Calvert and Johnson), the hardness (after Martens), induction (by the Hughes balance), tenacity

(after Roberts-Austen), and the elongation (after Thurston). The majority of these curves are



Fig. 25.—FORGED STEEL (1.24 per cent. carbon). Heated and quenched at 735°. Polish-attack. $V \times 1000$ diameters.

borrowed from Dr Stansfield. Many of them seem to indicate the existence of the definite compounds SnCu_3 and SnCu_4 , to say nothing of isolated inter-