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INTRODUCTION
TO
METALLOGRAPHY

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WITH ILLUSTRATIONS

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AUTHOR'S PREFACE

ALTHOUGH Metallography is a very young science, its study is by no means an easy task, partly due to the fact that in Germany the numerous papers on the subject have not yet undergone systematic collection. Moreover, the nomenclature of the micro-constituents, particularly that of the iron-carbon system, is not universally the same, and conflicting opinions still exist, so that the beginner is easily liable to be misled.

This little work proposes to introduce the learner to the somewhat unfamiliar phenomena of Physical Chemistry, so far as they need consideration for metallographical purposes, and to make it possible for him to obtain a glimpse of the methods of investigating metals and alloys.

The author is well aware that his work cannot claim to be complete, and solicits kind consideration at the hands of his *confrères* in pronouncing judgment on it.

The author is indebted to his esteemed teacher and chief, Prof. Wüst, for inciting him to the compilation of the work, and he hereby expresses his heartiest thanks for the advice and assistance rendered to him.

P. GOERENS.

AACHEN, June, 1906.

TRANSLATOR'S PREFACE

THE pleasure derived from a perusal of Herr Goerens' "Einfuhrung in die Metallographie" is the primary cause of the appearance of this English edition of the work.

The section on Iron and its Alloys differs from the original German in that it has been practically rewritten and thus brought up to date by the author, to whom the translator takes this opportunity of expressing his warmest thanks.

The translator's task was very much lightened by the assistance and advice generously tendered by his friend and colleague Mr. J. H. Wreaks, Demonstrator of Metallography at the University of Sheffield, without whose co-operation the appearance of this edition would have been very considerably delayed.

THE UNIVERSITY, SHEFFIELD,
February, 1908.

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THE PHYSICAL PROPERTIES OF MATTER

Allotropy.—The heat administered to a body is expended in the performance of external work, the elevation of temperature, and the increase of the potential energy of the body. The amount of heat available for doing external work, in the cases of solid and liquid substances, is so small in comparison with the other two, that it may be neglected. The rise in temperature of a body is an indication that its heat-contents have increased. If t denote the temperature in degrees Centigrade before heating, and T the temperature after heating, P the weight of the body in grams, c its specific heat, then the amount of heat taken up is

$$W = P \, . \, c \, (T - t) \text{ heat units} \quad . \quad . \quad . \quad . \quad (1)$$

The total internal energy of a body consists of two parts; the heat-contents expressed by formula (1) and that which may be called here "latent energy." The latter does not lend itself to direct measurement, although in many cases it appears as heat: in consequence it is spoken of as latent heat. If one gram of steam is cooled from about 150° C. under a pressure of one atmosphere, it begins to condense at 100° C. and disengage its latent heat of vaporization. When this has taken place, and 600 units of heat have been evolved into the surrounding medium, the steam at 100° C. has changed into water at 100° C. To change the water into steam again, 600 units of heat must be supplied; during the whole of this time the temperature remains constant at 100° C., although heat is being added. As soon as the condensation of the steam is ended, the temperature sinks regularly to 0° C. Another sudden decrease of the internal energy takes place at this point whilst the water changes to ice. In the converse occurrence, the change of ice into water, 80 units of heat must be supplied to one kilogram of ice at 0° C. in order to convert it into water at 0° C.

The points 0° and 100° are generally designated transition points. In the example chosen of ice, water, and steam, a change in the state of aggregation occurred at these points. Such changes we are able to perceive at once with our senses. According to the kinetic theory, the different states of aggregation are distinguished from one another by the difference in mobility and the corresponding arrangement of the molecules. In the solid state the molecules occupy a definite position at a definite distance from each other. If the distance is increased, or the position altered (extension, twisting), force is called into play, the force of cohesion, which opposes these changes. In the liquid state, the molecules are posited at a definite distance from one another but not in a definite position. Lastly, the molecules, in the gaseous state, are independent of one another in point of distance and position. A direct consequence of these properties of the different states of aggregation is that a solid body retains the shape once imparted to it, a liquid conforms to the shape of the vessel in which it is contained so far as its volume permits, whereas gases fill any space offered to them.

The specified differences in the internal energy of bodies, due to changes in the state of aggregation, are not the only ones, however, to which it is subject. An example will make this point clear. If 12 grams of diamond are burnt to carbon monoxide, 26·1 units of heat are liberated, whilst by using pure carbon obtained from sugar charcoal, 29·0 units are developed. In both cases 28 grams of carbon monoxide result. Although the chemical composition of the initial substance is the same, 12 grams of carbon, the amount of heat developed is different. The same body, carbon, has therefore at the same temperature different properties according to whether it is existent as diamond or as sugar charcoal. These two forms are described as allotropic modifications of carbon. The differences between the allotropic forms of a body are in general not so pronounced as those of the different states of aggregation, and certainly a fundamental difference between the single states of aggregation and the allotropic modifications is not so obvious. On this point Lothar Meyer[1] expresses himself as follows :—

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[1] Lothar Meyer in Watts' *Dictionary of Chemistry*, 2nd Ed., 1888, p. 128.

"The change of one allotropic modification is so similar to the change of one state of aggregation into another, that, strictly speaking, the three states of aggregation of any substance at all must be described as three allotropic modifications of it. . . . The melting of ice, for example, is the conversion of the light into the heavy modification (of water)."

Just as by the conversion of one state of aggregation into another, heat manifestations occur, so also is this the case in the change from one allotropic form into another ; and that which is designated in the former phenomenon latent heat of fusion or latent heat of vaporization, is called in the latter case heat of transformation (Umwandlungswärme).

The following elements occur in different allotropic modifications, and are therefore polymorphic[1]: antimony, arsenic, lead, iron, iridium, carbon, phosphorus, sulphur, selenium, silver, tellurium, zinc, tin.

As in the change from one state of aggregation into another, so also the change from one modification to another takes place at a definite temperature. In this respect the two changes are again very similar. It is well known that it is possible to cool water below 0° C. without freezing it ; this is spoken of as an under-cooling. Frequently a slight disturbance (*e.g.* the introduction of a small particle of ice) suffices to destroy this condition. The water then suddenly freezes to ice and the heat thereby liberated raises the temperature almost to 0° C. Further, the position of the freezing-point is influenced by the presence of a third body. Similarly, in allotropic transformations, under-coolings, as well as the effect of a third body, have been observed. The latter may be so large as to depress the transformation-point more than 100 degrees of temperature.

The position of the transformation points is clearly shown by graphic representation. Correspondingly, when a heated body is subjected to a slow cooling, a retardation in the fall of temperature takes place at those points at which heat was liberated. Time and temperature being selected as co-ordinates, the former as abscissæ and the latter as ordinates, the cooling curve of the body under observation is obtained by joining the separate points by a line.

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[1] Landoldt-Börnstein's *Physikalisch-chemische Tabellen*. Berlin. G. Springer. 1905.

Fig. 1 shows in this way the curve for pure platinum cooled from 1000° C. The behaviour of steam cooled from 150° C. is depicted in Fig. 2. The cooling is at first regular down to 100° C.; at this point condensation occurs, and for a period of *ab* minutes, during which the phenomenon lasts, the temperature remains constant at 100° C. When condensation is complete, the temperature again sinks regularly to 0° C., when water freezes to ice. Heat is again liberated by this occurrence, and the temperature remains constant at 0° C. until the whole mass has become solid. If under-cooling takes place, the curve continues regularly below 0° C., to rise at the moment of freezing almost to the freezing-point; this is indicated by the dotted part of the curve in Fig. 2.

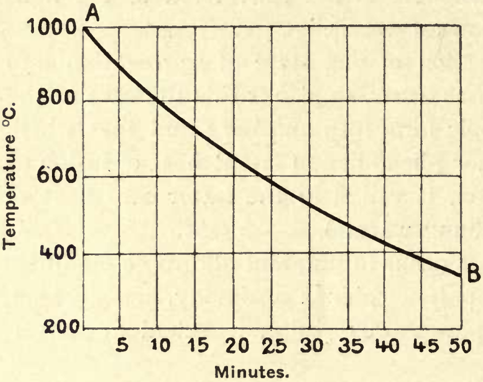

FIG. 1.—Cooling curve of pure platinum.

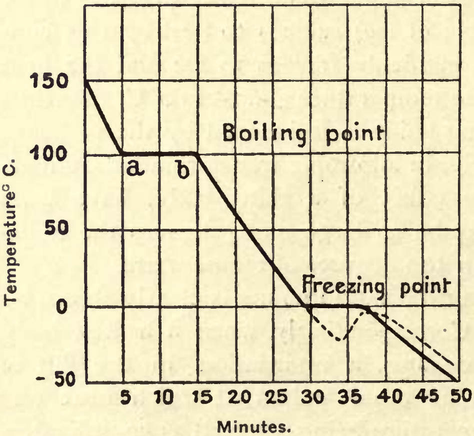

FIG. 2.—Cooling curve of water.

Should the material under observation undergo allotropic changes in addition to changes in the state of aggregation, they frequently find expression in the cooling curve. Fig. 3 shows the curve for chemically pure iron, to which we shall return later. The first break in this corresponds to the solidification point of iron, 1505° C., and between this temperature and 880° C., the iron exists as the γ-modification. This changes at 880° C. into the second or β-modification, which changes again at 780° into the third or α-modification. At the latter temperature iron acquires the property of being attracted by a magnet, which is not the case above it. The last two transformation points are denoted by the letters Ar_2 and Ar_3, according to Osmond's[1] original proposal. On heating a piece of iron retardations occur (see the dotted curve of Fig. 3) corresponding to both transformation points,

$$\alpha\text{-Iron} \rightarrow \beta\text{-iron and}$$
$$\beta\text{-Iron} \rightarrow \gamma\text{-iron}$$

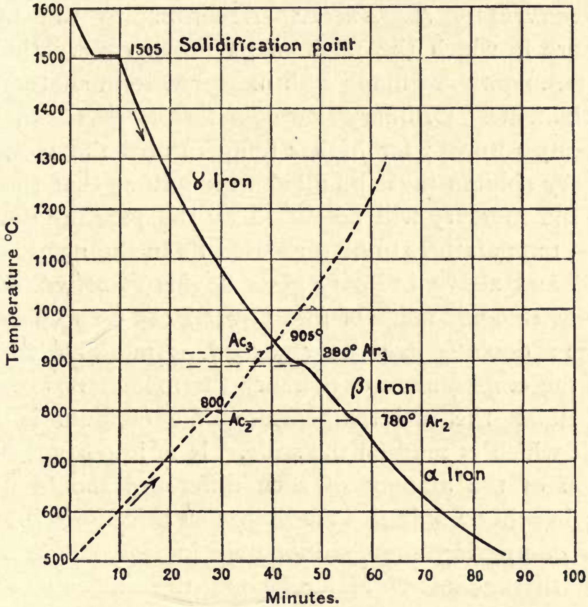

FIG. 3.—Cooling curve of pure iron.

although at a somewhat higher temperature than in the cooling, viz. at 800° C. and 905° C. These points are called Ac_3 and Ac_2. The difference in temperature between Ar and Ac is called hysteresis. According to Fig. 3, the hysteresis amounts to 20° and 25° C. respectively.

The heat-changes at the transformation points of a substance are not always sufficiently large to admit of establishing with certainty by means of temperature measurements. Nevertheless,

[1] Osmond, *Mikrographische analyse der Eisen-Kohlenstofflegierungen*, W. Knapp, Halle, 1906.

as in most cases, other physical properties, *e.g.* the specific gravity, the system of crystallization, the electric conductivity and the magnetic properties undergo a sudden change, the transformation points can frequently be determined with sufficient accuracy by their means.

Cooling curves.—As appears evident from the foregoing, the plotting of the cooling curve of a body affords a valuable means of determining possible critical points. For this purpose it is necessary to make a large number of consecutive measurements of temperature, with which matter we must therefore deal first.

Measurement of temperature.—According to the range of temperature in which the phenomena under observation occur, the measurements are made with mercury thermometers or with thermo-elements. Ordinary thermometers of glass can be used for low temperatures; for higher temperatures the space above the mercury column must be filled with gas, so that the boiling point of the mercury will be raised by the pressure developed. When the temperatures to be measured lie in the neighbourhood of 500° C. and above, ordinary glass begins to soften, on which account instruments made of fused quartz can be employed with advantage; 600° C. may be regarded as marking the upper limit for the employment of mercury thermometers.

In general, the real temperature of a medium is different from that which is read on the scale. It is important then that a decision of the amount of such difference should be forthcoming; in other words, the reading must be corrected. This is done by comparing the thermometer in use with a so-called "normal thermometer," and referring the indications of the former to those of the latter. This comparison is carried out practically by placing the instrument under investigation and the normal thermometer together in a liquid which is slowly and uniformly heated with continuous stirring; the corresponding values read off from the two scales are embodied in a table, from which in subsequent measurements the corrected temperature values can be read at once.

EXAMPLE I.—In the following table the corresponding readings of the two thermometers are placed opposite one another. What correction must be made for the thermometer *A* under investigation to reduce the values to those of the standard thermometer?

Normal thermometer Temperature t_n	Thermometer A Temperature t_A
100	100·5
101	101·5
105	105·5
150	150·5

It is seen that all the readings are 0·5° C. too high. Therefore for the thermometer A we have

$$t_n = t_A - 0{\cdot}5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

EXAMPLE 2.—The following table shows the same values for a thermometer B under investigation.

t_n	t_B	$t_B - t_n$
0	0·40	0·40
5	5·42	0·42
10	10·44	0·44
15	15·46	0·46
20	20·48	0·48
25	25·50	0·50
30	30·52	0·52

It is seen from the table that the initial difference of 0·40° is increased by 0·02° for a rise of 5° C. in temperature. As this is the case uniformly in the observed range of temperature, the correction formula

$$t_n = t_B - \frac{0{\cdot}02}{5} t_n - 0{\cdot}40 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

answers for the case submitted. From it we have

$$t_n = 0{\cdot}996 t_B - 0{\cdot}398 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

For exact work, a further correction must be made for the varying temperature of the mercury column, the so-called column correction. The normal thermometer is calibrated at a standardizing institution in such a way that the thread possesses the same temperature as that of the remainder of the mercury. As in most investigations which come under consideration here, the scale projects out of the heated material, the value

$$n\beta(T - t)^1$$

---

[1] Landoldt-Börnstein, *Physikalisch-Chemische Tabellen.* Dritte Auflage, 1905, Seite 195.

must be added to the reading. In this formula n represents in degrees the length of the projecting part of the mercury column, β the apparent coefficient of expansion of mercury in glass $\left(\beta = \frac{1}{6300}\right)$, T the measured temperature and t the mean temperature of the projecting column.

It suffices generally, however, at 100° C. to add 0·01° for each degree of the projecting thread, at 200° C. 0·02°, and correspondingly more for higher temperatures.

In all cases where the temperature to be measured lies above 500° C., the employment of a thermo-element for the measurement is to be recommended. This instrument depends upon the following principle. If two wires of different metals *A* and *B* (Fig. 4) whose ends are fused together at *C* whilst the other free ends *D* and *E* are connected by a leading wire, are heated at the point *C*, a current of electricity is developed in them, the electromotive force of which depends on the difference of temperature between *C* on the one hand, and *D*, *E* on the other.

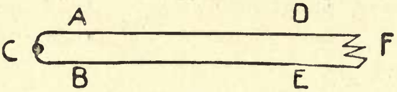

FIG. 4.

The Le Chatelier thermo-element consists of one wire of chemically pure platinum and a similar one of platinum alloyed with 10 per cent. of iridium or rhodium. Both wires are fused or twisted together at one end, so that there is intimate metallic contact. An indicating galvanometer (Fig. 5) serves to measure the current, and besides a scale *S′* for the electromotive force, it possesses a similar one, *S*, for the temperature, so that it is not necessary to make special calculations.

FIG. 5.—Millivoltmeter.

Whereas mercury thermometers are affected little or not at all by frequent usage, this may happen much more readily in the case of thermo-elements. Should the wires when heated be brought into contact with substances which change them chemically (vapour of sulphur and phosphorus, most molten metals), the electromotive force of the element alters, and, in consequence, the indicated temperature. In this connection gases containing carbon are particularly dangerous, as they impart carbon to the platinum and make it perfectly friable, so that it can no longer be used in the construction of a thermo-element. For this reason it must be specially noted, in fusing the ends of the wires together in the blowpipe flame, that the latter is always of an oxidizing nature and never contains an excess of hydrogen or of hydrocarbon. In general, it is better not to fuse the wires, but only to scrape them bright and twist them tightly round each other.

From the foregoing the necessity arises of frequently checking the indications of the pyrometer. This is best done by measuring the melting-point of known substances with the thermo-element under examination, and comparing the values obtained with the corresponding accurate ones given by the air thermometer. In the following table a number of such fixed points, according to the determinations of Holborn and Day,[1] are collected together.

Substance.	Melting-point 0° C.
Lead	327
Zinc	419
Antimony	630·5
Silver	961·5
Gold	1064

The prosecution of such a determination generally takes the following form. One wire of the thermo-element is isolated from the other by means of a very thin porcelain tube *A* which slides over it (Fig. 6). The whole stands in a wider tube *B* made of difficultly-fusible glass, glazed porcelain, silica glass, or similar material impervious to metallic vapours. A known amount of the substance employed is heated above its melting-point in a crucible *C* and the pyrometer fastened in the manner sketched, care being taken that the point *D* at which the wires are fused together, is in the centre of the mass. The cold ends of the wires are coupled up by means of brass clamps with copper leads (about

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[1] Holborn and Day, *Annalen der Physik*, 2, 505, 1900.

2 mm. thick) and placed in test tubes, which are immersed in a reservoir containing melting ice. The copper wires finally conduct the generated current to a galvanometer. Before connecting them with the terminals of the galvanometer, the latter must be set perfectly horizontal, for which purpose the spirit level *B* is attached to the instrument. The mechanism for arresting the needle is then released, and it can then be seen whether the indicator comes to rest at the zero point. If this is not the case, it must be set to zero. When the crucible is then allowed to cool slowly, the temperature remains constant for a time during the solidification of the mass. When it has begun to sink further, the crucible is re-heated, when a halt in the rising temperature is again observed during the melting. The heating and cooling must be conducted so slowly that both arrests take place at the same time. Possible under-cooling is prevented by stirring or by dropping in a small fragment of the solid substance (inoculation, seeding).

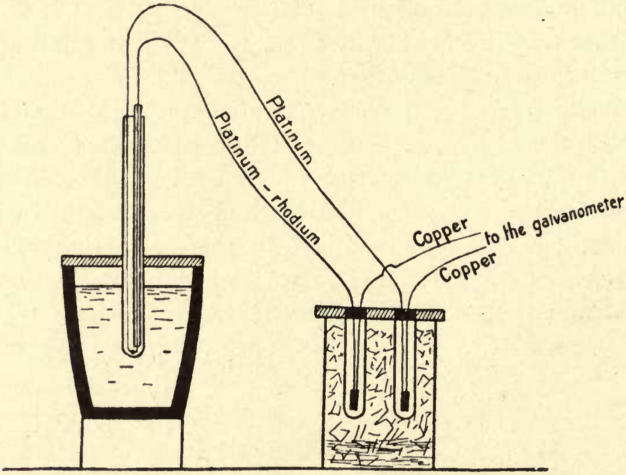

FIG. 6.

From the values thus obtained for the melting-points of different substances a correction table is projected similar to what we saw in the case of the mercury thermometer.

EXAMPLE.—By means of the thermo-element under investigation the following points were determined—

Melting-point of lead	320° C.
„ „ „ antimony . .	623° „
„ „ „ gold . . .	1053° „

According to the table on p. 9, the actual melting-points of the elements given by the air thermometer are, for lead 327°, antimony 630·5°, gold 1064° C.

The differences found amount therefore to—

$$
\begin{aligned}
327 - 300 &= 7^\circ \text{ C. at } 327^\circ \text{ C.} \\
630{\cdot}5 - 620 &= 7{\cdot}5^\circ \text{ C. „ } 630^\circ \text{ „} \\
1064 - 1053 &= 11^\circ \text{ C. „ } 1064^\circ \text{ „}
\end{aligned}
$$

Up to a temperature of 630° C., the addition of a constant number 7° C. to the values obtained gives a sufficient approximation. Above this, a further amount besides the 7° C., must be added, which is found as follows—

From 630° to 1064° there are added $11 - 7 = 4^\circ$ more, hence the correction amounts to 4° for a range of $1064 - 630 = 434^\circ$, giving a correction for 1° of $\frac{4}{434}$. In other words, for every degree above 630° C., there must be added, in addition to the constant 7°, the amount $\frac{4^\circ}{434}$. From this the formula for correction becomes—

$$T = t + 7 + \frac{4}{434}(t - 630)$$

where T denotes the temperature in 0° C. given by the air thermometer, and t denotes the temperature in 0° C. found by the pyrometer.

The preceding calculations give correct values only on the hypothesis that the cold ends of the wires, which are joined to the copper leads with clamps, are actually at 0° C. If ice is not available for the experiment, water is placed in the reservoir containing the test tubes instead. The galvanometer remains set at zero. By warming up to the room temperature a current is developed in the cold junction opposite to that proceeding from the hot junction. The electromotive force, a, of the new current nullifies a certain amount of the main current. These a volts represent on the scale a certain number of degrees, which is the smaller, the higher the temperature of the hot junction.

The correction to be made amounts therefore to a fraction only of the room temperature, and the factor, with sufficient accuracy, can be taken from the following table—

Temperature	k	Temperature	k
0°	1·00	600°	0·54
100°	0·89	700°	0·52
200°	0·76	800°	0·51
300°	0·65	900°	0·50
400°	0·59	1000°	0·49
500°	0·56		

The formula for correction reads, according to the foregoing

$$T = t + kt',$$

where T is the temperature of the hot junction referred to zero,
t the registered temperature,
t' the temperature of the cold junction,
k the factor, selected from the above table, for the temperature concerned.

Attention must be here directed to a still further correction. In drawing up cooling curves, an arrangement of the thermo-element like that represented in Fig. 7 is employed. Let us suppose that a thermo-element, protected by the tubes A and B, is immersed in a mass S, and that the whole system is at the temperature T_a°. At a given moment let the substance begin to cool, and the rate of cooling be uniformly a, *i.e.* in one second let the temperature fall a°. After a certain time, n seconds, the temperature of S will be—

$$T_b = T_a - na.$$

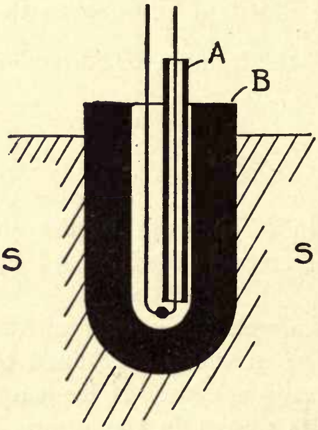

FIG. 7.

Now, usually the tube B is so poor a conductor of heat that it cannot give up its heat quickly enough; therefore, after the time n, its temperature will be rather higher than that of the mass S. The quicker the cooling, the greater this difference $T_c - T_b$. Hence it follows that—

$$T_c - T_b = ka \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In just the opposite manner, in the heating of S, the indicated temperature of the inner tube is lower than that of S.

Further, the amount is proportional to the rate of increase of temperature. If e is the rate of heating, T_b the temperature of S and T_d that of the inner tube, then—

$$T_b - T_d = ke \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2) it follows that—

$$\frac{T_b - T_d}{T_c - T_b} = \frac{e}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Another form of this expression is shown by the following formula—

$$T_b = \frac{e}{a + e} T_c + \frac{a}{a + e} T_d \quad . \quad . \quad . \quad (4)$$

GRAPHIC REPRESENTATION OF COOLING CURVES.

The simplest method of graphic representation consists in plotting temperature as a function of the time. To this end temperatures are read, say every 5 seconds, on the thermometer or galvanometer scale, and the points obtained joined by a continuous line.

EXAMPLE 1.—A molten mass of zinc, allowed to cool in a crucible, shows the following temperatures at the various time intervals.

Temperature 0° C.	Time in seconds after commencement of experiment.
480	0″
470	5″
461	10″
452	15″
443	20″
434	25″
425	30″
419	35″
419	40″
419	45″
415	50″
406	55″
397	60″

The readings must of course be corrected according to the rules given above. From the above table the cooling curve is constructed by choosing seconds for abscissæ and temperatures for ordinates, as is shown in Fig. 8.

This method of representation applies only to those cases in which the phenomena in question last long enough to admit of expression in a curve obtained in this manner. This is mostly the case in the phenomena of freezing but not so in many allotropic changes.

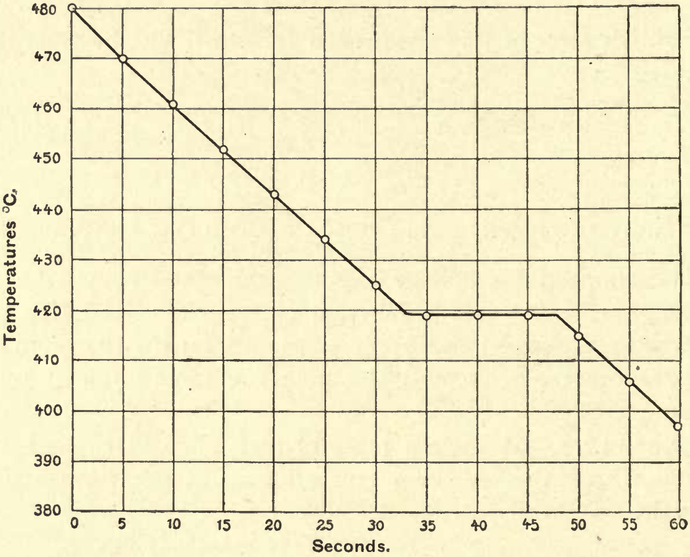

FIG. 8.

Osmond therefore depicts cooling curves in this way: temperatures are selected for the abscissæ and for ordinates the number of seconds taken in cooling the body through a definite interval of temperature.

EXAMPLE.—Fig. 9 shows a cooling curve (grey pig iron), drawn up from the following table in the manner just described.

Minutes from beginning of experiment.	Temperature 0° C.	Minutes from beginning of experiment.	Temperature 0° C.
0	1300	6	1154
2	1242	8	1135
4	1197	10	1130

Minutes from beginning of experiment.	Temperature 0° C.	Minutes from beginning of experiment.	Temperature 0° C.
12	1124	32	720
14	1120 arrest	34	702 arrest
16	1117	36	702
18	1065	38	685
20	1000	40	650
22	945	42	615
24	896	44	585
26	847	46	564
28	800	48	523
30	760	50	500

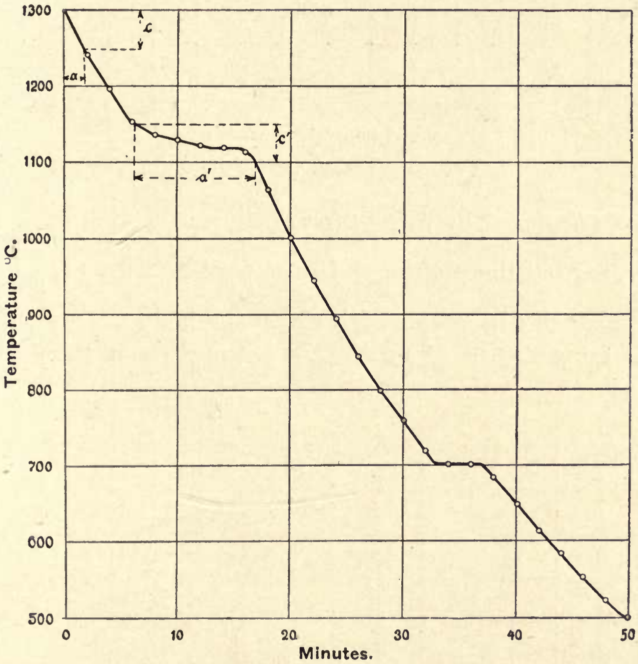

FIG. 9.

It is seen from Fig. 9 that *a* represents the number of minutes taken in cooling the body from 1300° C. to 1250° C., *a'* the number in cooling from 1150° C. to 1100°. Osmond's curve is derived by determining these values *a* every 10 degrees, and plotting them as ordinates in a system whose abscissæ show the corresponding temperatures. This is done in Fig. 10. One can see that this method yields a very striking diagram, but it does not, however, suffice for the accurate determination of the real positions of the arrest points, as the ordinates are the equivalents of temperature intervals and not of temperatures. Greater success is achieved by using the velocities of cooling as ordinates in carrying out the plotting. In the curve of Fig. 11, $\frac{c}{2}$ denotes the number of degrees through which the body cools per second at the temperature of 1300° C. During an arrest point the velocity is zero, and the curve will then reach the axis of abscissæ. Fig. 11 shows the velocity diagram corresponding to the curves of Figs. 9 and 10, and is important in connection with the automatic representation of cooling curves.

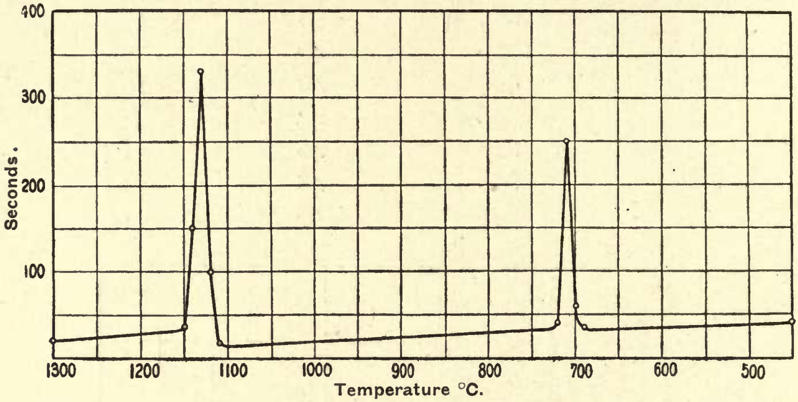

FIG. 10.—Cooling curve (Osmond).

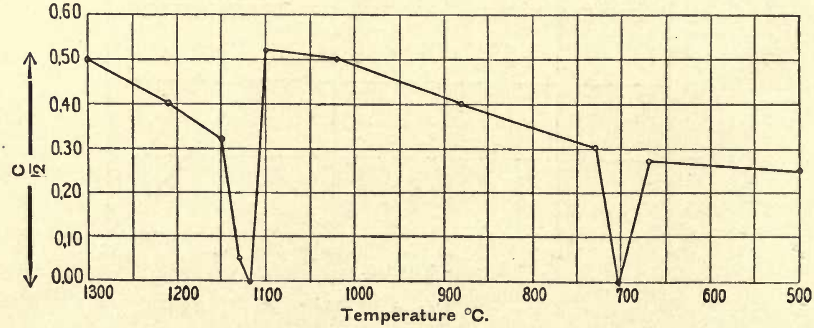

FIG. 11.—Curve showing rate of cooling.

PROSECUTION OF EXPERIMENTS.

When it is a question of plotting the cooling curve of melts which are liquid below 400–450° C., mercury thermometers can be employed for temperature measurements. In order to obtain comparable results, it is advisable to use constant weights of material in the whole series of experiments and to adhere as uniformly as possible to the conditions specified above. Fig. 12 shows an experimental arrangement suitable for the examination of lead, tin, bismuth, cadmium, and similar alloys. The weighed metals are placed in a test tube of hard glass *A* protected by an outer iron tube *B*, which is clamped to a retort stand. The space between *A* and *B* is filled with sand or finely powdered fire brick. The alloy, after adding a little wax, charcoal, or similar substance to protect the melt from the influence of the air, is melted by means of a bunsen burner. When the mass is thoroughly liquid, a glass rod *D*, whose lower end is fastened to a ring, is introduced to act as a stirrer, and then the previously warmed thermometer *C* is placed with its bulb in the middle of the bath of metal. When the heating has been carried somewhat beyond the point of fusion, the melt is allowed to stand whilst the stirrer is moved regularly up and down. At regular intervals, about every half minute, the temperature is read off. The stirring is continued throughout the readings, but only to the moment at which a decided resistance is experienced. When, namely, the freezing begins, further stirring would operate prejudicially by separating the crystals from the still liquid mass and preventing further reaction with them.

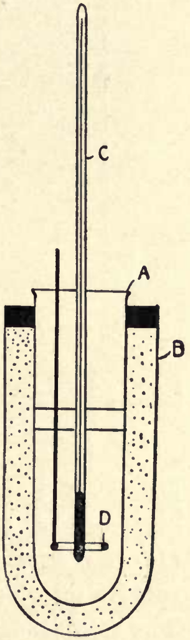

FIG. 12.

When the cooling conditions are to be investigated at temperatures below that of the room (freezing points of easily fusible amalgams) a Dewar vessel (Fig. 13) filled with solid carbon dioxide can be employed with advantage. This consists of a glass cylinder *D* with double walls, which is made vacuous. The vessel is filled with solid carbon dioxide and the test tube *K* introduced. Temperature observations and stirring are conducted as above.

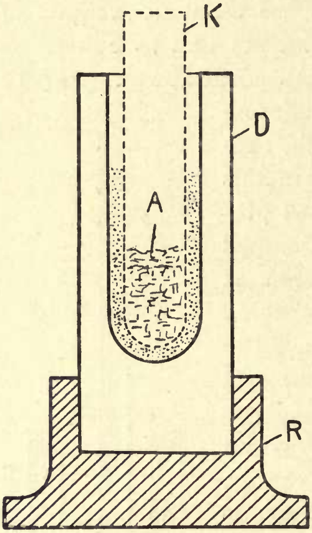

FIG. 13.—Dewar's vessel.

When the experiments must be carried out at temperatures which do not admit of the use of mercury thermometers, or if for any other reason they are inadmissible, a thermo-element is used with the arrangement of the experiment like that employed for calibration (Fig. 6, p. 10).

In many cases one is compelled to let the cooling proceed so rapidly that observations with a seconds watch do not suffice, on account of the large number of readings. In such cases a chronograph (Figs. 14 and 15) is employed for measuring time.

A cased-in clock-work mechanism, whose movement is controlled by the centrifugal regulator *R*, sets the drum *A* in uniform revolution by means of a pair of toothed wheels, *F*. The drum has a diameter of 300 mm., and makes one revolution per minute. On the axis of the first toothed wheel there is a leading spindle on which a square-threaded screw of 2 mm. pitch is cut. The spindle carries, as with turning lathes, a slide bearing the marking pencil *B*. To right and left of this pencil there is a pair of electro-magnets, *C*; when an electric circuit in these is completed, they attract the arm which carries the pencil, thus subjecting the latter to a deflection. When, therefore, the clock-work is in action, the pencil describes on a sheet of paper stretched over the drum a continuous spiral line of 2 mm. pitch; if the circuit is closed once, or several times, interruptions occur at the corresponding points of the line. During one minute the pencil describes the circumference of the drum once, and therefore draws a line of 300 mm. length. One second corresponds in consequence to 300 ÷ 60 = 5 mm. Therefore, should there be, *e.g.* two interruptions following one another at a distance of 35 mm., 35 ÷ 5 = 7 seconds have elapsed between the two closings of the circuit.

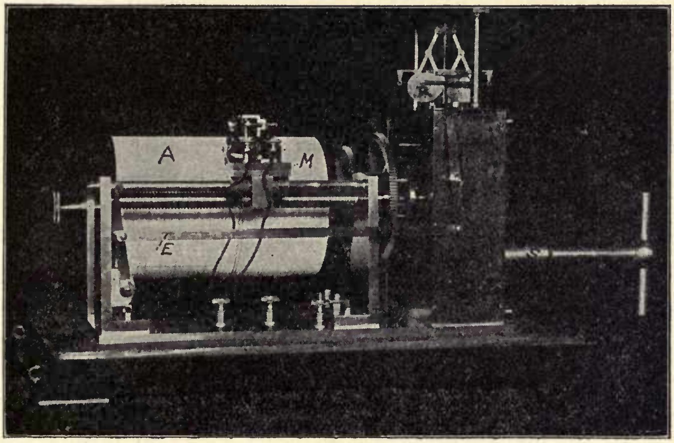

FIG. 14.—Richard's Chronograph (side elevation).

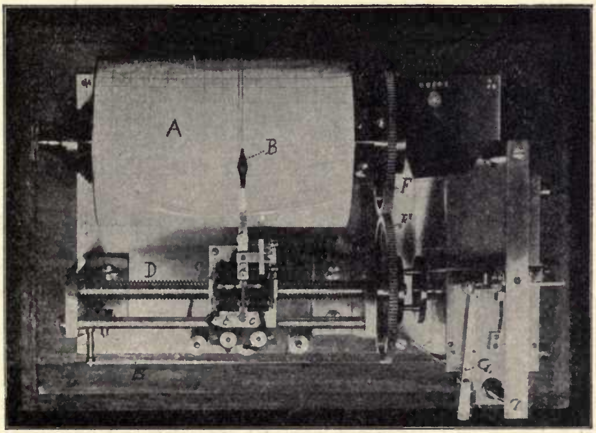

FIG. 15.—Richard's Chronograph (plan).

The starting and stopping of the clock-work is done by means of the lever *E G*, and the winding by the key *S*. When the slide has reached the end of its travel, it strikes against one arm of the lever *E* so that the clock-work is arrested automatically.

The following arrangement for carrying out experiments on cooling has become established.

When the crucible with its molten contents is ready to be removed from the furnace, the projecting tube of the thermo-element is heated at its end in the blow-pipe flame, so as to prevent its springing when inserted subsequently in the molten mass. The crucible being in position, the tube is introduced, and the crucible covered with a lid divided into two pieces. At the same time the clock work is set in motion by releasing the brake. The wires of the thermo-couple lead from the tube to an ice chest where their ends are connected to copper leads of at least 1 mm. in thickness by means of brass clamps; the copper wires lead to the galvanometer which stands in a place not subjected to vibration. The galvanometer needle is then observed through a magnifying glass. Each time it passes a division on the scale of temperatures, the current (from three cells) is completed through the electro-magnets by striking the lever of the contact-maker with the hand. The needle is thereby deflected, and this is repeated every 10° C.

When the cooling is finished, the paper is cut away from the drum, the temperature corresponding to each interruption entered, and the distances between them measured. The fifth part of these distances expressed in millimetres gives the number of seconds taken by the mass in cooling down through 10° C.

All the methods described up to the present necessitate individual observations, and are therefore subject to unavoidable errors. To eliminate these, efforts were made to hit upon arrangements which would make possible an automatic registration of cooling curves. To the credit of Roberts-Austen in particular must be placed the construction and perfecting of this apparatus; he described his various installations in detail in the Fifth Report of the Alloys Research Committee of the Institution of Mechanical Engineers (see footnote on p. 22).

The principle of his first arrangement consisted in leading the current generated in the wires of a Le Chatelier thermo-couple to the actuating coil of a mirror galvanometer. A beam of light which fell on the mirror was reflected by it upon a sensitive plate, and moved in a horizontal direction by the rotation of the mirror. Simultaneously the plate was made to move by a special contrivance in a vertical direction, so that the curve traced on the plate by the beam of light showed both time and temperature changes.

It proved, however, that the cooling curves developed in this manner did not register distinctly slight deviations in the fall of temperature. The employment of a more sensitive galvanometer was impossible, on account of the altogether too large impulses for greater differences of temperature, as on the one hand the suspension wires of the coil were then strained too much and the zero point was inconstant, and on the other hand, the apparatus became unwieldy on account of the necessarily large dimensions of the plate.

A greater improvement consisted in directing a constant current in opposition to the current in the thermo-couple, so that only the difference between both reached the galvanometer, which could then be made sufficiently sensitive.

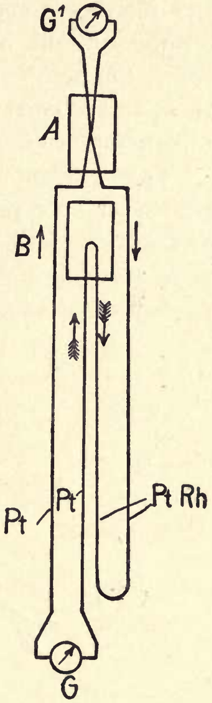

FIG. 16. — Compensation arrangement for determination of cooling curves (Roberts-Austen).

Finally, Roberts-Austen undertook a further improvement, which is described in his fifth and last report, and which we shall here discuss further. The following is the principle: let *A* be a body (Fig. 16) which exhibits no critical points in the range of temperature under consideration. Into this a thermo-element is introduced in which, if *A* be heated, a current is generated which has the direction platinum to platinum-rhodium at the junction (smooth arrows). Let *B* be the body under investigation also provided with a thermo-couple; the current generated in this is indicated by the feathered arrows. When both thermo-elements are coupled up in opposition, *i.e.* platinum connected to platinum and platinum-rhodium to platinum-rhodium, the whole system acts as a thermo-couple one of whose junctions is at *A* and the other at *B*. The current through the system gives, therefore, the difference of temperature between *A* and *B*; this is zero so long as *A* and *B* are at equal temperatures. Should a retardation of the fall of temperature *B* occur, the temperature of *A* will sink more quickly than that of *B*, and a current is generated which can be measured in the galvanometer *G*.

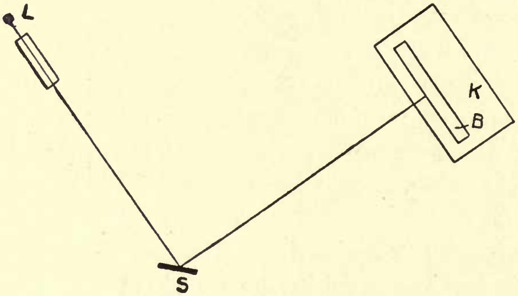

FIG. 17.

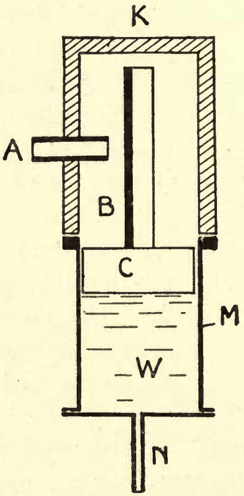

FIG. 18.

The galvanometer deflections were registered on a photographic plate, which was subjected to a uniform displacement in a vertical direction. Roberts-Austen employed for this purpose the following contrivance: A source of light, *L* (Fig. 17), projects the image of a narrow vertical slit upon the mirror *S* of the galvanometer which reflects the light upon the side of a box, *K*, containing a horizontal slit, *A* (Fig. 18). The light passes through the latter and falls upon a sensitive plate, *B*. This is fixed in an upright position upon a box, *C*, which floats on a water-bath *W*. When water is conducted into the box at a uniform rate, the level rises regularly and raises the box, *C*, and the plate. The curve thus obtained is the combination of the time with the difference of temperature of the bodies *A* and *B*. In order to determine at what temperatures of *B* the recalescence takes place, the temperature curve must be taken at the same time as that of the difference of temperature. This can, for instance, be done as follows: a third thermo-element is introduced into the system (Fig. 16) and the current is measured by a less sensitive galvanometer, *G'*. The latter can be set up in such a way (Fig. 19) that its mirror throws the image of a second source of light upon the same plate, whereupon two curves are now recorded, which have one of the co-ordinates (that of time) in common.

The use of a third thermo-element can be obviated by switching off the current coming from *B* and leading it direct into a galvanometer *G'*, as Roberts - Austen[1] does.

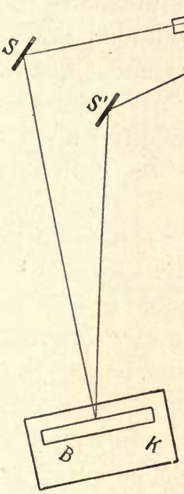

FIG. 19.

Professor Heyn[2] has given to the whole arrangement a form through which possible larger differences in the temperature readings evoked by the great distance between the two pieces *A* and *B* may be avoided. In Fig. 20, I. represents the sample under experiment, II. a similar body made of porcelain. The bodies are joined and worked together so that the whole possesses a cylindrical form, whereby the radiation becomes very uniform.

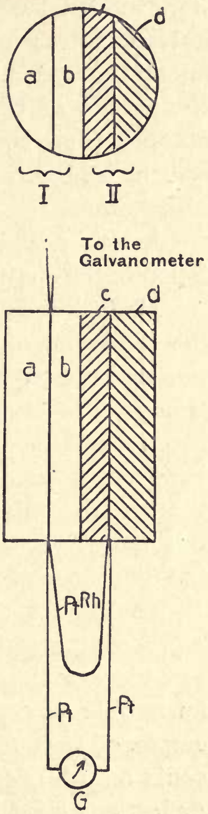

FIG. 20.—Compensation arrangement for determination of cooling curves (Heyn).

A further method for the determination of the cooling curve with time and temperature as co-ordinates was introduced by Charpy.

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[1] Roberts-Austen, "Five Reports to the Institution of Mechanical Engineers." *Proceedings*, 1891, p. 543; 1895, p. 238; 1893. p. 102; 1897, p. 31; 1899, February.

[2] E. Heyn, *I. Bericht über die mikroskopische Untersuchung der, etc. Verh. des Ver. zur Bef. d. Gewerbefleisses.* November, 1904, Berlin.

For the production of a regular movement he employs clockwork similar to the chronograph previously described, which sets in regular motion a cylinder covered with sensitive paper and contained in a light-tight box. The axis of this cylinder is horizontal. Two pencils of light fall upon the mirror of the galvanometer; one is so directed upon the cylinder that it enters through a narrow slit and can trace a continuous line on the surface of the regularly rotating cylinder. The rays proceeding from the second source of light are reflected upon a screen, and are in this way made accessible to individual observation.

A very neat experimental arrangement was constructed by Saladin, the engineer at the Creuzot works, and Le Chatelier.[1]

The methods hitherto described make it possible to indicate the difference of temperature between the body under examination and the comparison body as a function of time only. If it is desired to express it as a function of the temperature, then two records are needed, viz. the curve of the difference of temperature as a function of the time, and the cooling curve, *i.e.* the actual temperature as a function of the time. From these two there can then be constructed point by point the curve of the difference of temperature as a function of the temperature.

The direct recording of a curve of which the abscissæ represent temperatures, the ordinates, the differences of temperature between the test piece and the comparison body, was hitherto impossible, because the very sensitive galvanometers necessarily employed were furnished with vertical suspension, and therefore could only be deflected in a horizontal plane, whereas one of the deflections must be vertical.

Now Saladin makes use of the property of a 45° mirror to give a vertical image of a horizontal straight line. If, for instance, s is the reflecting surface in Fig. 21, $d = 45°$, then the image of ab must lie at $a'b'$, and it is vertical if ab lies horizontally. Instead of a mirror Saladin uses a prism arranged for total reflection. Fig. 22 shows the scheme of the entire contrivance; s is the mirror of the galvanometer which is deflected by the thermo-electric current which serves to measure

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[1] H. Le Chatelier, "Nouveau dispositif expérimental de la méthode de M. Saladin pour l'enrégistrement des points critiques." *Revue de métallurgie*, 1904. Paris, Dunod 49, quai des Grands-Augustins.

the temperature. A screen, having a hole of 0·1 to 0·2 mm. diameter, is placed at the focus *F* of the achromatic lens *A* and immediately before the source of light *L* which may be, *e.g.* a Nernst lamp. The divergent pencil of light issuing from the opening in the screen is changed by the lens *A* into one of parallel rays which fall upon the first mirror *s*. This reflects them into the obliquely placed prism *P*. By the deflection of the mirror *s*, the rays *B* are displaced in a horizontal plane, after passing through *P* they move in a vertical plane. The mirror *s'* of the second sensitive galvanometer, which is deflected by the current due to the difference of temperature of the two bodies, must be sufficiently high to catch the rays displaced in the vertical plane which may still fall upon it. By the deflection of the latter galvanometer the light is again displaced horizontally and finally concentrated to a point by means of the lens *A'* at its focus. At this point a photographic plate is placed which records the movement of the point of light. Since this movement registers the resultant of the deflections of the two galvanometers there is a curve upon the plate showing the difference in temperature of the two bodies as a function of the temperature.

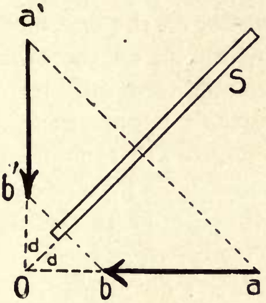

FIG. 21.—Action of the oblique prism in the Saladin-Le Chatelier apparatus.

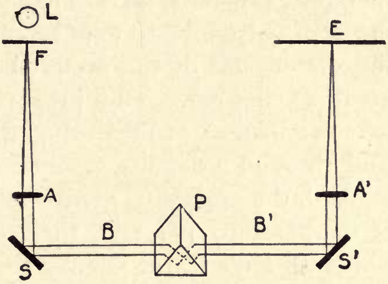

FIG. 22.—Path of the light rays in the Saladin-Le Chatelier apparatus.

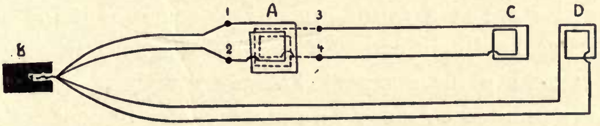

FIG. 23.—Scheme for a registering apparatus for cooling curves (Dejean).

The arrangement described above possesses the disadvantage that the size of the bodies under research is very limited. Moreover it is extremely difficult and in many cases impossible to carry out a melting-point determination because of the difficulties created by the arrangement of the comparison body. Dejean,[1] therefore, proposes an arrangement by which, on the one hand, the comparison body may be dispensed with, and on the other, the dimensions of the material under examination may be as great as desired. The principle of Dejean's apparatus is as follows: instead of measuring the times which are required to cool through a definite interval of temperature as in Osmond's method, the apparatus gives the reciprocal value, *i.e.* the change of temperature per unit time, or the velocity, the diagram of which we have learnt already (p. 15 and Fig. 11 on p. 16). The apparatus consists of a kind of Desprez-d'Arsonval galvanometer *A*, the actuating coil of which carries two windings, insulated from one another, which are connected to the four binding screws 1, 2, 3, 4. The binding screws 1 and 2 of the first (inducting) winding are connected up to a Le Chatelier thermo-couple, the hot junction of which is inserted in the sample for examination, *B*. During the heating and cooling the coil is twisted in the magnetic field about its point of suspension ; this motion induces a current in the second winding, the strength of which is proportional to the velocity of the coil's movement, and consequently to the velocity of heating or cooling of the sample. This current is conducted to the sensitive mirror galvanometer *C* of the Saladin-Le Chatelier apparatus. The deflections of this galvanometer are at a minimum or become zero if the velocity of cooling or heating decreases or becomes zero, that is to say, when a critical point occurs. The temperatures at which this appears are yielded by a second galvanometer in connection with a second thermo-couple. It follows, therefore, that the curve described on p. 16 Fig. 11 is automatically obtained, and shows the velocity of the change of temperature as a function of the temperature.

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[1] M. Dejean, "Galvanomètre d'induction pour l'étude des points de solidification et points critiques." *Revue de métallurgie Mémoires*, 1905.

THE PHYSICAL MIXTURE.[1]

Between the elements, the molecules of which consist of atoms of the same kind, and compounds, whose molecules consist of atoms combined according to their valency values, on the one hand, and mechanical mixtures, the individual components of which can be separated by mechanical means on the other hand, there stands a class of substances which we group under the name "physical mixtures." With elements and compounds they share the property of perfectly uniform composition throughout their mass; they differ from them in that this composition is not governed by the laws of valency. The physical mixture is to be met with in the solid, liquid, and gaseous states of aggregation.

In general, the properties of the mixture are not strictly additive, that is to say, a particular property of the mixture is not exactly the mean of the same property of its components; they change with the composition.

As one would expect from the constitution of gases, the relations are of the simplest kind in mixtures of gases in which no chemical change occurs. Since in such mixtures each gas behaves, as is well known, as though it alone were present, the properties can easily be deduced by a simple "partnership" calculation. The relations are different in liquid mixtures. To convince ourselves of the importance of these differences we will consider briefly how the regular distribution of the single components is conditioned.

In a gas, as we have seen previously, the individual molecules are not held together at a definite distance, but endeavour to occupy the greatest available space. Consequently, as soon as two or more gases meet together in a defined space, each one

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[1] W. Nernst, *Theoretische Chemie.* Translated by C. S. Palmer. (Macmillan.)

strives to fill it completely, independently of the other gases present. From this it follows that all gases mix together in all proportions, supposing that no chemical change takes place.

In the liquid state, on the contrary, perfect miscibility, from what has been said previously, cannot be expected. If two suitable liquids, say a litre of each, be poured together into a vessel, the specifically heavier one will occupy the lower part and the lighter one the upper part of the vessel, and the sum of the volumes will amount to two litres, as before mixing. Oil and water, for instance, conduct themselves in this way.

Now physics teaches that forces operate between the individual molecules of the same body as well as between those of different bodies, cohesion in the former case and adhesion in the latter. It is therefore clear that if oil and water are stratified, the cohesion which holds the individual molecules of oil together as well as that which binds the water molecules, must be greater than the adhesion between the water and oil molecules.

If, on the other hand, we select sulphuric acid and water, the following takes place. The water molecule is subjected to the influence of two forces, the cohesion of the nearest water molecules and the attraction (adhesion) of the nearest sulphuric acid molecules. Now the adhesion between sulphuric acid and water is greater than the cohesion of water molecules as well as that of sulphuric acid molecules. Consequently the water molecule under consideration yields to the adhesion, is severed from the surrounding water molecules, and passes into the sulphuric acid. This movement will repeat itself until the force of adhesion is neutralized, *i.e.* until one substance is saturated with respect to the other.

Quite the same reasoning applies to the case of solid-liquid as well as to solid-solid bodies. The degree of mutual interpenetration depends upon how much adhesion exceeds cohesion, and this is nothing else but an expression for the solubility of one body in the other.

From the point of view thus stated it directly follows that we cannot in general speak of the dissolved body and the solvent, but of the mutual solution of the two bodies. In those cases, where one of the components is present in large excess, it is frequently designated the solvent.

In opposition to gas mixtures, in which the solubility (if one may so describe the complete mutual interpenetration) is independent of temperature, pressure, and the nature of the components, in liquid and solid mixtures this is largely influenced by the factors mentioned. The changes resulting from the building up of the mixture will be considered more closely in what follows.

In order to arrange the subject clearly, mixtures may be divided up as follows:—

I. Aqueous solutions ;
II. Fused salt mixtures ;
III. Fused alloys.

We shall see that these three classes exhibit so great a similarity in all respects that this division appears somewhat arbitrary. It must however be noted, on the other hand, that this similarity or rather identity only became known later ; it is always interesting to trace the evolution of a law, for one thereby becomes more thoroughly conversant with its meaning. In consequence the identity of the groups will be deduced here from their common properties.

Aqueous Solutions.—The cooling curve of pure water exhibits, as we have seen earlier, a point of arrest at 0° C. which corresponds to the formation of ice. This curve in Fig 24. is 0. If a 10 per cent. solution of salt is made, in addition to the point of arrest *e* at $-4°$ C., another one *k* can be observed at $-22°$ C. (curve 1) ; 15 per cent. of salt lowers the position of the first point *e* still further, whilst the second occurs at the same temperature $-22°$ C. (curve 2). With 23 per cent. of salt the first point has fallen also to $-22°$ C., so that this mixture possesses only one such point of arrest. Solutions with more than 23 per cent. of salt show two points again, the first of which *s* rises with increasing amounts of salt, whilst the second remains constant at $-22°$ C.

To make the significance of these arrest-points clear, observations of the changes which the mixture undergoes at them can be made. At 0° C. water freezes to ice ; from a solution consisting of 10 per cent. NaCl and 90 per cent. H_2O, crystals separate out at the first point which prove on analysis to consist of pure ice. This fact leads to the generalization that the freezing-point of water is depressed by the presence of salt ; the amount of this depression increases at first with the amount of salt. If the small crystals of ice which have formed be carefully removed, there remains a solution (mother-liquor) which possesses a correspondingly higher percentage of salt. Consequently the freezing-point of this solution is lower than that of the first and more crystals, which prove to consist of pure ice free from salt, separate out only by cooling further. By removing these crystals also, the solution becomes richer and richer in salt, the temperature at which crystallization takes place falls further and further, until finally at – 22° C. the whole mass suddenly solidifies. When this solid is analyzed, it proves to consist of 23·5 per cent. salt and 76·5 per cent. water. If another concentration is selected for the original solution, say 18 per cent. NaCl and 82 per cent. H_2O, the process is strictly analogous, only that the first ice crystals occur later, at about – 10° C. The mixture remaining liquid until the last, which solidifies suddenly at – 22° C. possesses again the same composition 23·5 NaCl, 76·5 H_2O.

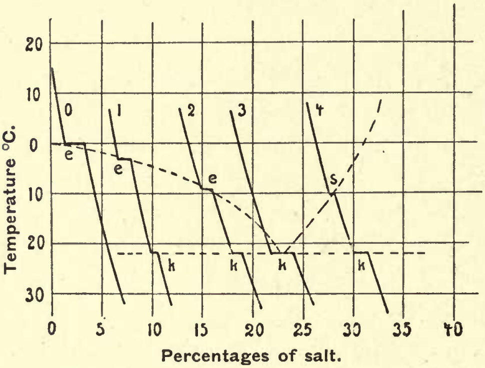

FIG. 24.

If the solution possesses this composition to begin with, it has only the one freezing-point at – 22° C. In solutions which contain more than 23·5 per cent. of salt, another point of arrest again appears above this temperature. A mixture, for instance, containing 25 per cent. NaCl, 75 per cent. water begins to deposit at its first arrest point *s* crystals which analysis shows to consist of pure salt. The remaining mother-liquor consequently becomes poorer in salt until the amount 23·5 NaCl, 76·5 H_2O is reached, solidifying at – 22° C.

This mixture, which always has the same composition, possesses a constant freezing-point, and remains liquid longest from the whole series of salt-water mixtures is called "eutectic mixture" or "eutectic."

The properties of the eutectic, viz. its possession of constant composition and melting-point led formerly to its being regarded as a chemical compound. From more exact investigations, however, it resulted that the components were not in molecular proportions, and therefore the chief requirement for a chemical combination was not fulfilled. Further, the microscope established the fact that the eutectic consists of innumerable plates of water and ice placed in mechanical justaposition.

In order to depict the solidification and cooling relations of the whole series of salt solutions comprehensively, the graphic representation is also made use of. In Fig. 24 the cooling curves of solutions of different salt contents are set out side by side. The points *e* collectively denote the temperature at which ice separates out, the points *k* the solidification of the eutectic mixture, whilst the points *s* correspond to the separation of salt from the solution. If now all the points, *e*, *k*, *s*, are joined together by a continuous line (the dotted line of Fig. 24), the diagram Fig. 25 is obtained. Following Heyn's[1] precedent, it is called the freezing-point diagram, and it is therefore nothing but the locus of all the critical points of a series of solutions of increasing salt contents. In the freezing curve, Fig 25, *AB* therefore corresponds to the separation of pure ice, *BC* to the separation of salt, and *DD* to the separation of eutectic water-salt. From the diagram the condition of any selected salt mixture can be read off, as soon as the concentration and the temperature are given. A solution consisting of 10 per cent. NaCl and 90 per cent. of water, as is seen from the diagram, begins to deposit ice crystals at the temperature *a*. When the surrounding temperature has fallen to about – 10° C., so much water has already separated as ice that the remaining mother-liquor contains *de* per cent. of salt.

Proceeding from the following consideration, the relative amounts (of the two substances) may be clearly deduced. Suppose that the flakelets of ice present at any instant are separated from the mass, so that the solution only is left. Then if the temperature falls only to the extent of an infinitesimally small amount, a small fresh quantity of ice will freeze out. Hence the solution at – 10° C. is a saturated one, and we obtain its composition by drawing a horizontal line through the ordinate at – 10° C., cutting *AB* in *e*. The abscissa *de* of this point gives

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[1] Heyn, *Die Metallographie im Dienste der Hüttenkunde.* Freiberg, Craz. u. Gerlach,

us the amount of salt in the mother-liquor, for this is the only one of the whole series of salt solutions which begins to deposit ice at – 10° C. It is possible now to calculate how much ice has separated at this point. M being the total weight of the

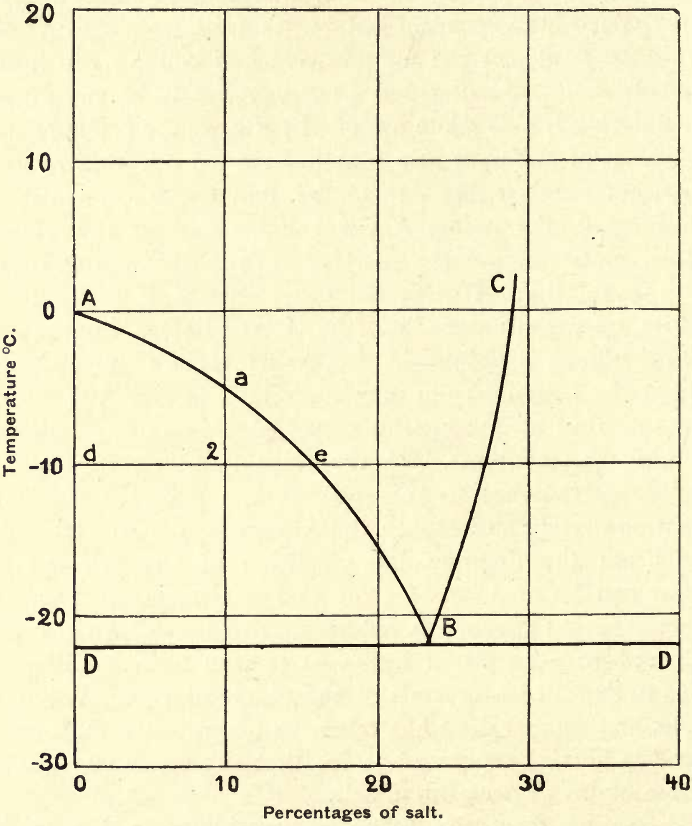

FIG. 25.—Freezing diagram of ice and salt solutions.

solution, its salt content $d2$ = 10 per cent., then the amount of salt in the solution is

$$\frac{M \cdot d2}{100} \text{ grams } \quad . \; . \; . \; . \; . \; . \quad (1)$$

If x be the required amount of ice, the mass of the mother-liquor is $M - x$. This contains, as we saw above de per cent. of salt. The total amount of salt contained in it is therefore

$$\frac{(M - x)\, de}{100} \text{ grams } \quad . \; . \; . \; . \quad (2)$$

As the crystals of ice are free from salt, the fractions (1) and (2) must be equal, hence—

$$\frac{Md2}{100} = \frac{(M - x)de}{100}$$

$$Md2 = Mde - xde$$

$$xde = M(de - d2) = M . 2e$$

$$\frac{x}{M} = \frac{2e}{de}$$

That is, the amount of ice separated at a particular temperature bears to the total amount of the mixture the proportion expressed by the lengths *2e* : *de* into which the vertical line drawn through the percentage of salt divides the horizontal line through the temperature ordinate.

The phenomena of freezing are not always so simple as they have been described here in the example of salt and water. It has been supposed that pure salt separated along the line *BC*, and that the eutectic consisted of lamellæ of ice and salt deposited side by side. This is not always the case. Much more frequently chemical compounds with the water separate out instead of the pure salt, and to each particular hydrate there corresponds a particular branch of the line *BC*.

As an example of this kind of freezing, the solutions of ferric chloride, which were first systematically investigated by Roozeboom[1] will be discussed. Ferric chloride forms with water the following hydrates:—

$Fe_2Cl_6 . 4H_2O$; $Fe_2Cl_6 . 5H_2O$; $Fe_2Cl_6 . 7H_2O$; $Fe_2Cl_6 . 12H_2O$.

Imagine now each one of these salts to be in the liquid condition, then on cooling there will be a point at which its whole mass solidifies, viz. the melting or freezing-point of the salt. The melting-point of the hydrate $Fe_2Cl_6 . 4H_2O$ lies at 73·5° C. By adding anhydrous ferric chloride to the liquid hydrate, the melting-point is depressed until at 66° C. the eutectic ferric chloride-hydrate$_4$ appears. (For the sake of brevity the hydrate is represented by the index number corresponding to the number of molecules of water per molecule of ferric chloride. Hydrate$_4$

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[1] Bakhuis Roozeboom, "Über die Hydrate des Eisenchlorids." *Zeitschrift für physikalische Chemie*, 10, s. 477 (1892).

therefore means $Fe_2Cl_6 . 4H_2O$) The diagram of freezing, Fig. 26, is identical with that of salt-water. Therefore we have

Along *JK* separation of the pure hydrate$_4$,
„ *KL* separation of pure ferric chloride,
„ *KK* freezing of the eutectic mixture hydrate$_4$-ferric chloride.

Fig 27 represents the freezing curve of hydrate$_4$ and hydrate$_5$ and needs no further explanation.

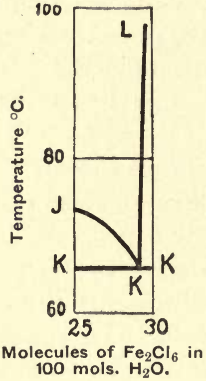

FIG. 26.

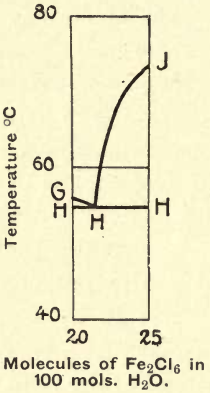

FIG. 27.

To represent clearly the whole diagram for the system water-ferric chloride, the collected separate portions are put together. Fig. 28, in which each cross-hatched area represents a division, shows the whole arrangement. With respect to the co-ordinates it should be noted, however, that the ordinates represent temperatures as usual and the abscissæ, instead of the percentage amount of ferric chloride, give the number of molecules of ferric chloride in 100 molecules of water. This representation furnishes in many cases a more lucid diagram than the former.

The advantage of such a representation is at once proved if the occurrences are to be traced when one of the components is gradually removed; for example, when the water is evaporated. For the sake of simplicity, it will be supposed that the temperature remains constant at about 30° C. The changing composition will then be given by a horizontal line drawn through the ordinate 30. At first the whole system is liquid until so much water has evaporated that there is one molecule of ferric chloride to twelve molecules of water; this is the composition of the hydrate$_{12}$ and as its melting-point is higher, viz. 37° C., the whole mass solidifies to a conglomerate of crystals of the hydrate$_{12}$; by further evaporation of water the region in which a liquid mixture of water and hydrate$_7$ exists is reached; at the point *d* the hydrate$_7$ begins to solidify, becoming under increasing temperature a liquid mixture hydrate$_5$-water and then solid hydrate$_5$.

From the complete freezing diagram it can be seen that each definite compound corresponds to a maximum in the curve. Certainly Roozeboom proceeded conversely; he first established the curve for the water-ferric chloride system and argued the existence of the various compounds from the occurrence of

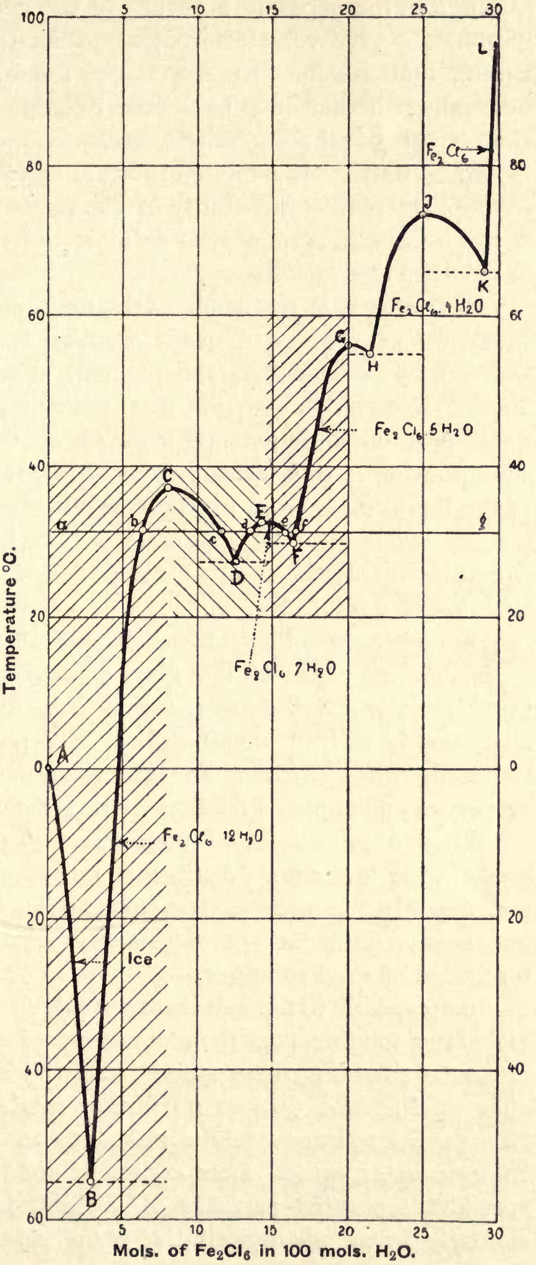

Fig. 28.—Solubility curve of ferric chloride in water (Bakhuis Roozeboom).

maxima in the separate branches of the curve. These investigations are very valuable from a systematic point of view. A similar method, for instance, serves for mixtures of metals to determine whether definite chemical compounds of the separate components of an alloy exist.

Fused Salts.—If a molten mixture of two salts is allowed to solidify, the perfect miscibility of the two components obtaining at the time may remain after solidification or it may be wholly or partially destroyed.

Supposing that the whole of the molecules of the liquid mass occurring at a given moment were to remain in the position which they possessed at the moment, a solid body would be formed characterized by this, that its molecules occupy a definite fixed position and distance from each other (see p. 2). The configuration of this solid body would then be the same as that of the liquid mass from which it resulted; the individual components would not be separable by mechanical means; they would be dissolved. The solid complex would possess the constitution of a solid solution.

By melting together lime, silica, and alkali, a glass is formed. Now the properties of the glass change according to the proportions in which the constituents named enter together, and continuously with the composition. The possibility of changing the composition without an accompanying sudden change of properties constitutes a leading characteristic of solid solutions.

When a solid solution possesses the property of forming crystals, the latter are described as mixed crystals of both components. In the main, isomorphous bodies form mixed crystals, but isomorphism is not necessarily a *sine quâ non* for the formation of solid solutions.

In opposition to the salt mixtures, which form a homogeneous mass after solidification, the components of which therefore enter into solid solutions, there stand those the components of which after solidification possess no further solubility for each other. In aqueous solutions this corresponds to the system sodium chloride-water, which after complete solidification consists of spacially separated particles of salt and ice. Such salt-melts similarly break up quantitatively on solidification into their components.

Between these two extreme cases, the complete solubility and the complete insolubility of the components after solidification, a series of intermediate substances is possible. In these cases the solubility suddenly decreases considerably at the moment of solidification, without however becoming nil. In many cases, also, the solubility decreases still further in the process of cooling, which gives rise to the separation of a corresponding amount of one of the pure components in the interior of the solid mass.

Further, it is possible for definite chemical compounds to form between the two components, the so-called double salts, corresponding to the hydrates in the system ferric chloride-water (p. 33); then, just as in those, these double salts can be considered as new components which give rise to the same phenomena as have been already discussed for the single salts.

Now according to the type of solidification, there are distinguished, in solidified salt mixtures:—

I. *Systems, which do not form double salts.*
   (*a*) The two components form a continuous series of mixed crystals of the same kind.
   (*b*) The two components do not form a continuous series of mixed crystals of the same kind.
   (*c*) The two components form a discontinuous series of mixed crystals of different kinds.

II. *Systems, which form double salts.*

I. SYSTEMS WHICH DO NOT FORM DOUBLE SALTS.

(*a*) *The two components form a continuous series of mixed crystals of the same kind.*

Imagine two substances A and B which are perfectly soluble in one another in the liquid as well as in the solid condition. According to the researches of B. Roozeboom[1] the phenomenon of solidification of such a solution is not so simple as was formerly supposed for such bodies. In general the solidification does not take place at a definite temperature but during an interval of

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[1] B. Roozeboom, "Erstarrungspunkte der Mischkristalle zweier Stoffe." *Zeitschrift f. physikalische Chemie*, 1899, Bd. 30, s. 385.

temperature. This depends upon the fact that the crystals first formed have not the same composition as the liquid solution out of which they separate. In by far the most cases, the liquid, in comparison with the mixed crystals, possesses a greater amount of that component by whose presence the freezing temperature is lowered.

Roozeboom employs the following graphic representation for illustrating this (Fig. 29). Let *AC* and *BD* be the melting-points of the two components *A* and *B*. In the co-ordinate system, the abscissæ denote the percentage contents of the *B* constituent, and the ordinates temperatures. There is now for each melt a temperature at which mixed crystals begin to separate out. The locus of these points is marked C_L (liquidus); in Fig. 29 this is the line *CpnD*. Further there exists a second point at which freezing is at an end; these points joined by a line give C_s (solidus); in Fig. 29 *CgoD*. A certain solution *m* solidifies as follows: at the temperature *n* mixed crystals begin to separate, the *A* content of which, according to the statement expressed above, is smaller than that of the liquid. According to Roozeboom this content is found by drawing a horizontal line through *n* which cuts C_s in the point *o*. The abscissa of this point gives the *B* content of the mixed crystals.

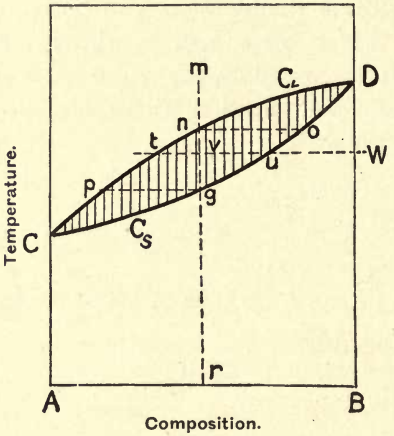

FIG. 29.—Solidification diagram of a system, the components of which form a continuous series of mixed crystals of the same kind.

By the separation of the crystals rich in *B* from the solution, this has become richer in *A* and hence its solidification point falls. At a given instant let this, *e.g.* be *t*; the crystals separating out at this moment have the composition *u*. The mass of the mother-liquor decreases in proportion to the separation of the mixed crystals until finally at the temperature *q* it has become zero. The crystals separating last of all of the composition *q* were crystallized from a mother-liquor of the composition *p*.

The originally separated crystals which were poorer in A equalize their composition little by little as they absorb from the mother-liquor a corresponding amount of A, so that finally the whole mass consists of homogeneous mixed crystals of the composition m. To this end it is of course necessary that the cooling proceeds so slowly that this enrichment of the already solid mass by diffusion of the constituent A is possible. If this does not take place, the ensuing aggregate of mixed crystals is heterogeneous and the freezing temperature of the latter falls lower than expected from the concentration.

The representation allows one to establish the amount of the mixed crystals at any instant, which have already separated out. Let the total amount of the melt be 100, the composition in the liquid state m, and the temperature at the moment be t. According to the above statements the composition of the separated mixed crystals $= u$, that of the remaining liquid $= t$. Let now

$$\begin{aligned} \text{mass of crystals} &= x \\ \text{then mass of melt} &= 100 - x \\ A\text{-content of the crystals} &= x\overline{uw} \\ A\text{-content of the melt} &= (100 - x)\,\overline{tw} \\ \text{But total } A \text{ content of the mass} &= 100\,\overline{vw} \end{aligned}$$

$$\text{Hence } x.\overline{uw} + (100 - x)\,\overline{tw} = 100\,\overline{vw}.$$

$$\text{Whence } \frac{x}{100 - x} = \frac{tv}{vu} = \frac{\text{mass of mixed crystals.}}{\text{mass of remaining liquid.}}$$

Roozeboom has denoted this kind of freezing as Type I. In the group of homogeneous mixed crystals Roozeboom distinguishes two further types in which, between the freezing-points of the components the curves C_s and C_L show a maximum or a minimum. We can, however, leave both these cases out of consideration here, since up to now no examples have been established with certainty.

(*b*) *The liquid solidifies to a discontinuous series of mixed crystals of the same kind.*

The case may occur in which one component A possesses only a limited solubility for B and *vice versâ*. Fig. 30 shows the freezing diagram for this case, which was designated Type IV. by Roozeboom. At the temperature t of the transition point, the meaning of which will be discussed further in the sequel, the solubility of *B* in *A* may be taken equal to the abscissa of the point *F*, that of *A* in *B* equal to *G*. At the temperature 0°, let these solubility capacities be smaller still and equal to *AH* and *KB*.

Melts between *eD* solidify as follows: As soon as the line *ED* is reached during the cooling, mixed crystals separate out, the composition of which as described under (*a*), is yielded by the abscissa of the point of intersection of *GD* with the horizontal drawn through the point in *ED*. By further cooling no other change occurs, as at the temperature 0° the solubility of *B* for *A* is equal to *KB*.

A liquid of the composition *c* separates on cooling at first mixed crystals *d*; liquid and crystals alter their composition from *c* to *E* and from *d* to *G* respectively. Now in order that by further cooling, the composition of the liquid can be altered further along *EC* and that of the separated mixed crystals along *FC*, the whole complex of the *G* mixed crystals present must be converted into *F* mixed crystals. This takes place at constant temperature *t* by the reaction:

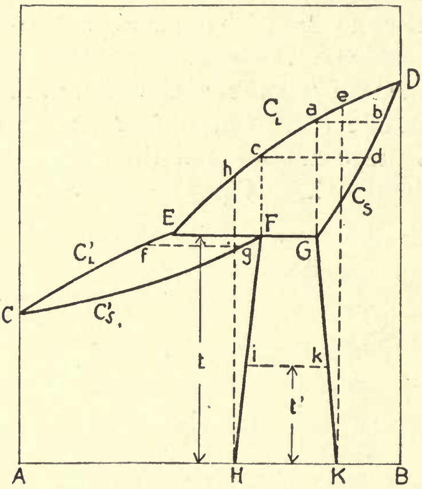

Fig. 30.—Freezing diagram of a system, the components of which form a discontinuous series of mixed crystals of the same kind.

$$\text{Liquid } E + \text{mixed crystals } G = \text{mixed crystals } F \quad . \quad (1)$$

If mother-liquor remains after this reaction, it freezes along *EC* with separation of mixed crystals along *FC*; this is the case for all melts from *E* to *c*. If more mixed crystals than mother-liquor are present in order to complete the reaction (1), the latter will be quite saturated, and the mass consists later of mixed crystals *G* and *F*. This is the case for melts between *c* and *a*. It was supposed above that the solubility gap *FC* increases with falling temperature and is equal to *HK* at 0° C. In consequence of this, all those complexes which at the temperature *t* contain mixed crystals with more than *AH* per cent. *B* or *KB* per cent. *A* intersect the lines *FH* and *GK* during the cooling, and further separation occurs.

For the readier understanding of these rather complicated phenomena, a number of cooling curves (see p. 4) are schematically shown in Fig. 31. The thick lines show those parts of the curve during which any change takes place, whilst the thin lines correspond to normal cooling.

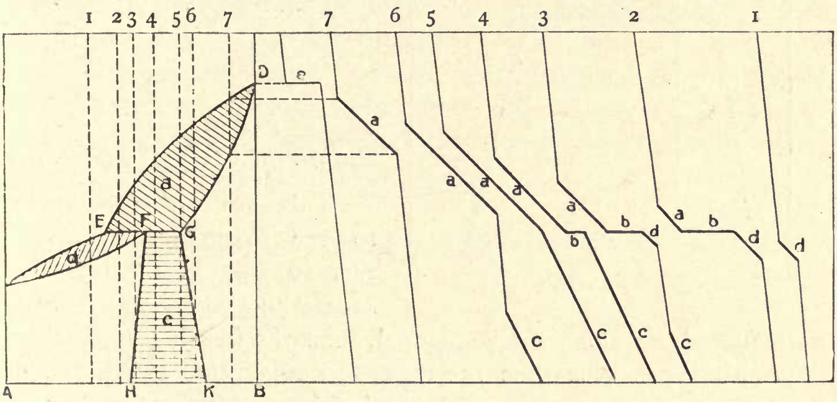

FIG. 31.

In Fig. 31 therefore—

a = the temperature interval during which mixed crystals separate along *DG* ;

b = the point at which the change mixed crystals *G* + liquid *E* = mixed crystals *F* takes place ;

c = the temperature interval during which "limit-crystals" *GK* and *FH* respectively separate ;

d = the interval during which mixed crystals *CF* separate ;

e = the freezing of the pure substance *B*.

If the gap of solubility is very large, Type V. occurs which is represented in Fig. 32.

The course of the freezing does not differ essentially from that of Type IV. Whilst the liquid melts pass through the compositions *DE* or *CE*, the separated mixed crystals simultaneously change according to *DG* and *CF* respectively. Melts lying between *F* and *G* solidify simultaneously at temperature *t* to an intimate mixture of crystals *G* and crystals *F*. *E* is, however, a eutectic point. In this case also what has been said for Type IV. applies. The gap *FG* can increase with falling temperature so that in the course of the cooling a further separation can take place. Examples of this type are found in the systems iron-carbon, and potassium nitrate-thallium nitrate.

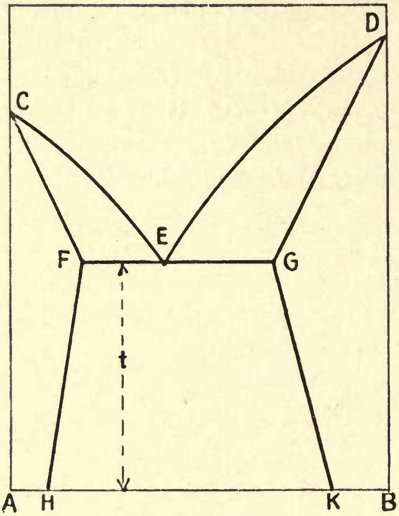

FIG. 32.

(*c*) *The liquids solidify to two different kinds of crystals.*

This case carries one back to the foregoing. Imagine that in Fig. 32 the crystals separating along *DG* are regular, those along *CF* hexagonal, then the freezing is exactly of this type. *t* is then the eutectic temperature at which an intimate mixture of hexagonal and regular crystals simultaneously falls out. In this category all those systems fall whose components are completely insoluble in each other and of which the system $\frac{\mathrm{KCl}}{\mathrm{NaCl}}$ presents an example.

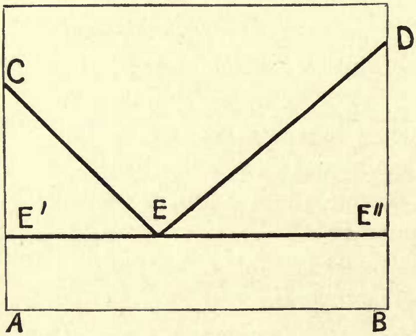

FIG. 33.

If in Fig. 32 the point *F* moves back to the ordinate *A*, *G* to the ordinate *B*, the type reproduced in Fig. 33, which may be designated Type Va, ensues.

As is evident, this is absolutely identical with the salt water type of freezing. The phenomena which the diagram illustrates are exactly like those in the freezing of the salt-water system. Hence in Fig. 33—

CE represents the separation of the pure component *A*
ED represents the separation of the pure component *B*
E′E″ represents the freezing of the eutectic mixture *AB*.

II. SYSTEMS WHICH FORM DOUBLE SALTS.

The systems falling under this head form an analogue to the ferric chloride-water system previously described. The separated double salts can form further one or several kinds of crystals amongst themselves and with the components, and can mix partially or completely, so that of the previously mentioned types several may occur together or be repeated. On this account the interpretation of the freezing curves can become a very difficult matter under some circumstances, particularly when the results cannot be tested chemically, optically, or in some other manner.

It was supposed earlier, that neither the components nor the mixed crystals underwent further changes after freezing. These (changes) are, however, very frequent, as has been described in an earlier chapter. From the great similarity existing between allotropic transformations and freezing phenomena, it may be concluded that the same phenomena, which have been described for freezing in the foregoing, can be repeated. In point of fact, Roozeboom has developed theoretically all possible cases of these transformations, and has demonstrated them for various systems.[1] It would lead us too far to discuss Roozeboom's very interesting researches at this point; only one characteristic example, the system potassium nitrate-thallium nitrate[2] will be selected.

Potassium nitrate and thallium nitrate when chemically pure both possess transformation points, potassium nitrate at 126° C. and thallium nitrate at 142° C. Above 126° C. potassium nitrate exists in the α-condition and forms rhombohedral crystals; below this temperature it exists in the β-condition and the crystals are

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[1] B. Roozeboom, "Umwandlungspunkte bei Mischkristallen." *Zeit. f. physik. Chem.* 1899, Bd. 30 s. 414.

[2] C. van Eyk, "Über die Bildung und Umwandlung der Mischkristalle von Kaluimnitrat und Thalliumnitrat." *Ztsch. f. physik. Chem.* 1899, Bd. 30 s. 430.

rhombic. For thallium nitrate the α-condition also corresponds to the rhombohedral and the β-condition to the rhombic crystals.

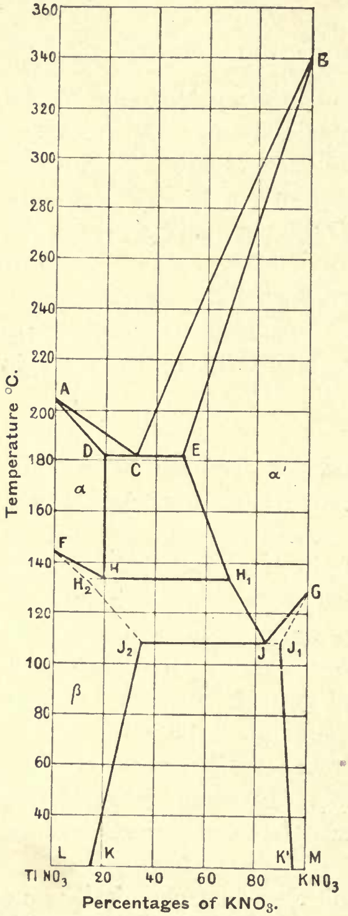

FIG. 34.—Diagram of freezing and allotropic transformation of the system potassium nitrate-thallium nitrate (Van Eyk).

Fig. 34 shows the freezing diagram for the whole series of mixtures. It corresponds to the freezing-type IV, that is to say, the series of mixed crystals which separate in freezing is discontinuous, and has a gap between *D* and *E* (20 and 50 per cent. of potassium nitrate). The melts lying between these limits freeze therefore to a conglomerate of mixed crystals, one containing 20 and the other 50 per cent. of potassium nitrate. At the moment of their formation the mixed crystals are rhombohedral: they change, however, at a definite temperature into the rhombic form. The temperature of the mixed crystals sinks continuously between *F* and *H* from the transformation point of the pure thallium nitrate to that of the final crystals. As in the freezing, this re-crystallization is spread over a definite interval, as would be indicated by the line FH_2 (corresponding to *AD* in the freezing. From the point *H* we have a conglomerate of mixed crystals containing 20 per cent. and a similar one containing 50 per cent. of potassium nitrate. As the transformation of the rhombohedral into the rhombic type extends only to the 20 per cent. crystals, the transformation temperature must remain constant and expressed by the straight horizontal line HH_1.

Whilst by further cooling on the thallium nitrate side, the limit crystals retain their concentration of 20 per cent., those above 50 per cent. potassium nitrate separate according to the line EH_1J. The transformation of the rhombohedral crystals α' begins along the line GJ and is completed along GJ_1: in the point J the limiting or saturation point is reached. Consequently the transformation of further crystals must follow at a constant temperature. Along the horizontal straight line JJ_2 the remaining rhombohedral crystals are transformed, and below J_2J_1 the mass consists of a conglomerate of rhombic crystals only, with J_2 and J_1 per cent. of potassium nitrate. These limits are, as before, displaced at a lower temperature so that after the end of all the transformations, a conglomerate of crystals K and K' exists. Collecting together all the results again, we have existing—

1. Above ACB: liquid.
2. Inside ACD: rhombohedral mixed crystals AD and liquid AC.
3. Inside CBE: rhombohedral mixed crystals BE and liquid BC.
4. Inside $ADHF$: rhombohedral mixed crystals α.
5. Inside BEH_1JG: rhombohedral mixed crystals α'.
6. Inside $HDEH_1$: rhombohedral mixed crystals α and rhombohedral mixed crystals α'.
7. Inside FHH_2: rhombohedral mixed crystals FH and corresponding rhombic crystals FH_2.
8. Inside GJJ_1: rhombohedral mixed crystals GJ and corresponding rhombic crystals GJ_1.
9. Inside $H_2HH_1JJ_2$: rhombic mixed crystals β and rhombohedral mixed crystals α'.
10. Inside FH_2J_2KL: rhombic mixed crystals β.
11. Inside $J_2JJ_1K'K$: rhombic mixed crystals β and rhombic mixed crystals β'.
12. Inside GJ_1K': rhombic mixed crystals β'.

Alloys.—It is only of late years that the alloys of so much technical importance fell into the sphere of systematic scientific research. Thanks to the work of commissions formed in several industrial states, whose business it was to investigate the genesis as well as the properties of metals and their alloys, there are to-day sufficient paths open to us to explore with success a domain which was formerly of an extraordinarily problematical character.

One can say that the study of metallic alloys first received a remarkable impetus at the time when Graham furnished the proof that the laws valid in general for aqueous solutions, can be employed unaltered for molten metallic solutions, as we have already learnt.

The closer study of the phenomena of freezing and transformation of alloys has shown that Roozeboom's views on the formation and transformation of mixed crystals must be invoked in explanation. To this investigator we owe a system which first made it possible for us to perceive and interpret the transformation phenomena of the highly important technical alloys (iron-carbon, brass, bronze). In the theoretical development, he set out from the stand-point of Gibbs' Phase Rule, with which so far as concerns our purpose, we will first of all occupy ourselves.

Imagine in Fig. 35 we have two molten metals, one above the other according to their specific gravities. If, as an example, *A* is lead and *B* iron, no change takes place in the system, as both metals are completely insoluble in one another. If, on the contrary, both metals possess a certain solubility the one for the other, the phenomenon of diffusion begins, as for example in the system lead-bismuth. *A* diffuses into the metal *B*, in spite of its density, whilst a portion of *B* passes into *A*. If this phenomenon lasts long enough for both metals to be dissolved completely in each other, so that at every point of the volume *abcd* the composition is equal, the metals are said to possess perfect solubility for each other. Frequently however the process is such that only a certain amount of *B* passes into *A* and of *A* into *B*. In this case both metals possess a limited solubility for one another. Suppose that from *A*, *x* parts pass into *B*, and from *B*, *y* parts into *A*; a further alteration of the contents does not take place so long as both resulting mixtures are in contact. The

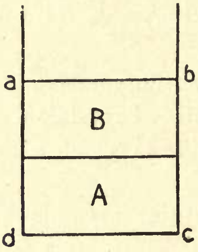

FIG. 35.

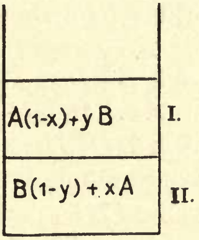

FIG. 36.

composition of the two solutions is now $A\ (1-x)+yB$ and $B\ (1-y)+xA$ (Fig. 36).

In the language of the phase rule the various complexes are designated as follows :—

The metals A and B are the *components* of the system *abcd*, that is to say, those constituents of the system which remain chemically unaltered under the given circumstances.

The solutions $A\ (1-x)+yB$ and $B\ (1-y)+xA$ are called *phases*, that is to say, those constituents of the system which can be separated from each other by physical means. In the case under consideration both phases are liquid; they could thus be separated by skimming off the specifically lighter one. We have supposed that as soon as the given composition of the two phases is reached, further changes are excluded; this is expressed by saying that phase I is in equilibrium with phase II. This equilibrium can be destroyed by various means. If, for example, the system is heated to another temperature t', the composition of both phases alters until equilibrium corresponding to the temperature t' is reached. The new concentrations may be called I′ and II′. Generally the solubility of the components A and B for each other increases with the temperature, until finally at some given moment the composition of both phases is the same, and the system therefore consists of one phase only.

A further factor which influences the composition of the phases which are in equilibrium is the pressure on the system. As this however is constant in all phenomena to be considered in the sequel and equal to one atmosphere, it may be left out of consideration.

Now there are certain relations between the number of components and phases, the temperature and the pressure, which must be satisfied in order that the system may be in equilibrium. The phase rule explains these relations. At this point it must be clearly set down that the phase rule only explains the qualitative and not the quantitative conditions. It is therefore only of value when perfect equilibrium is reached; the phase rule has nothing to say about uncompleted reactions and the products resulting therefrom. Now the materials employed for technical purposes are for the most part products which correspond to such incompleted reactions. The sole applicability of the phase rule to practice consists therefore in determining whether perfect equilibrium is reached or not, and this is, at any rate, important in many cases.

Leaving pressure out of consideration, the phase rule states that

$$F = n + 1 - \phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

where F denotes the number of degrees of freedom, *i.e.* "possibilities of change," n the number of components, and ϕ the number of phases.

A few examples will make this equation clear.

1. Suppose that a system consists of one component, pure iron, then $n = 1$. Let the number of phases be also $= 1$, *e.g.* suppose the iron to be completely liquefied, a condition which obtains at 1700° C. Then the phase rule states—

$$F = n + 1 - \phi = 1 + 1 - 1 = 1 \quad . \quad . \qquad (1')$$

The system has one degree of freedom. That is to say, of the factors which can influence the system, one can be altered without producing a change in the system. As it is assumed that the pressure is left out of consideration, the temperature only can exercise an influence. It is seen from equation (1′) that the temperature can be changed without producing change in the system.

2. Let another system consist of one component, pure iron, and two phases, liquid and solid iron. Then equation (1) gives—

$$F = 1 + 1 - 2 = 0,$$

that is, the number of degrees of freedom is 0. There is therefore only one single temperature at which solid and liquid iron can co-exist in equilibrium—the melting-point of iron.

3. A system of two components, tin and lead, consists of one phase, the liquid melt. Then—

$$F = n + 1 - \phi = 2 + 1 - 1 = 2.$$

The system can therefore be altered in two ways without destroying the equilibrium. Temperature and concentration can therefore have different values and the system will consist as before of one phase.

4. The same system consists of two phases, liquid melt and separated lead crystals. Then $F = 1$. That is to say, either the temperature or the concentration can be suitably chosen. If the temperature, for instance, is chosen = 250° C., the one degree of

freedom has been made use of, and the corresponding concentration is therefore determined. In point of fact, only the system 65 per cent. lead and 35 per cent. tin can consist at 250° C. of solid lead and molten solution. Every other system at that particular temperature is either perfectly solid or perfectly liquid.

5. The same system consists of three phases, solid lead, solid tin, and liquid melt. Here $F = 0$. There is therefore only one definite temperature and concentration at which this system is possible. Experience shows that only the eutectic mixture (32 per cent. lead and 68 per cent. tin) can exist along with the liquid melt at 180° C.

6. Suppose that the metallographic investigation of a section shows the phases, pure iron, pure carbon, and iron carbide at various temperatures.

$$F = n + 1 - \phi = 2 + 1 - 3 = 0.$$

The phase rule teaches that this system is only possible at one particular temperature. But as experience shows that the system (grey iron) is capable of existence at very different temperatures, a disagreement between law and actual fact apparently occurs in this case. The difficulty is easily removed, since the phase rule does not apply to the system under consideration for it is not in a state of (stable) equilibrium; that is to say, all the changes which should have taken place have either not done so or have not proceeded to completion.

These laws apply equally to solid as to liquid mixtures. As has been experimentally demonstrated by Roberts-Austen[1] for the system gold, lead, etc., solid metals and metalloids can diffuse into one another. The diffusion of carbon into solid iron is turned to account technically in the cementation process.

For a survey of the solubility relationships of two components at different temperatures, graphic representation may with advantage be employed. Let *AB*, Fig. 37, denote the system of two metals *A* and *B*. Each point on this line represents a definite alloy of the two components; thus, for example, *C* represents a mixture of *AC* per cent. of the metal *B* and *CB* per cent. of the body *A*. If now the two liquid layers sketched in Fig. 36 are analyzed for each temperature, it results for instance, that at the temperature $t = AH$, one layer consists of *HF* per

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[1] Roberts-Austen, *Phil. Trans. Royal Soc.*, 1896, CLXXXVII, p. 383.

cent. of *B* and *FI* per cent. of *A*, the other of *HG* per cent. of *B* and *GI* per cent. of *A*. Employing in Fig. 37 ordinates for temperatures and abscissæ for the compositions of the phases, a curve *CFDGE* is obtained, the solubilty curve of the system *AB*. To learn the composition of the different liquid phases of the system at a given temperature, it is only necessary to draw a horizontal line at a height *AH* corresponding to the temperature *t*. The points of intersection, *F* and *G*, of the latter with the solubility curve give the desired compositions. It follows from this that only the systems whose temperatures and concentrations correspond to the un-sectioned part *CFDGE* consist of two phases,. whilst the systems lying in the sectioned portion consist of one phase only.

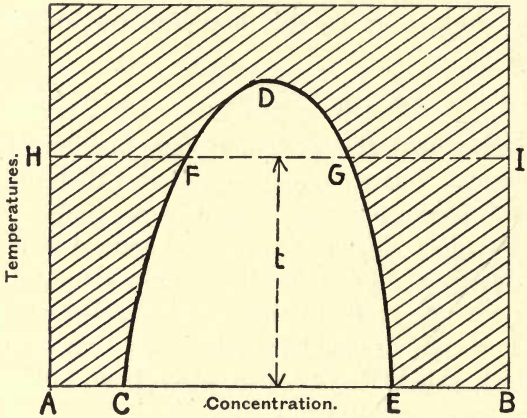

FIG. 37.

The graphic method employed in Fig. 37 is only suitable for binary systems, that is, for systems in which the number of components is two. If a third is introduced, the system of triangular co-ordinates described in the following is employed for representation.

If any point *P* be taken in the equilateral triangle *ABC* (Fig. 38), the sum of its distances from the three sides is constant and equal to the height of the triangle. That is

$$Pb + Pa + Pc = Be$$

[Proof: Draw through *P* a line *A′B′* parallel to *AB*, *B′b′* perpendicular to *AC*, *Pd* parallel to *AC*. From the equality of the triangles *PB′d* and *PB′a* it follows that $Pa = B'd$. From the equality of the triangles *BB′f* and *cPg* it follows that $Pc = Bf$. Also $Pb = db'$. Hence

$$Pb + Pa + Pc = db' + dB' + fB = Be.]$$

Thus every alloy can be represented by a point inside the equilateral triangle ABC. The corners of the triangle represent the pure metals whilst the straight line perpendicular to a side gives the percentage amount of the individual metals. Hence—

Pa = amount of A per cent.
Pb = „ B „
Pc = „ C „

In order to represent the equilibrium relations of such a ternary system graphically, suppose that through the lines AB, BC and CA planes $ABWU$, $BCWV$ and $ACUV$ are drawn perpendicular to the plane of the triangle, which would give the direction of the temperature axes.

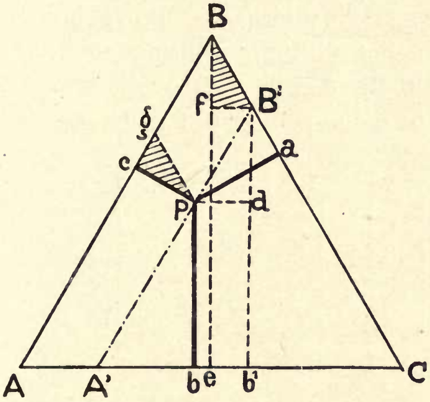

FIG. 38.—Triangular co-ordinates for representing ternary alloys.

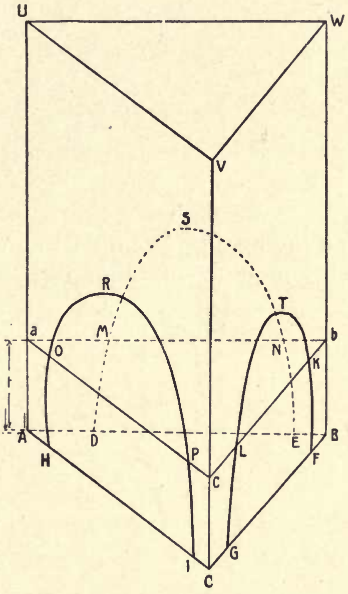

FIG. 39.

The solubility curves $DMSNE$, $FKTLG$, and $IPROH$ of the separate pairs of components can be traced out in the newly obtained planes exactly in the same way as that of Fig. 37.

Inside the prism $ABCVWU$ there is now a surface which gives the solubility relations of the different alloys, and is bounded by the three solubility curves. To determine the form of this "solubility surface" inside the prism, imagine this to be cut by horizontal planes. Such a section taken at a height t is shown in Fig. 40; the shaded part of this denotes the province of those alloys which at the temperature $t°$ consist of one phase only. If the solubility relations of such systems be determined at various temperatures, the solubility surface can be determined with sufficient accuracy by placing the figures obtained on one another. According to the relative positions of a point with respect to this surface, the corresponding alloy will consist of one or more phases. The alloy *A* (Fig. 40) for instance, consists of the two phases *A′* and *A″*, which are obtained by drawing a line parallel to *ac;* the points of intersection *A′* and *A″* with the bounding lines give the compositions of the two phases.

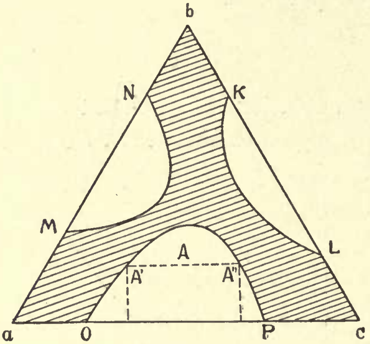

FIG. 40.

Lead-Zinc.

The lead-zinc alloys present an interesting example of metallic mixtures whose solubility in the molten condition is markedly variable. According to the experiments of Spring and Romanoff[1] the miscibility of both molten metals is unlimited above a temperature of 920° C.,

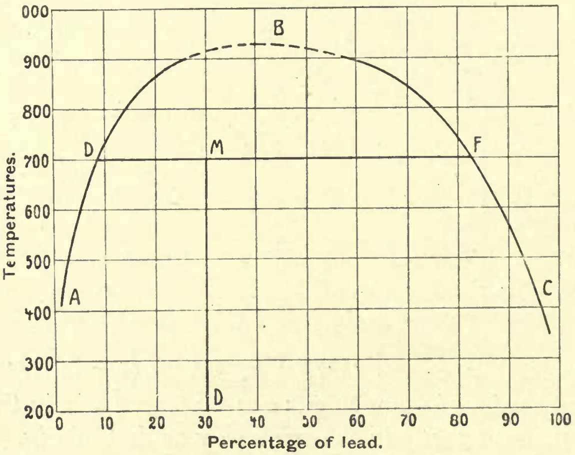

FIG. 41.—Solubility curve of lead and zinc (Spring and Romanoff).

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[1] Spring and Romanoff, "Über die Löslichkeit von Blei und Wismut in Zink. Nachweis einer Kritischen Temperatur." *Zeitschrift für anorganische Chemie*, 13, 1896, s. 29.

whilst it decreases with falling temperature. The conditions governing this are graphically shown in Fig. 41. After the explanation on p. 50 this diagram is clear without further description; all alloys above the line *ABC* consist of a homogeneous liquid mass which separates, however, into two layers as soon as the temperature falls below *ABC*. A melt with 30 per cent. of lead and 70 per cent. of zinc, shown at 700° C. by the point *M*, consists of two layers, one of which contains 8 per cent. of lead and 92 per cent. of zinc, the other 81 per cent. lead and 19 per cent. zinc. If the two metals separate entirely from one another above the freezing-point, the freezing-point curve of the lead-zinc alloys will consist of two horizontal straight lines only, which begin at the melting-points of the two metals.

It is possible now to divide the large number of alloys into groups according to the conditions determining their existence in the solid condition. Binary and ternary alloys only will be considered here. The systems with more than three components, on account of their possible complications, are very difficult, and have still been investigated little or not at all. The following classification will be taken.

I. Binary Alloys.

A. *No chemical compounds of the two components exist.*

1. The two components form a continuous series of solid solutions. (They are completely soluble in each other.)
2. The two components form a mechanical mixture after solidification. (They are perfectly insoluble in each other.)
3. The two components are partly soluble in each other; the alloy after solidification consists of solid solutions or mechanical mixtures of solid solutions.

B. *The two components form one or several compounds with each other.*

1. The compounds are wholly or partly soluble in the components or in one another.
2. The compounds are completely insoluble, reciprocally as well as in the components.

II. **Ternary Alloys.**

The possibilities of the different groups is indicated by the subdivision given under I. without further description. It can be seen that the number of groups thus obtainable is very large, since here also there is the possibility of definite compounds, and the perfect or imperfect solubility of all the components in each other and in their compounds. Indeed the case in which a ternary alloy *abc* can contain only three compounds *ab*, *ac*, *bc*, gives an immeasurable number of different possible combinations. On this account only a very few simple cases have been studied up to now, in which the three components form no chemical compound amongst themselves and are perfectly insoluble in one another.

I. THE BINARY ALLOYS.

A. *The components form no chemical compound with each other.*

1. The two components form a continuous series of solid solutions.

The phenomena of freezing of the systems comprised under this heading correspond to the type I. of Roozeboom explained on p. 37. The following only need be added.

According to the view of Roozeboom, mixed crystals separate at the commencement of freezing, containing a small amount of that constituent by which the melting-point is lowered. In consequence the complete solidification does not take place at a definite temperature but extends over a longer interval. Now this is not always the case with alloys. According to Roberts-Austen's experiments, crystals separate from certain alloys of the noble metals which possess exactly the same composition as that of the mother-liquor out of which they originate. This observation can perhaps be made to harmonize with Roozeboom's view by supposing the temperature interval to be so small that it easily escapes direct determination.

The structure of this class of alloys is quite homogeneous, since every part of it has the same composition. If, notwithstanding, a heterogeneous structure occurs in many cases under the microscope, this is because the crystals first separated cannot attain a regular composition sufficiently quickly, and thus after the freezing have a composition differing from that of the remainder of the mixed crystals. Such occurrences are largely avoided by protracted cooling.

Antimony-Bismuth.

The curve of the beginning of freezing *BiASb* (Fig. 42), published by Gautier[1] slopes continuously between the melting-points *Bi*, *Sb* of the pure metals. The properties also of the various alloys vary continuously with the composition.

The microscopic investigation of the series, pursued by Charpy[2] and by Hüttner and Tammann[3] confirm the progress of the freezing of mixed crystals as contended by Roozeboom. That is to say, according to the rule mentioned on p. 38 the mixed crystals which separate at first are always poorer in that body on account of whose presence the freezing-point is lowered; in this case, bismuth. To represent the complete progress of the freezing it is necessary to add a second curve (shown dotted in Fig. 42) showing the end of the solidification. A melt containing 50 per cent. of antimony would begin to deposit at the point *A*, 500° C., mixed crystals with *B* per cent. of antimony. The remaining mass, poorer in antimony, would cool further with a continual separation of ever-increasing bismuth contents, until finally at C° solidification is ended. The frozen mass, however, consists of homogeneous mixed crystals containing 50 per cent.

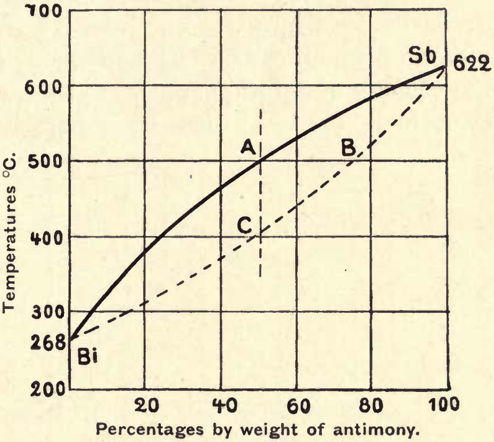

FIG. 42.—Freezing curve of the antimony-bismuth alloys (Gautier).

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[1] Gautier, "Recherches sur la fusibilité des alliages métalliques." *Bulletin de la Soc. d'Enc. p. l'Ind. nationale*, 1896. Also in *Contribution à l'étude des alliages.* Paris, Chamerot et Renouard, 1901, p. 133.

[2] Charpy, "Étude microscopique des alliages métalliques." *Bull. Soc. d'Enc.*, 1897. Also in *Contrib. à l'ét d. all.*, p. 121.

[3] Hüttner und Tammann, "Über die Legierungen des Antimons und Wismuts." *Ztschr. f. anorgan. Chem.*, Bd., 44, s. 131.

of antimony, only in case the earliest crystals, poor in bismuth, can enrich themselves with this metal sufficiently quickly during the process of freezing. This is not the case, however, according to what is found by the microscope. By polishing the sample parts are shown in relief which exhibit no sharp edges; it appears therefore that the hardness of the crystals varies continuously just like their composition. The crystals standing in relief correspond to the mixed crystals, precipitated first which are hard and rich in antimony; to these are attached softer crystals of gradually increasing bismuth contents. By heat-tinting, brighter and darker parts may be seen on such a polished surface, which gradually fade into one another. It is impossible to obtain a uniform bismuth content by subsequent prolonged heating, since the velocity of diffusion appears to be extraordinarily low. However, it is observed that at a higher temperature, the softer portions melt and run together into small globules, whilst the hard edges retain their shape.

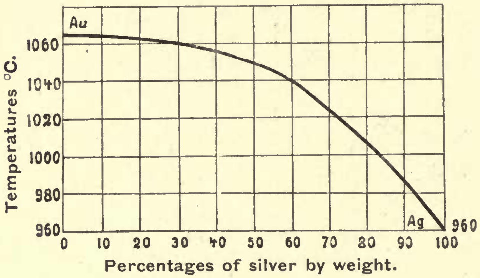

FIG. 43.—Freezing curve of gold-silver alloys. (Roberts-Austen and Kirke-Rose.)

Gold-Silver.

The curve of the commencement of freezing of gold-silver alloys runs continuously between the melting-points of the two metals. Fig. 43 shows the freezing-point curve published by Roberts-Austen and Kirke-Rose.[1] It can be seen from it that small amounts of silver lower the freezing-point of gold only slightly or not at all, and that the melting-point of an alloy containing 50 atoms per cent. of silver lies only 3° C. lower than that of gold.

Gold-Platinum.

According to the researches of Erhard and Schertel[2] the curve of the initial freezing of gold-platinum alloys runs continuously

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[1] Roberts-Austen and Kirke-Rose; "On certain properties of the alloys of the gold-silver series." *Chemical News* 87, 1903, p. 2.

[2] Erhard and Schertel, "Jahrbuch für Berg-und Hüttenwesen Sachsen," s. 17.

and almost in a straight line between the freezing-points of the pure metals, as shown in Fig. 44.

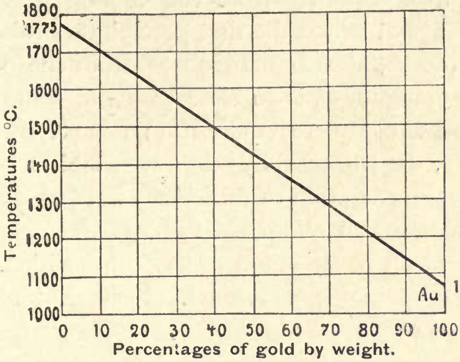

FIG. 44.—Freezing curve of gold-platinum alloys (Erhard and Schertel).

Iron-Manganese.

The freezing-point curve of iron-manganese alloys, as determined by Levin and Tammann[1] is reproduced in Fig. 45. It is evident from this that the two metals form a continuous uninterrupted series of mixed crystals. Only the full-lined curve of

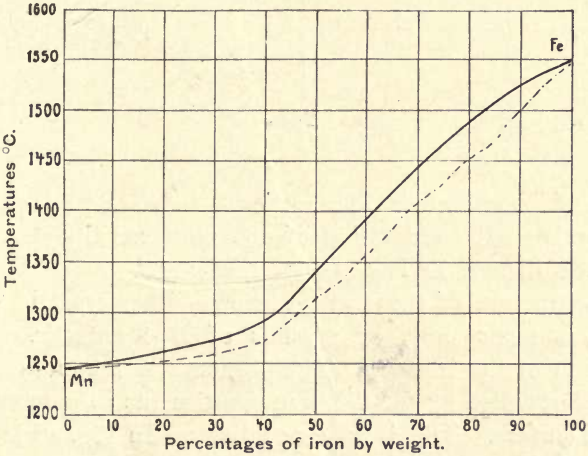

FIG. 45.—Freezing curve of iron-manganese alloys. (Levin and Tammann.)

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[1] Levin u. Tammann, "Über Manganeisenlegierungen." *Zeitschrift für anorganische Chemie*, Bd. 47, heft 1, s. 136.

the commencement of freezing (Fig. 45) however, has been determined with certainty; that of the completion of freezing cannot be established with certainty from the cooling curves. In this case again, the rate at which the first precipitated mixed crystals, poorer in manganese, absorb manganese from the fluid mother-liquor richer in manganese, is so slow that the temperature falls too quickly and a complete equilibrium cannot be established. Correspondingly, the frozen alloys do not exhibit a homogeneous structure, but an aggregation of mixed crystals of differing compositions. A longer annealing of the heterogeneous mass, however, brings about an equalization of the composition.

2. The two components form a mechanical mixture after solidification.

The freezing curve of this group of alloys corresponds to the type Va of Roozeboom's classification. In Fig. 46, therefore, *ac* corresponds to the separation of one pure constituent *A*, *bc* to that of the other *B*, and *de* to the eutectic *AB*.

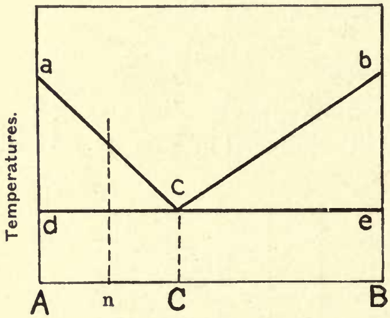

FIG. 46.

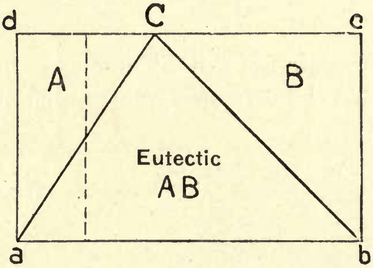

FIG. 47.

The structure of these alloys shows either crystals of *A* + eutectic, eutectic only, or crystals of *B* + eutectic. In the description of the micro-photographs, care is taken to estimate the areas occupied by the different constituents as percentages of the total surface. This is done as follows. In Fig. 46 let $AC = m$ represent the percentage amount of *B* in the eutectic. The areas occupied by *A* and the eutectic in a plane section through an alloy containing *n* per cent. of *B* are calculated as follows.

Let x be the surface occupied by the constituent A, y that occupied by the eutectic, both being expressed in percentages of the total sectional area. Then we have first:

$$x + y = 100 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Further, the *B*-contents of the eutectic must be equal to the total *B*-contents of the alloy, since the constituent *A* already separated is entirely free from *B*; thus:—

$$\frac{y.m}{100} = n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2) we have

$$x = \frac{100}{m}(m-n)$$

$$y = \frac{100n}{m}$$

If we suppose, as is the case in Figs. 46 and 47 that the alloy contains 20 per cent. of *B*, the eutectic 40 per cent. of *B*, then will

$$x = 50$$
$$y = 50$$

that is, the areas occupied by the two constituents are equal.

In order to perceive at a glance the area occupied by each constituent in a whole series, the graphic representation introduced by Sauveur[1] is advantageously employed.

In Fig. 47 upon the line *ab* the *B*-contents of the alloy are plotted and upon the abscissa *ad* the composition of the structure in percentages of the total area. At the eutectic point *C* the mass consists entirely of eutectic, that is, 100 per cent. of the surface is occupied by the eutectic mixture; at the points *a* and *b* the structure shows pure metals only, that is, the mass of the eutectic = 0 per cent. The course of the line *aCb* indicates therefore that part of the rectangle *abcd* in which the eutectic appears. The amount of the latter is found by drawing a vertical line through the point in the abscissa corresponding to the alloy. (The dotted line of Fig. 47). The parts into which this line is divided give the percentages of the surface occupied by eutectic and *A* respectively. It is seen that in the case of the example chosen, *i.e.* an alloy with 20 per cent. of *B*, the intercepted parts on the vertical line are equal; that is, the alloy consists of 50 per cent. of *A* and 50 per cent. of eutectic.

On the other hand, if the proportion of the surface occupied by a single constituent is known, the composition of the alloy may be deduced therefrom. The equations (1) and (2) would

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[1] A. Sauveur, *The Metallographist*, vol. i.

serve for this calculation with the difference only that x and y are known, and n is unknown.

For the experimental determination of the portion occupied by a single constituent a planimeter is used, as different investigators, viz. Sauveur, Heyn and Benedicks have suggested. To reduce the errors of reading to as small an amount as possible, it is advisable to trace round the separate fields in one journey, and in passing from one to another, to follow the same line going and returning. In Fig. 48 the course which the tracing point of the planimeter should follow is indicated by arrows, *A* being the supposed starting point.

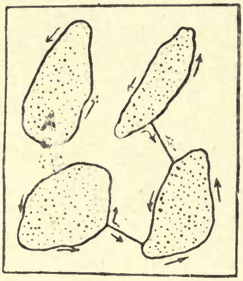

FIG. 48.

Antimony-Lead.

The freezing-point curve of antimony lead alloys reproduced in Fig. 49 was published by Roland-Gosselin.[1] It follows from this that the eutectic consists of 13 per cent. of lead and 87 per cent. of antimony, and freezes at 228° C.[2] The microscopic

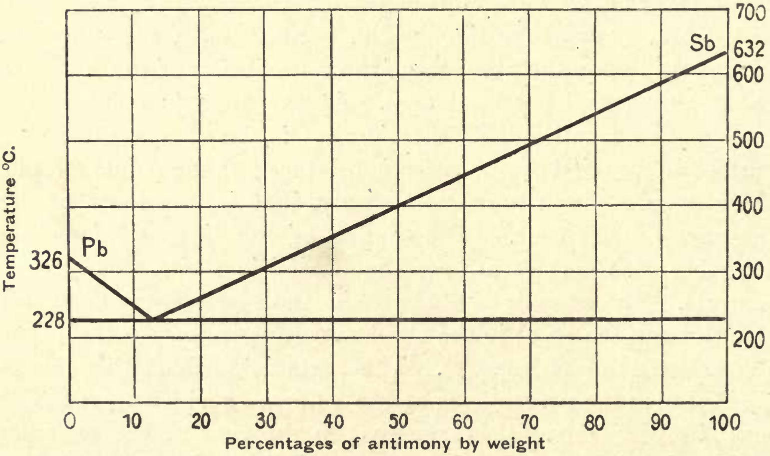

FIG. 49.—Freezing curve of antimony-lead alloys. (Roland-Gosselin.)

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[1] Gautier, " Recherches sur la fusibilité des alliages métalliques." *Bulletin de la Société d'Encouragement pour l'Industrie nationale*, 1896. Also in *Contribution à l'étude des alliages*, p. 93.

[2] In this, as well as in all the rest of the thermal investigations, the

investigation, pursued by Charpy,[1] is in agreement with the thermal research. Alloys with less than 13 per cent. of antimony consist of lead crystals embedded in eutectic; if the antimony contents exceed the eutectic composition, free antimony crystals appear, surrounded by eutectic. Nitric and hydrochloric acids are to be recommended as etching media, the latter colouring the lead white.

Lead-Tin.

According to the investigations of Guthrie,[2] Roberts-Austen,[3] and others, the lead-tin alloys yield the freezing curve (Roberts-Austen) reproduced in Fig. 50. The eutectic consists of 70 per cent. of tin and 30 per cent. of lead. Its freezing-point is 180° C. Hypo-eutectic alloys, that is, those containing less than 70 per cent. of tin, are composed of lead crystals surrounded by eutectic; hyper-eutectic alloys consist of tin crystals which lie in the eutectic.

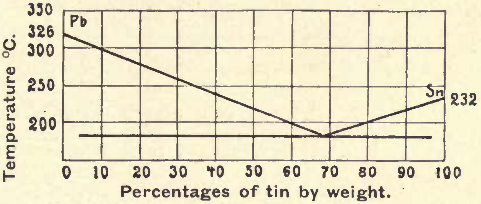

FIG. 50.—Freezing point curve of lead-tin alloys. (Guthrie.)

Microscopic investigation is by no means easy, as the alloys are difficult to polish on account of their softness. Assistance is afforded by pouring the molten alloy upon a polished steel plate (or its equivalent) and etching the plane surface so obtained directly. According to Charpy's[4] experiments, hydrochloric and nitric acids are to be recommended for this purpose. The same observer found that the structures agreed perfectly with the requirements of the freezing-point curve.

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temperatures given by the authors are reproduced unchanged. It appeared unnecessary to correct the numbers by the air-thermometer, since no assurance of the purity of the original materials was given in the older experiments.

[1] G. Charpy, "Étude microscopique des alliages métalliques." *Contribution à l'étude des alliages* 1901, p. 107. Paris, Chamerot et Renouard.

[2] Guthrie, "On Eutexia." *Philosophical Magazine*, vol. XVII. 1884, p. 462.

[3] Roberts-Austen, *Engineering*, 1897, 63, p. 223.

[4] Charpy, "Étude microscopique des alliages métalliques." *Bull. Soc. d'Enc.*, 1897. *Contribution à l'étude des alliages*, 1901, p. 121.

Cadmium-Zinc

The two metals crystallize out pure, side by side, as Fig. 51, the freezing curve plotted according to the researches of H. Gautier,[1] shows. The physical properties of the alloys lie between those of the components. The horizontal eutectic line is drawn in Fig. 51 from 0 to 100 per cent. zinc. Heycock and Neville,[2] however, who also made thermal investigations of this system, were able to trace the eutectic line between about 24 and 50 per cent. zinc only, so that it is quite possible that zinc and cadmium might form a continuous series of mixed crystals. Of this point further supplementary investigations must be made.

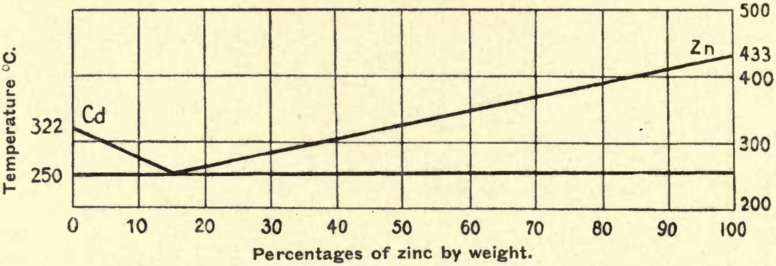

FIG. 51.—Freezing curve of cadmium-zinc alloys. (Gautier.)

Lead-Silver.

The freezing-point curve of lead-silver alloys, determined by Heycock and Neville,[3] is reproduced in Fig. 52. This shows a eutectic point *B* at a weight percentage of 96 lead and 4 silver. The branch *AgB*, which corresponds to the separation of pure silver from the melt, bends markedly. This is explained on the supposition that the molecular volume of the dissolved lead varies with the concentration. It is possible however that the lead-silver alloys stand upon the dividing line between the alloys which are perfectly miscible and those which are imperfectly miscible in the liquid state. In fact the latter always show a more or less

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[1] H. Gautier, "Recherches sur la fusibilité des alliages métalliques." *Contribution à l'étude des alliages*, 1901, p. 93.

[2] T. Heycock and H. Neville, "The freezing-points of alloys containing zinc and another metal." *Journal of the Chemical Society*, 1897, I., p. 383.

[3] Heycock and Neville, "Complete freezing-point curves of binary alloys." *Philosophical Transactions*, 1897, 189A., p. 137.

extended horizontal part in one of the branches. A dip towards the horizontal which is seen on *AgB* in Fig. 52 would thus indicate a slight separation already in the fluid condition. Which of the two explanations holds good for this case is still undecided.

Silver-Tin.

The freezing-point curves, Figs. 53 and 54, drawn up by Gautier[1] and Heycock and Neville[2] show that the branch lying on the side of the silver is not straight, but runs in a curve. Unfortunately in these determinations, observations upon the beginning and ending of the appearance of the eutectic are remiss, so that the existence of a chemical compound cannot be decided

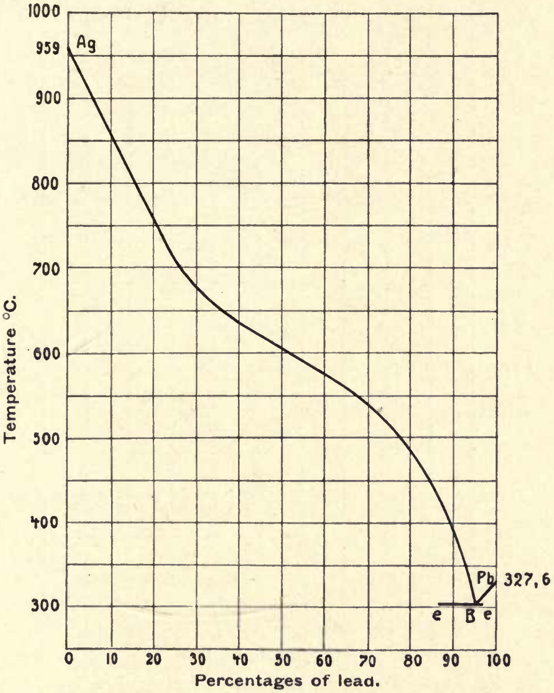

Fig. 52.—Freezing-point curve of lead-silver alloys. (Heycock and Neville.)

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[1] H. Gautier, "Recherches sur la fusibilité des alliages métalliques." *Bull. Soc. d'Enc.*, 1896. Also in *Contribution à l'étude des alliages*, 1901. Paris, Chamerot de Renouard.

[2] Heycock and Neville, see "lead-silver," p. 62.

with certainty from the freezing-point curve. Behrens,[1] from a metallographic examination of a series of silver-tin alloys, comes to the conclusion that silver and tin enter into the following combinations with each other:

Ag_6Sn, Ag_4Sn, Ag_3Sn, Ag_2Sn, $AgSn$, Ag_2Sn_3, $AgSn_2$.

Behrens bases his conclusion on the fact that all these melts consist of homogeneous crystal conglomerates, but it must be noted that the freezing-point curve shows nothing that would lead one to assume the existence of such a large array of chemical compounds. Charpy[2] quite rightly points out that the uniform crystallization can be explained just as well by supposing that silver and tin form a compound which is isomorphous with

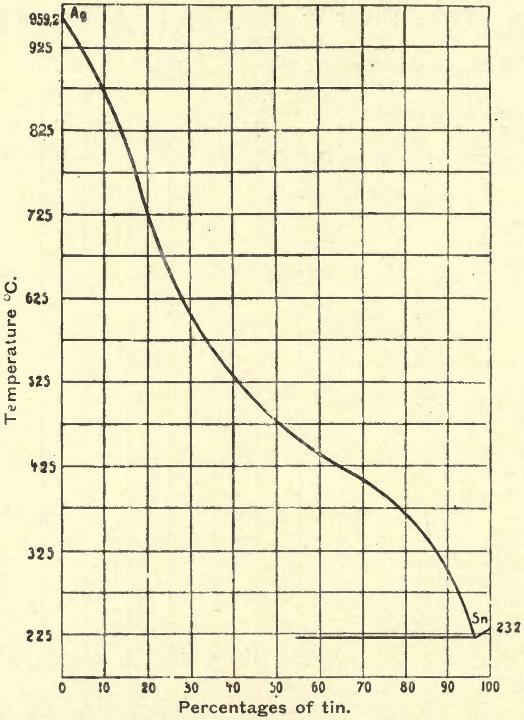

FIG. 53.—Freezing-point curve of silver-tin alloys. (Heycock and Neville.)

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[1] Behrens, "Das mikroskopische Gefüge der metalle und Legierungen."

[2] Charpy, "Étude microscopique des alliages métalliques." *Contribution à l'étude des alliages*, 1901, p. 153.

silver. From the microscopic researches of Charpy, it follows that all alloys up to 65 per cent. of silver show eutectic. This would correspond to the compound Ag_2Sn, which can therefore build homogeneous mixed crystals with the silver. For microscopic investigation Charpy recommends diluted hydrochloric acid as an etching medium.

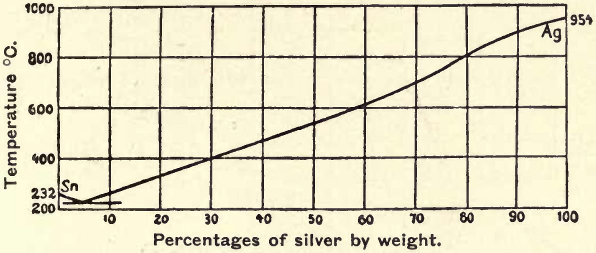

FIG. 54.—Freezing-point curve of the silver-tin alloys. (Gautier.)

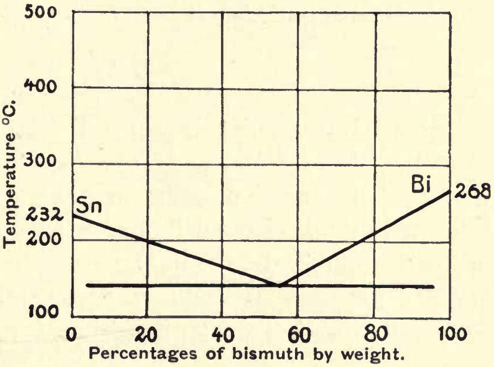

FIG. 55.—Freezing-point curve of bismuth-tin alloys. (Gautier.)

Bismuth-Tin.

The freezing-point curve (Fig. 55) shows a eutectic point, at 143° C., according to Gautier.[1] The eutectic has the following composition: Bismuth 55 per cent., tin 45 per cent. The microscopic investigations prosecuted by Charpy[2] give corresponding results; free bismuth or free tin surrounded by eutectic mixture according as the composition of the alloy lies to the right or left of the eutectic point. Dilute hydrochloric acid is recommended as a suitable etching medium.

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[1] H. Gautier, "Recherches sur la fusibilité des alliages métalliques." *Bull. Soc. d'Enc.*, 1896. Also, *Contr. à l'ét. d. All.*, p. 133.

[2] Charpy, "Étude microscopique des alliages métalliques." *Bull. Soc. d'Enc.*, 1897. Also, *Contr. a l'ét. All.*, p. 157.

Zinc-Tin.

Fig. 56 shows the freezing-point diagram of zinc-tin alloys, according to the determinations of Heycock and Neville.[1, 2] Composition of the eutectic: zinc 16 per cent., tin 84 per cent.; eutectic temperature 190° C. As the eutectic horizontal line has not been observed at any great distance on both sides of the eutectic point, the two metals may possibly form mixed crystals, which could be determined by additional metallographic investigations.

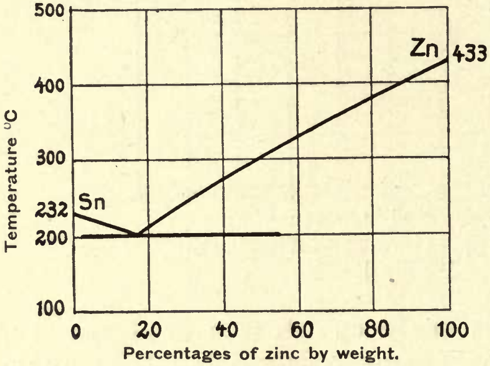

FIG. 56.—Freezing-point curve of zinc-tin alloys. (Heycock and Neville.)

Gold-Thallium.

The freezing-point curve of gold-thallium alloys, as determined by Levin,[3] is reproduced in Fig. 57. As pure thallium possesses a transition point at 225°, an arrest-point which is indicated by a horizontal line at this temperature can be observed in the domain of the thallium crystals in all alloys which contain primary precipitated thallium. Iron-carbon alloys in the solid condition exhibit a similar behaviour (see p. 166).

Gold-Copper.

Fig. 58 shows the freezing-point curve of gold-copper alloys according to the determinations of Roberts-Austen[4] and

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[1] Heycock and Neville, "The freezing-points of alloys containing zinc and another metal." *Journal of the Chemical Society*, 1897, p. 383.

[2] Heycock and Neville, *Journal Chem. Soc.*, 65, 1894, p. 31.

[3] Levin, "Über Gold-Thalliumlegierungen." *Zeitschr. f. anorg. Chemie*, Bd. 45, 1905, p. 31.

[4] Roberts-Austen and Osmond, "Recherches sur la structure des métaux, sa genèse et ses transformations." *Contr. à l'ét. d. All.*, 1901, p. 71.

Kirke-Rose.[1] The eutectic point lies at 82 per cent. gold and 905° C.

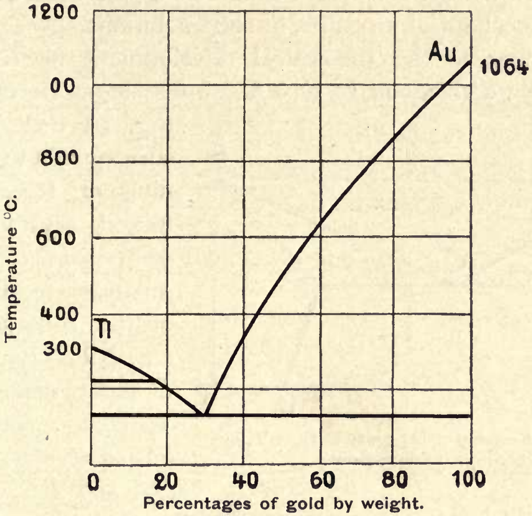

FIG. 57.—Freezing-point curve of gold-thallium alloys (Levin.)

Copper-Silver.

The freezing-point curve of copper-silver alloys, which is also plotted in Fig. 58 according to the determinations of Roberts-Austen and Kirke-Rose, is quite similar to the preceding. In all the alloys which are used in coinage, there appears to be a certain degree of solubility in the solid state.

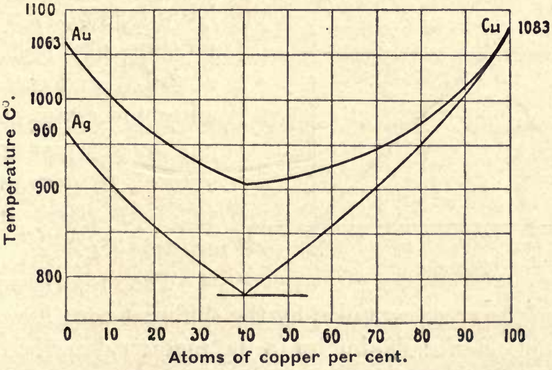

FIG. 58.—Freezing-point curve of gold-copper and silver-copper alloys. (Roberts-Austen and Kirke-Rose .)

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[1] Roberts-Austen and Kirke-Rose, *Proc. Royal Soc.*, 67, 1900, p. 105.

3. The two components are partially soluble in each other; the alloy consists, after freezing, of solid solutions or mechanical mixtures of solid solutions.

According to the theoretical development by Roozeboom, these alloys correspond to type V. of freezing. In the diagram Fig. 59 therefore, *ACB* corresponds to the beginning of freezing, when mixed crystals of the compositions *AD*, *BE*, separate from solutions of the composition *AC*, *CB*. Alloys lying between *D* and *E* deposit at *t*° C. a eutectic consisting of mixed crystals *D* and *E*. *DF* and *EG* correspond to the changes in concentration during further cooling, from which finally the mixed crystals *F* and *G* result. In a manner quite analogous to what was seen in the case of the alloys of group 2 (see p. 58), the composition of the structure may be determined. In Fig. 60 *afih* represents the domain of existence of homogeneous mixed crystals of changing composition. Alloys lying between *f* and *g* are a mixture of "limit-crystals" *F* and *G* and eutectic. An alloy for example containing 40 per cent. of *B* consists of 70 parts of eutectic and 30 parts of "limit-crystals" *F*.

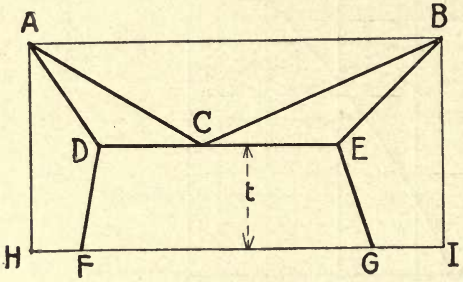

FIG. 59.—Freezing-point curve of type V. of freezing. (Roozeboom.)

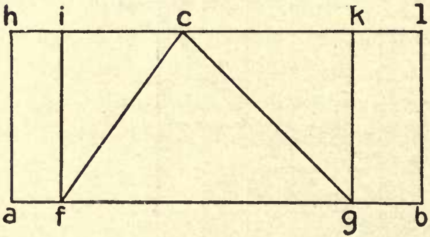

FIG. 60.

The experimental determination of the areas occupied by the different constituents can be made by means of a planimeter in the manner described on p. 60.

Aluminum-Zinc.

The curve of the commencement of the freezing of the aluminium-zinc alloys, established by Roland-Gosselin,[1] showed

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[1] H. Gautier, "Recherches sur la fusibilité des alliages métalliques." *Bull. Soc. d'Enc. pour l Ind. nat.*, 1896 Also in *Contribution à l'étude des alliages*, 1901, p. 133.

that it consisted of two branches intersecting at an angle. Later researches by Heycock and Neville,[1] and particularly Shepherd,[2] proved that on the one hand the eutectic line vanished at a certain aluminium content, but also on the other, that the structure of many aluminium-zinc alloys was entirely homogeneous. Fig. 61 shows the freezing-point diagram (Zustandsdiagram) reproduced from the researches of Shepherd. From this it follows that above the outline *ZnAAl*, the alloys are homogeneous fluids. In the region *ZnAa* mixed crystals of the composition *Zna* exist in equilibrium with molten alloy *ZnA*. In like manner primary aluminium crystals coexist in the region *AAlb* with molten alloy *AlA*. At the temperature of the straight line *aAb* the eutectic mixture of mixed crystals of the composition *a* with those of composition *b* separates out. The mutual solubility of the two metals changes to some extent with falling temperature, corresponding to the lines *ad* and *bc*. According to Fig 61 therefore, the following phases exist in the different domains—

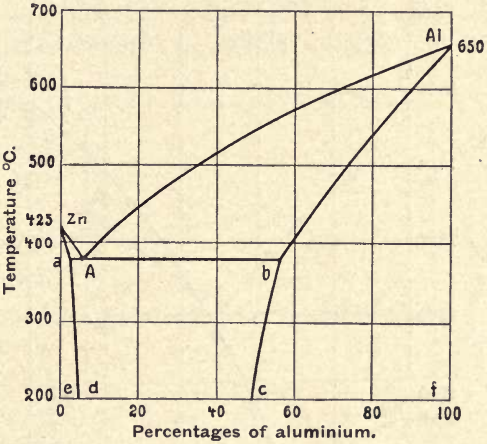

FIG. 61.—Freezing-point curve of aluminium-zinc alloys. (Shepherd.)

Znade: mixed crystals Zn(Al),
aAbcd: mixed crystals Zn(Al) + Al(Zn),
cbAlf: mixed crystals Al(Zn).

The microscopic investigation of the aluminium-zinc alloys by Charpy[3] and Shepherd shows complete agreement with the

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[1] Heycock and Neville, "The freezing-points of alloys containing zinc and another metal." *Journal of the Chemical Society*, 71, 1897, p. 383.

[2] E. S. Shepherd, "Aluminium-Zinc Alloys." *Journal of Physical Chemistry*, 1905, 9, p. 504; also *Metallurgie*, 1905, p. 86.

[3] Charpy, "Étude microscopique des alliages métalliques." *Bull. Soc. d'Enc.*, 1897. Also in *Contr. à l'étude d. All.*, p. 13.

indications of the diagram, since only the alloys between 4 per cent. and 45 per cent. of aluminium consist of two constituents. For developing the structure potash solution is recommended, which tints the aluminium dark.

Gold-Nickel.

The diagram of the gold-nickel alloys, reproduced in Fig. 62 from the researches of Levin,[1] shows that the two metals form mixed crystals, the series of which is interrupted by a gap. According to the views of Roozeboom, the freezing would therefore run as follows.

At the temperature of the line *AuA* mixed crystals begin to separate, the composition of which would be given by the line (shown dotted) running somewhat like *AuB*. The latter like *NiC* could not and has not yet been determined with certainty. This is because the mixed crystals first separated react with the remaining mass too slowly. Equilibrium in consequence is not attained. Correspondingly, it is found that the micro-structure of the mixed crystals is not homogeneous, but continuously variable. By a prolonged exposure to a high temperature, an equalization of the composition of the frozen mass takes place.

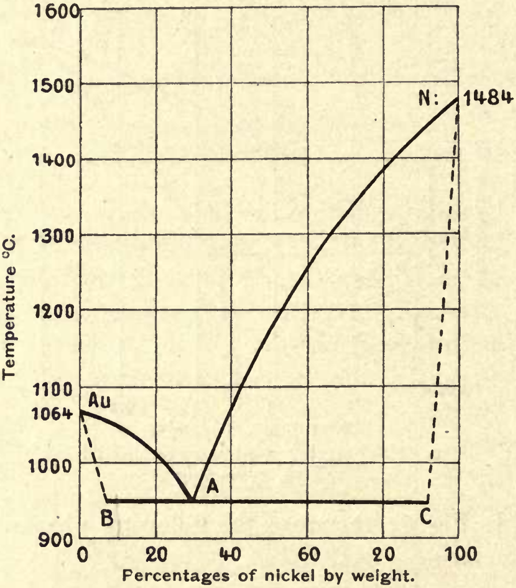

FIG. 62.—Freezing-point curve of gold nickel alloys. (Levin.)

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[1] M. Levin, "Über Gold-Nickellegierungen." *Zeitschrift für anorganische Chemie*, 1905, 45, p. 238.

B. *The two components form one or several chemical compounds with each other.*

1. The compounds are as completely insoluble in the components as in each other.

In order that an alloy of two components may be referred to as a chemical compound the following stipulations, with the exception of a case to be discussed later, must be fulfilled:

(*a*) The alloy must freeze completely at a definite temperature which remains constant during the interval of crystallization.

(*b*) The proportions in which the components occur must be constant and stochiometric, *i.e.* whole multiples of the atomic weights.

(*c*) The structure of the frozen alloy can show only one constituent.

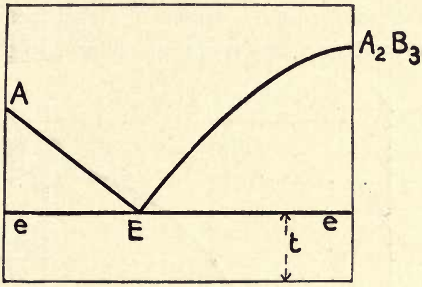

FIG. 63.

The theoretical deductions from the different possible kinds of freezing of Roozeboom show that the systems of two components possess two freezing-points, the upper one corresponding to the separation of one pure component and the second to that of the eutectic. But the eutectic mixture is the only one which possesses a constant freezing-point and constant composition. Thus of the three conditions specified above, the eutectic solution fulfils only the first, but not those of stochiometric ratio and of homogeneous structure; for this reason the eutectic alloys must not be considered as compounds, as frequently occurred earlier.

The existence of a definite compound will nevertheless be exhibited on the freezing-point curve. Imagine two components A and B which form a definite chemical compound A_2B_3 with each other. The series of all the possible alloys can be divided into two groups; those alloys which contain more and those which contain less of the constituent B than corresponds to the pure compound.

Let us first consider the first of these two groups. Its freezing-point curve can have, for example, the form shown in Fig. 63: *A* corresponds to the melting-point of one of the pure components *A* and by the addition of A_2B_3 will be depressed down to the eutectic temperature *E*. $\mathrm{A_2B_3}$ is the melting-point of A_2B_3, which on its part is likewise depressed towards *E* by the presence of *A*. Finally *eEe* is the line of the eutectic A,A_2B_3. In a similar manner, the freezing-point curve of the second class can be drawn (Fig. 64). In this case a eutectic B,A_2B_3 appears which freezes at the temperature t'. If now, these two freezing curves, Figs. 63 and 64, be combined in one, a complete freezing-point curve of the system is obtained (Fig. 65). In this, therefore—

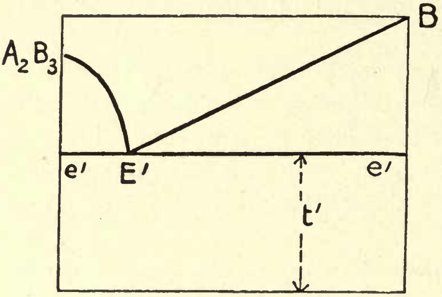

FIG. 64.

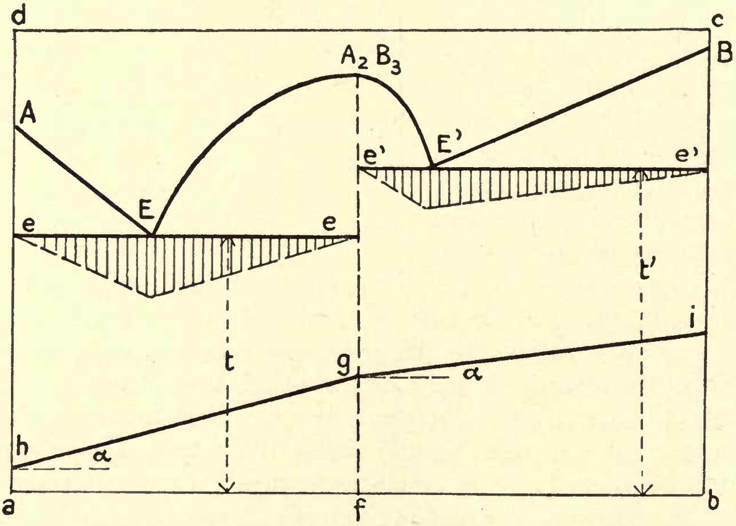

FIG. 65.

AE corresponds to the separation of the pure component *A* ;
EA_2B_3E' " " " compound A_2B_3 ;
$E'B$ " " " pure component *B* ;

ee corresponds to the separation of the eutectic A,A_2B_3;
e'e' „ „ „ eutectic B,A_2B_3.

Fig. 66 shows the proportions of the different constituents of the structure. From this it follows that alloys

between *a* and *b* consist of pure component A and eutectic A,A_2B_3;
„ *b* „ *c* „ „ compound A_2B_3 and eutectic A,A_2B_3;
„ *c* „ *d* „ „ compound A_2B_3 and eutectic B,A_2B_3;
„ *d* „ *e* „ „ component B and eutectic B,A_2B_3.

In the experimental establishment of such a freezing-point curve, difficulties are frequently encountered which militate against the exact determination of the single points. Tammann[1] is to be thanked for the introduction of certain methods of investigation to overcome these difficulties.

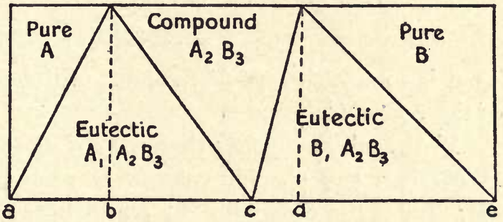

FIG. 66.

According to Fig. 66, the alloys between *a* and *b* contain an increasing amount of eutectic. As it must be assumed that the amounts of heat developed on freezing are proportional to the weights of the separated eutectic, so also the time, during which the temperature remains constant on the formation of the eutectic, will also be proportional to these weights. At the compositions *a*, *c*, and *e* the amount of the separated eutectic is nil. The cooling curves of these alloys will therefore exhibit no eutectic point. At the compositions *b* and *d*, on the contrary, the duration of the arrest-point will show two maxima. In Fig. 65 the straight lines drawn at right angles to *ee*, *e'e'* indicate the times during which the temperature remains constant at the eutectic temperatures *t* and *t'*. From the disappearance of the eutectic arrest-point at *e* (Fig. 65) therefore, the existence of a chemical compound may be assumed.

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[1] G. Tammann, "Über die Ermittelung der Zusammensetzung chemischer Verbindungen ohne Hilfe der Analyse." *Ztschr. f. anorganische Chemie*, Bd. 37, 1903, s. 302.

The determination of the point A_2B_3, moreover, can be brought about by the determination of the specific volume of the different alloys. Tammann[1] deduces this as follows :—

Let v be the volume of an alloy of two components M,N.

v_1 the specific volume of the component A

v_2 „ „ „ „ B

x the mass of the body A

y „ „ „ B.

v being the specific volume of the alloy, we have

$$v(x+y) = xv_1 + yv_2$$

$$\text{From this } v = v_1 + (v_2 - v_1)\frac{y}{y+x} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{The proportion } \frac{y}{x+y} = \frac{\text{mass of body } B}{\text{total mass of alloy}} = \text{concentration} = C.$$

This gives for equation (1)

$$v = v_1 + (v_2 - v_1)\,C \quad . \quad . \quad . \quad . \quad . \quad . \quad (1')$$

That is to say, the specific volume of the alloy is a linear function of the concentration.

If the alloy consists therefore of the two constituents A and A_2B_3, then the specific volume is represented by a straight line *hg;* this is the case with all alloys between *a* and *f*. Between *f* and *b* the alloys consist of the components A_2B_3 and B; the specific volumes of these are also represented by a straight line *gi.* The inclinations of the two lines *hg* and *gi* to the horizontal are different, since they are dependent upon v_2, v_1, and v.

Quite the same considerations are involved when instead of the one maximum, A_2B_3, several such occur, that is, when several compounds of the two components exist. The tin-sodium alloys[2] present a case in point.

To obtain a rapid survey of the structure of the different alloys of a given system, a diagram showing the prevailing conditions (Zustandsdiagram) should be constructed. By this is understood a figure divided by lines into separate domains of which each contains a definite group of phases. The upper limiting line of such a diagram will be in all cases the curve of the commencement of freezing, since for the one phase, fluid melt, a second, solid crystals, begins to make its appearance (for instance Fig. 61, p. 69).

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[1] See p. 73.

[2] See p. 81.

Lead-Magnesium.

The diagram of the lead-magnesium alloys, constructed by Grube,[1] is reproduced in Fig. 67. It follows from this that the two metals enter into chemical combination with one another according to the formula $PbMg_2$ corresponding to the maximum C. The phases corresponding to the separate fields are indicated in the diagram.

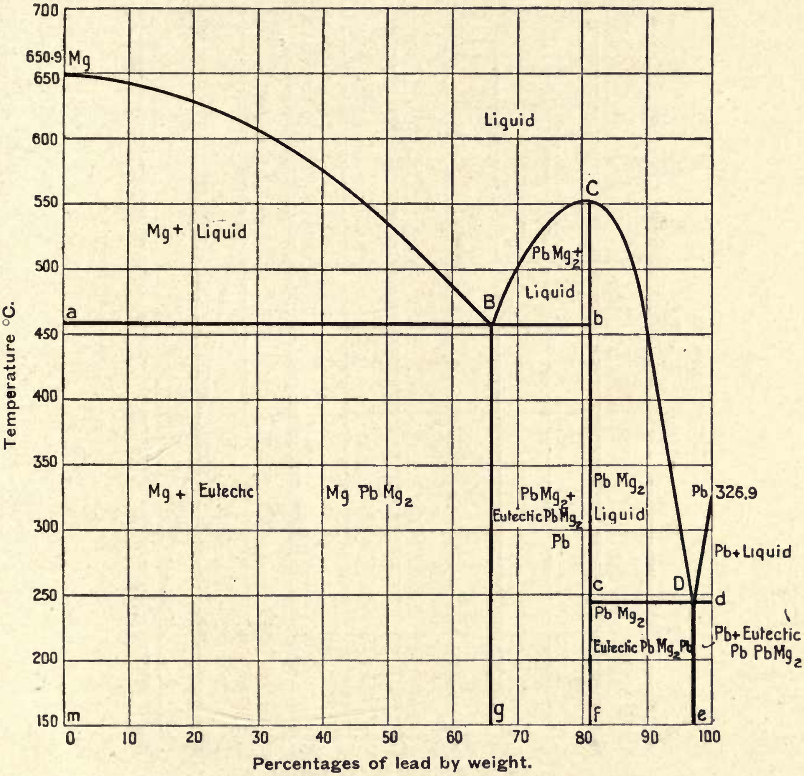

FIG. 67.—Diagram (Zustandsdiagram) of the lead-magnesium alloys (Grube).

The metallographic research, also conducted by Grube, of the lead-magnesium alloys, yielded perfect agreement with the diagram of Fig. 67. A simple exposure to moist air, which at once attacks the cut surface, suffices to render the structure discernible.

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[1] G. Grube, "Über Magnesium-Bleilegierungen." *Zeitschrift f. anorg Chemie*, 1905, Bd. 44, s. 117.

Magnesium-Tin.

A complete diagram for the magnesium-tin alloys was produced by G. Grube.[1]

In Fig. 67A, *MgABCSn* is the curve of the commencement of freezing, which has at *A* and *C* two eutectic points and at *B* a maximum corresponding to the compound $SnMg_2$. The branch *MgA* shows the temperature at which magnesium crystals begin to separate, *ABC* corresponds to the initial formation of $SnMg_2$ crystals, and *CSn* finally of free tin.

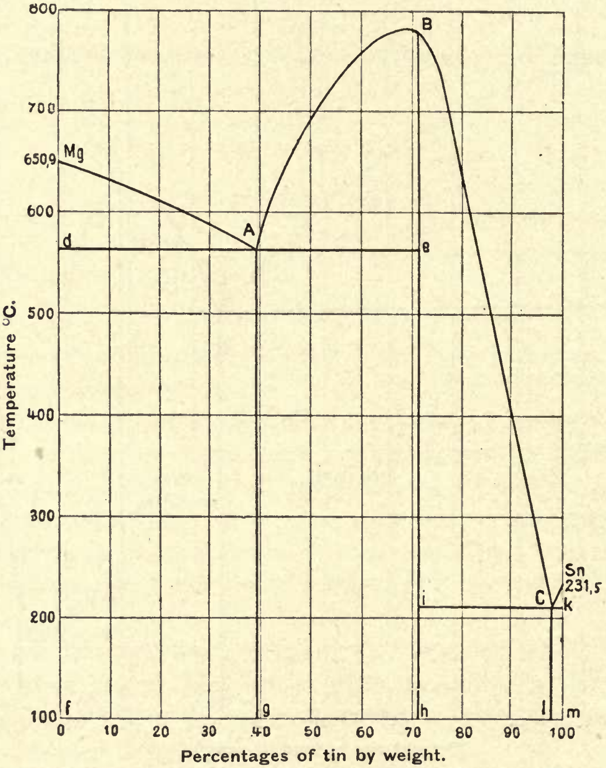

FIG. 67A.—Diagram for the magnesium-tin alloys (Grube).

Consequently the different fields of Fig. 67A contain the following phases:—

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[1] G. Grube, "Über die Legierungen des Magnesiums mit Zinn und Thallium." *Zeitschrift f. anorg. Chemie*, 1905, Bd. 46, s. 76.

I. The region above *MgABCSn* – homogeneous liquid alloy.
II. *MgAd* – primary magnesium crystals + fluid ;
ABe,iBC – primary $SnMg_2$ crystals + fluid ;
CSnk – primary tin crystals + fluid.

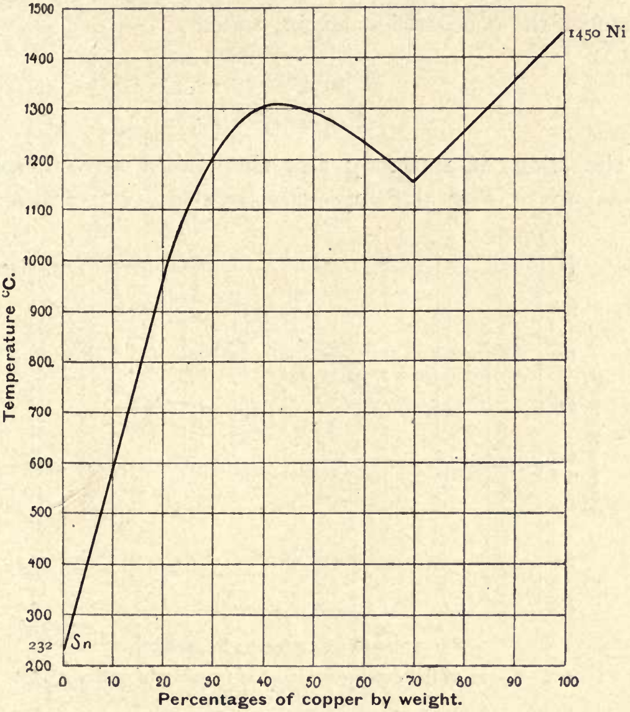

FIG. 68.—Freezing-point diagram of the nickel-tin alloys (Gautier).

III. *dAgf* – primary magnesium crystals + eutectic *A* (61 per cent. Al, 39 per cent. Sn) ;
gAeh – primary Mg_2Sn crystals + eutectic *A*
iClh – primary Mg_2Sn crystals + eutectic *C*
Ckml – primary tin crystals + eutectic *C*.

Nickel-Tin.

Tin and nickel form the compound Ni_3Sn_2, as is seen from the freezing-point curve of Fig. 68, plotted from the determinations of Gautier.[1] The two eutectic mixtures freeze at 231° C. and 1160° C.

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[1] See p. 60, footnote 1.

They contain 0·01 per cent. and 70 per cent. of nickel. The alloys with small quantities of tin are considerably harder than pure nickel. Charpy[1] has prosecuted the microscopic investigation of the series and has established the fact that up to about 35 per cent. of nickel, increasing amounts of a hard crystalline constituent of the composition Ni_3Sn_2 appear.

Antimony-Zinc.

The alloys of antimony and zinc afford an example of the appearance of several compounds between two metals, and the corresponding maxima in the curve of the commencement of freezing. The first determination of this curve by Roland-Gosselin[2] (Fig. 69) showed only one such maximum, but later experiments by Mönkemeyer[3] yielded the diagram reproduced in Fig. 70.

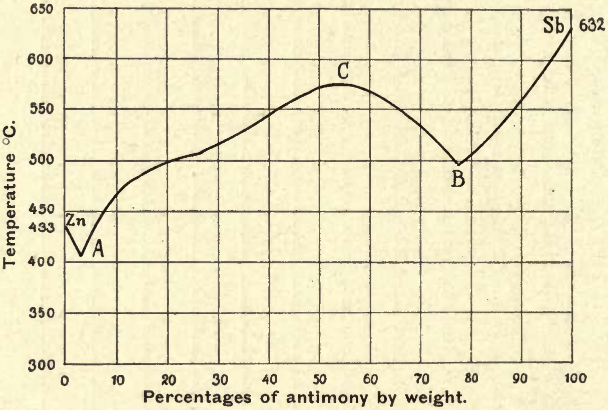

FIG. 69.—Curve of the commencement of freezing of antimony-zinc alloys (Roland-Gosselin).

The explanation of Fig. 70 follows from the earlier examples[4] and no more is necessary.

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[1] See p. 61, footnote 1.

[2] Gautier, "Recherches sur la fusibilité des alliages métalliques." *Contributions à l'étude des alliages*, 1901, p. 101.

[3] Mönkemeyer, "Über Zink-Antimonlegierungen." *Zeitschrift f. anorg. Chemie*, 1905, Bd. 43, p. 182.

[4] Heycock and Neville, "The freezing-points of alloys containing zinc and another metal." *Journal of the Chem. Soc.*, 1897, 71, I., p. 394.

ZnA – shows the separation of zinc.
ABC – separation of Zn_3Sb_2.
CDE – separation of ZnSb.
ESb – separation of antimony.

At the temperatures *A*, *C*, *E* the eutectic mixtures

Zn, Zn_3Sb_2
$Zn_3Sb_2, ZnSb$
and Sb,ZnSb

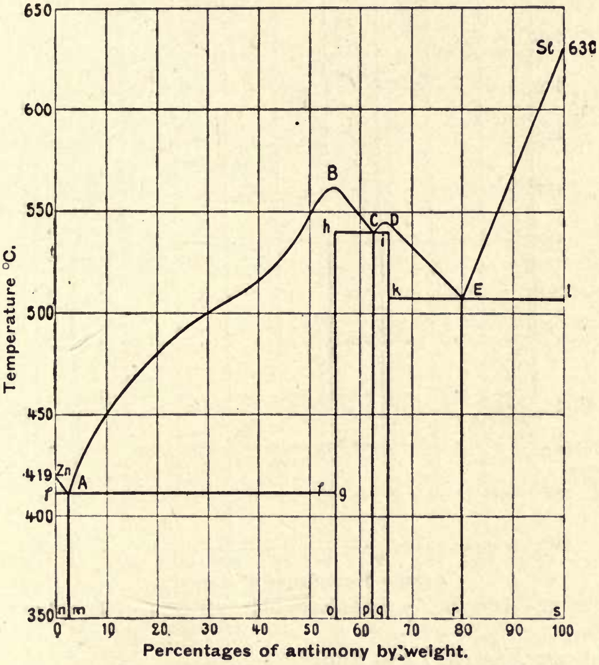

FIG. 70.—Diagram for the antimony-zinc alloys (Mönkemeyer).

freeze, and correspondingly the different antimony-zinc alloys are compounded as follows:

Between *n* and *m* – zinc + eutectic *A*.
Between *m* and *o* – Zn_3Sb_2 + eutectic *A*.
Between *o* and *p* – Zn_3Sb_2 + eutectic *C*.
Between *p* and *q* – ZnSb + eutectic *C*.
Between *q* and *r* – ZnSb + eutectic *E*.
Between *r* and *s* – antimony + eutectic *E*.

Tellurium-Bismuth.

The diagram of the tellurium-bismuth alloys, drawn up by Mönkemeyer,[1] is reproduced in Fig 71. It shows the type of freezing of Fig. 65 in its simplest form.

The following table gives the phases corresponding to the different fields.

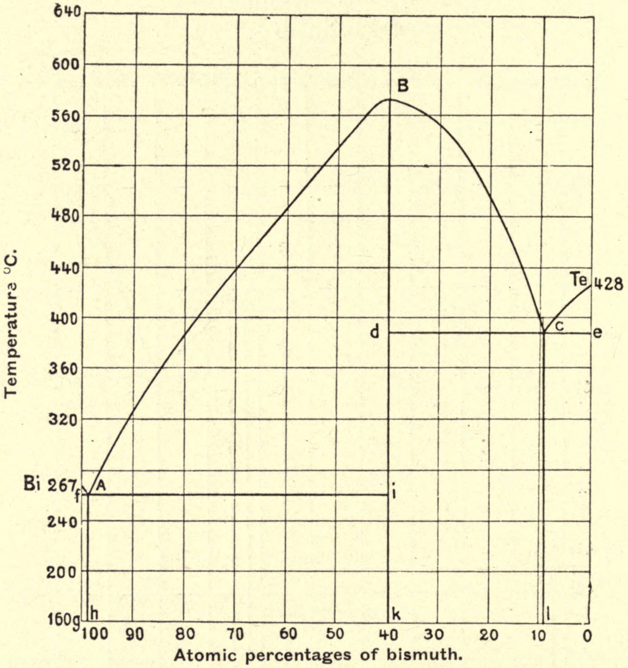

FIG. 71.—Diagram for the tellurium-bismuth alloys (Mönkemeyer).

Above *BiABCTe* – liquid ;
BiAf – Bi + liquid ;
ABi – Bi_2Te_3 + liquid ;
BCd – Bi_2Te_3 + liquid ;
CTee – Te + liquid ;
fAhg – Bi + eutectic *A* (Bi, Bi_2Te_3) ;
hAik – Bi_2Te_3 + eutectic *A* ;
kdCl – Bi_2Te_3 + eutectic *C* (Bi_2Te_3, Te) ;
lCeo – Te + eutectic *C*.

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[1] Mönkemeyer, "Über Tellur-Wismut." *Zeitschrift f. anorg. Chemie*, 1905, Bd. 46, s. 415.

Sodium-Tin.

The diagram for the sodium-tin alloys, established by Mathewson[1] is reproduced in Fig. 72. As in this case a series of interesting examples of freezing and transformation phenomena of alloys occur, it will be somewhat more fully treated.

The line *NaBCDEFGHSn* indicates the temperatures of the commencement of freezing. At *C* and *F* two maxima occur corresponding to the compounds Na_2Sn and NaSn. Moreover, the curve of the beginning of freezing possesses at the points *B*, *E* and *G* "kinks" (knicke) which correspond to the three concealed maxima[2] of the compounds Na_4Sn, Na_4Sn_3 and $NaSn_2$. In order to explain the diagram more clearly, some characteristic alloys will be selected in the following, and their freezing and transformation phenomena described.

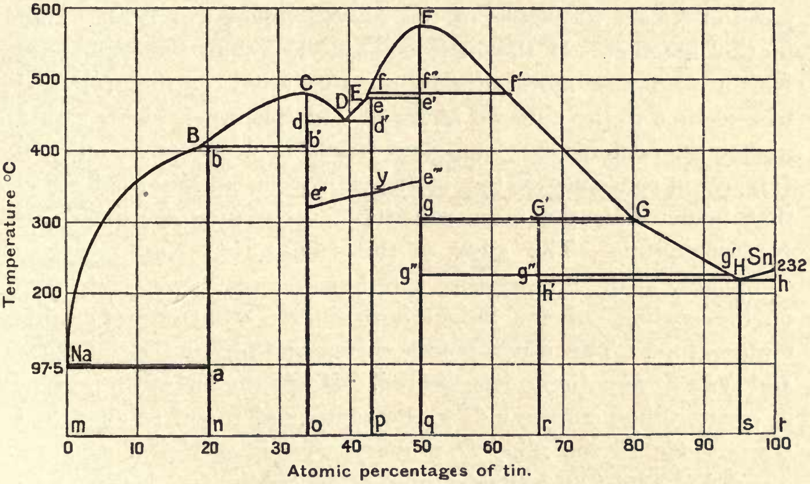

FIG. 72.—Diagram for the sodium-tin alloys (Mathewson).

Pure sodium melts at 97·5° C. By the addition of small amounts of tin, its freezing-point is inappreciably depressed, so that the first eutectic point, corresponding to the eutectic Na – Na_4Sn, will practically coincide with *Na*. A further addition of tin raises the freezing-temperature. All alloys between *Na* and

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[1] C. H. Mathewson, "Über die Verbindungen von Natrium mit Zinn." *Zeitschrift f. anorg. Chemie*, 46, s. 94 (1905).

[2] See p. 83.

B begin to precipitate crystals of Na_4Sn on the line *NaB*. The freezing is completed at the temperature of the horizontal line *Naa* by the formation of a eutectic consisting of Na and Na_4Sn.

A melt which corresponds exactly to the formula Na_4Sn freezes as follows. At a temperature lying on the *BC* branch of the curve crystals of the composition Na_2Sn separate out. When the line *Bb* is reached, these react with the still fluid mother-liquor according to the equation

$$Na_2Sn + \text{liquid alloy} \rightarrow Na_4Sn \quad . \quad . \quad . \quad . \quad (1)$$

As it was assumed that the original melt possesses the composition Na_4Sn, the whole of the mother-liquor will be used up by this reaction. If the melt contains less than the compound Na_4Sn demands, mother-liquor remains after reaction (1), and freezes then to the eutectic at *Naa.* On the other hand, with a higher tin content the compound Na_2Sn is in excess in reaction (1), and in consequence the mother-liquor is entirely used up, so that below *Bbb'* the mass consists of a mixture of Na_2Sn and Na_4Sn crystals. The alloy of the composition Na_2Sn freezes completely at the temperature *C* to homogeneous crystals, so that on the cooling curve a longer horizontal portion occurs at this temperature. The arrest-points corresponding to the line *Bbb'* and *Naa* have entirely disappeared. If the amount of tin present is greater than corresponds to the compound *C* and smaller than corresponds to the alloy *D*, primary crystals of Na_2Sn separate along *CD*, whilst an intimate mixture of Na_2Sn and Na_4Sn_3 proceeds to freeze on the eutectic line *dDd'*. *DE* corresponds to the primary crystallization of Na_4Sn_3. Now this latter compound possesses a transition point at the temperature *y*. The crystals of β-Na_4Sn_3 change into α-Na_4Sn_3 crystals with an increase in volume ; indeed, the increase is so considerable in the case of the alloys richer in tin, that the glass vessel which contains them is burst. All alloys which contain the compound Na_4Sn_3 must therefore show the transition point in the neighbourhood of *y*, which fact is indicated by the line *e''e'''*. The sloping direction of this may possibly be accounted for by internal stresses and consequent depression of the transformation point.

As also the compound Na_4Sn_3 decomposes below its melting-point into liquid and a kind of crystal of the formula NaSn, the same phenomena are repeated as in the formation of Na_4Sn ; that is to say, at the temperature of the horizontal Ee' the following reaction takes place:

$$\mathrm{NaSn} + \text{liquid} \rightarrow \mathrm{Na_4Sn_3} \quad . \quad . \quad . \quad . \quad (2)$$

An alloy lying between E and F would therefore freeze as follows. On the branch EF primary crystals of β-NaSn separate. These have a transition point at $ff'f''$, at which they are transformed into the α-modification. Finally these αNaSn crystals are changed at Ee' according to equation (2). The resulting compound β-Na_4Sn_3 changes at $e''e'''$ into the α-modification.

Further, the compound $NaSn_2$ separates primarily only along GH. $GG'g$ gives the temperature at which the compound $NaSn_2$ results from NaSn crystals and liquid, and according to the following equation:

$$\mathrm{NaSn} + \text{liquid} \rightarrow \mathrm{NaSn_2} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$NaSn_2$ is transformed at $g'''g''g'$ into an allotropic modification. HSn finally corresponds to the primary separation of tin, $h'h$ to that of the eutectic $NaSn_2$,Sn.

It is not always possible, however, to deduce the existence of a chemical compound from the collective arrangement of the critical points of a number of alloys. This is especially difficult when the compound decomposes before it melts. In most cases, nevertheless, the formula of the compound is arrived at by a suitable interpretation of the cooling phenomena, and by metallographic investigation, as Tammann[1] has shown in an ingenious manner.

Fig. 73 shows the freezing-point curve of the system A, B.

ac_1 represents the separation of the component A,
c_1c_2 „ „ „ compound $A_m B_n$,
c_2b „ „ „ component B,
t_1t_1 „ „ „ eutectic A, $A_m B_n$,
t_2 „ formation of $A_m B_n$ and separation of the eutectic $A_m B_n$, B.

The two bodies A and B may form the compound $A_m B_n$ with one another. This may, however, only be stable below the temperature $t_2°$, its melting-point, that is, when the pure compound

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[1] G. Tammann, "Über die Anwendung der thermischen Analyse in abnormen Fällen." *Zeitschrift f. anorg. Chemie*, 1905, Bd. 45, s. 24.

is heated, it will not melt to a homogeneous liquid but decompose at the temperature t°_2 according to the equation

$$A_m B_n \rightleftarrows aB + [(n - a) B + mA] \quad . \quad . \quad . \quad . \quad (1)$$

into crystals of the body B and a liquid $(n - a) B + mA$. Conversely, if the system $aB + [(n - a) B + mA]$ is allowed to cool, its separate components interact at t_2°, and reaction (1) proceeds from right to left.

Let it be assumed next that this reaction proceeds to completion. Melts of which the composition lies between C_2 and A_mB_n will freeze as follows. At the temperature given by C_2b crystals of B commence to separate by which the liquid becomes poorer in B. When the composition C_2 and simultaneously the temperature t_2 is reached, the reaction (1) proceeds from right to left, that is, crystals of A_mB_n are formed from the B crystals already separated and the still fluid material. Obviously the amount of the $A_m B_n$ crystals resulting in this way is greatest when the original solution possessed the composition $A_m B_n$.

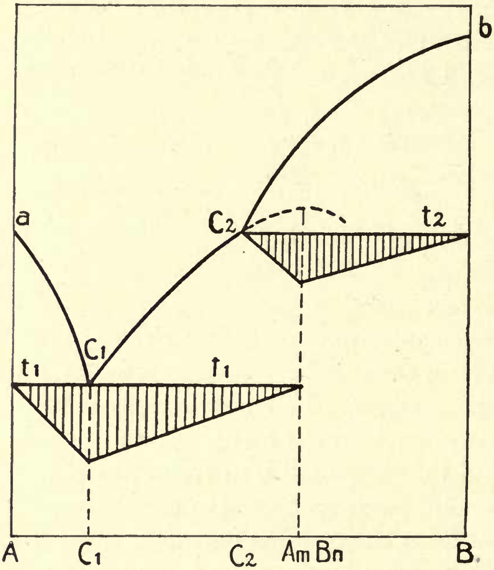

FIG. 73.—Composition.

The point $A_m B_n$ can be established by observing the duration of the arrest-point at t_1°. In a melt of the composition C_1 the duration of the arrest at t_1° will show a maximum, whilst at A and $A_m B_n$ the eutectic, and with this the arrest-point, will disappear. If the prevailing time of the eutectic arrest-point is plotted at right angles to the lines t_1 and t_2, the maximum of t_2 must coincide with the zero point of t_1.

The latter is not always the case, however, since reaction (1) can, under certain conditions, proceed only to partial completion.

The occurrence can, for instance, proceed in various ways. (1) Crystals of $A_m B_n$ can separate from the fluid melt still existing at the temperature t_2, whilst simultaneously the B-crystals already separated are dissolved therein. In this case the completion of the reaction would be attained with the greatest certainty. (2) The material A contained in the fluid C_2 can diffuse into the separated B crystals. Now it is possible in both cases that envelopes may form round the B crystals, which would prevent the contact of B with the fluid melt. The enveloped crystals are, in consequence, withdrawn from reaction (1). Thus this will not last so long, but instead an arrest-point will appear at t_1, since the concentration of the melt has been displaced towards the left by the withdrawal of the B crystals. This irregular procedure it will be possible to demonstrate, however, by a study of the structure, as the latter contains three kinds of crystals instead of the normal two. How such an abnormal process of crystallisation can be prevented must be decided case by case. Very frequently it is possible to suspend it by pulverising the solid mass and heating it for a sufficiently long time.

Often there are alloys, containing definite chemical compounds, amenable to chemical analysis, as certain reagents have no effect on the compound whilst the remaining material is attacked and dissolved. The compound now isolated, after being carefully cleaned, can be analyzed for its formula.

Thus, in order to determine definite chemical compounds in alloys, the following means are at our disposal:—

(1) The aspect of the freezing-point curve; maxima in the curve of the beginning of freezing correspond to definite compounds. Should this maximum be obscured by some side reaction or other, its position can be determined either by the graphic extrapolation of the branches (of the curve), by interpolation of the maximum of the transformation point, or by the determination of the point where the eutectic arrest-points disappear.

(2) The determination of the specific volumes of the whole series. These will be displayed by a broken line in which each angular point corresponds to a definite compound, in case the system contains no solid solutions.

(3) Chemical analysis.

Lead-Gold.

The first complete "melt-diagram," which was worked out by Vogel,[1] is reproduced in Fig. 74. From this it follows that the curve of the commencement of freezing *AuBCDPb* possesses two concealed maxima, which correspond to the compounds Au_2Pb and $AuPb_2$. The latter possesses a transition-point at 211°C; the freezing and cooling phenomena of the series will therefore eventuate as follow.

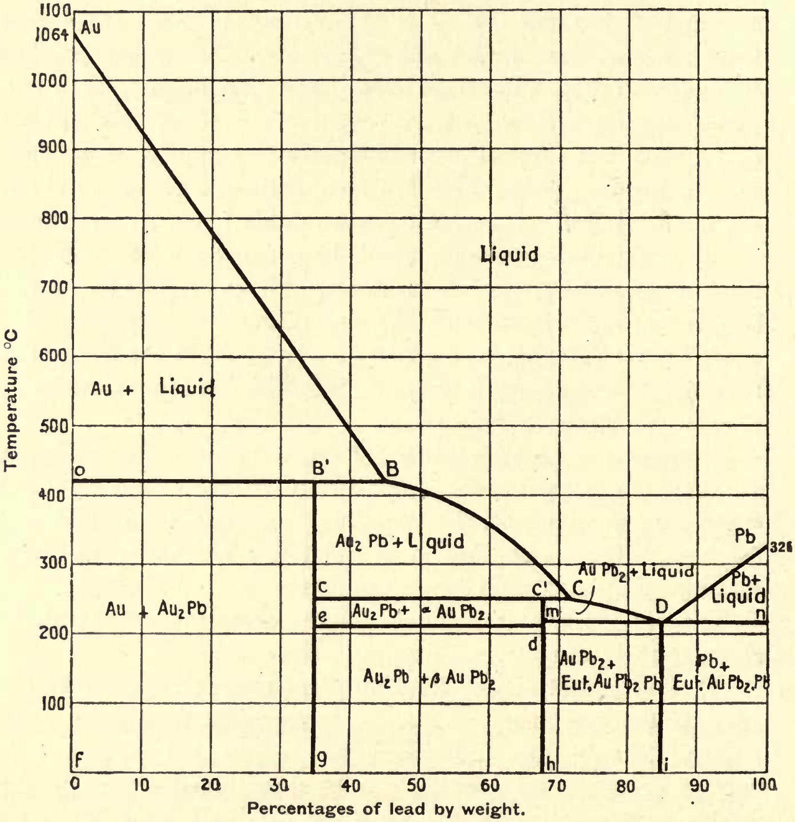

FIG. 74.—Diagram for the lead-gold alloys (Vogel).

On the line *AuB* separation of pure Au; on *BC* separation

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[1] R. Vogel, "Über Gold-Bleilegierungen." *Zeitschr. f. anorg. Chemie,* 1905, Bd. 45, s. 11.

of Au_2Pb; on *CD* separation of $AuPb_2$; on *DPb* separation of pure Pb.

The pure compounds Au_2Pb and $AuPb_2$ liquefy on warming, not to a homogeneous fluid, but decompose into a kind of crystal and a liquid. In cooling a molten alloy of the composition Au_2Pb, the separation of pure gold is first obtained. Should the temperature sink to *OB*, the gold already separated reacts with the fluid rich in lead to form Au_2Pb. This envelopes the gold crystals and withdraws them from further reaction, so that the change is incomplete. Similar phenomena appear in concentrations between *C* and *D*.

(2) *The compounds are wholly or partially soluble in the components or in one another.*

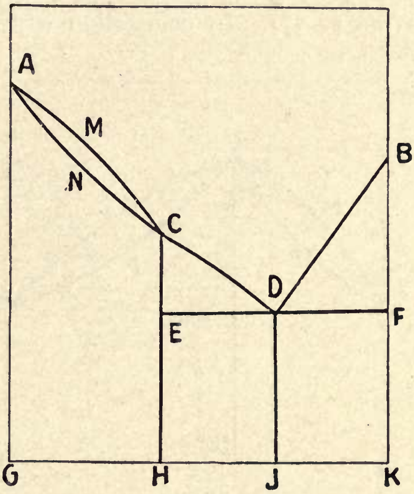

FIG. 75.

The phenomena of freezing and transformation are in general less decided and are frequently spread over very great intervals, which renders the accurate determination of the corresponding temperatures by thermal methods a matter of great difficulty. The changes which the primary mixed crystals undergo during the subsequent cooling are for the most part very slow and too small to result in a measurable heat disturbance. There is here, therefore, a special field for the microscopic study of the structures.

The appearance or disappearance of the separate constituents is proportionately easy to determine under the microscope, and therefore also the spheres of existence of the individual components. The researches of Heycock and Neville (see p. 111) on the copper-tin alloys are, in this connection, classical.

The theoretically possible freezing-point curves will be discussed here only in the simple case where the components *A* and *B* can form but one compound $A_m B_n$ with one another. Thus there are the following cases to differentiate.

(*a*) $A_m B_n$ is completely soluble in A, completely insoluble in B.

(*b*) $A_m B_n$ is completely soluble in A and in B.

(*c*) $A_m B_n$ is partially soluble in A and in B.

(*d*) $A_m B_n$ is completely soluble in A, partially soluble in B.

(*e*) $A_m B_n$ is partially soluble in A, wholly insoluble in B.

Several freezing-point curves of these five groups are shown in Figs. 75 to 77. It is evident, without further treatment, that these consist only of a juxtaposition of the various simple types of freezing as Roozeboom has developed them theoretically (see p. 37). In connection with this, $A_m B_n$ can, in a way, be considered as a new body which can occur alone or with one of the components only, but never with both together at the same time.

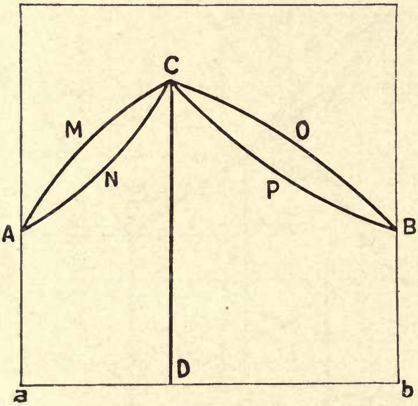

FIG. 76.

(*a*) According to the freezing-point curve Fig. 75 the whole melt is liquid above *AMCDB*. At the commencement of freezing mixed crystals *ANC* separate from the molten mass *AMC;* from the molten mass *CD* the pure compound $A_m B_n$, and corresponding to the eutectic line *EF*, the eutectic $A_m B_n$, B; *DB* corresponds to the separation of the pure substance *B*.

Corresponding to the freezing phenomena, there appear in the frozen alloy the following constituents:—

Between *G* and *H* – homogeneous mixed crystals A, $A_m B_n$.

At *H* – crystals $A_m B_n$.

Between *H* and *J* – crystals $A_m B_n$ and eutectic $A_m B_n$, B.

Between *J* and *K* – crystals B and eutectic $A_m B_n$ B.

(*b*) Exclusive of the composition *D* which corresponds to the compound $A_m B_n$, mixed crystals *ANCPB* separate from melts *AMCOB;* correspondingly, all the frozen alloys consist of homogeneous mixed crystals.

(*c*) The freezing-point curve Fig. 77 shows that mixed crystals *AF*, consisting of a solid solution of the compound $A_m B_n$ in the component *A* crystallize out from the melts *AC*. *C* corresponds to the eutectic of mixed crystals *F* and *G*, *E* to the pure compound *E*, and there is a repetition of the phenomena between *E* and *B* for the compound A_mB_n and the component *B*.

Alloys between *O* and *K* consist of homogeneous mixed crystals of the composition of the molten material; between *K* and *L* there is a mass of mixed crystals *K*, *L*; from *L* to *Q* homogeneous mixed crystals; at *Q* the pure compound A_mB_n; between *Q* and *M*, mixed crystals; *M* and *N* a mass of mixed crystals *M* and *N*; *N* and *P*, homogeneous mixed crystals.

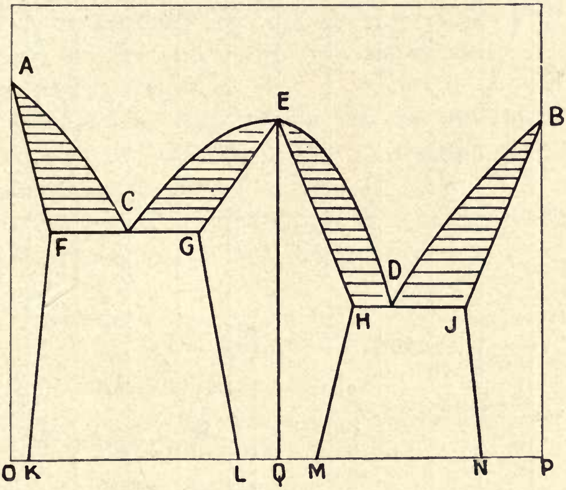

FIG. 77.

It is an easy matter to deduce the constitution of the alloys in the two remaining cases by drawing up the corresponding freezing-point curves.

Aluminium-Magnesium.

This series of alloys, frequently employed technically under the name "magnalium," were first thoroughly investigated by Boudouard.[1] From the freezing-point curve he deduced the existence of three chemical compounds of the formulæ Al_4Mg, $AlMg$, $AlMg_2$. The proof of this he found in the composition of the residue after treating certain alloys with hydrochloric acid

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[1] Boudouard, *Comptes rendus*, 132, p. 1325; 133, p. 1003.

and ammoniun chloride solution. As the formulæ of these alloys did not agree sufficiently well with the results of thermal analysis, Grube[1] repeated the experiments and established the freezing-point curve of Fig. 78.

This shows two minima *A* and *C* as well as a maximum *B*, which corresponds to the compound Al_3Mg_4. The part to the right of *B* exhibits the *Va* type of freezing (salt-water); *BC* corresponds to the separation of the compound Al_3Mg_4, *CMg* to that of magnesium, and lastly *gk* to that of the eutectic $Mg - Al_3Mg_4$.

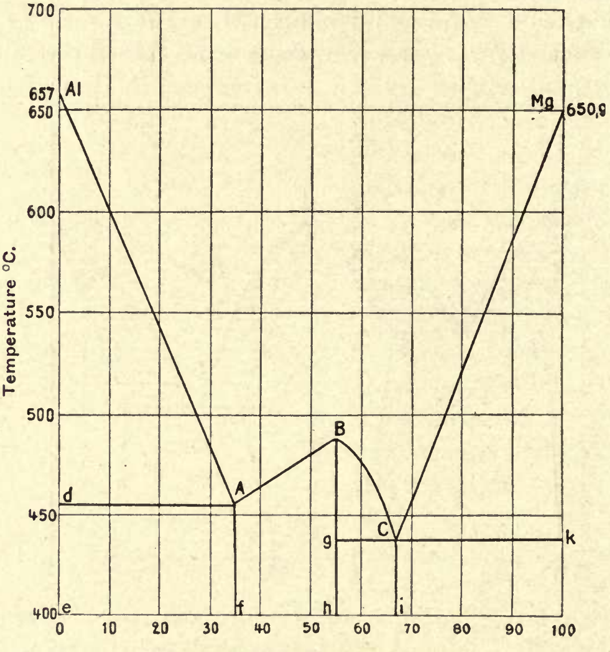

FIG. 78.—Diagram for the aluminium-magnesium alloys (Grube).

The part of the freezing-point curve lying upon the left side of *B* runs essentially differently. All the alloys between *A* and *B* freeze like chemical compounds, that is, completely at a definite temperature, which rises from *A* to *B*. This is possible only when mixed crystals of Al_3Mg_4 and Al form between *A* and *B*,

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[1] G. Grube, "Über Magnesium-Aluminiumlegierungen." *Zeitschrift für anorganische Chemie*, 1905, Bd. 45, s. 225.

or similar crystals of Al_3Mg_4 and another compound Al_2Mg_4, which must correspond to the composition *f*. As the latter does not comform to the law of multiple proportions, Grube assumes that it is a question of the separation of mixed crystals $Al_3Mg_4 - Al$ upon *AB*.

Now it has been shown earlier, that in the freezing of mixed-crystals, the crystals separating from the molten mass have a composition different from that of the molten liquor. The change in concentration resulting from this causes a lowering of the melting-point whereby the process of freezing is distributed over a more or less large interval of temperature.

It must be assumed that the curve of complete solidification practically coincides with that of the commencement of freezing of mixed crystals *AB*.

The line *Ad* in Fig. 78 will now be the eutectic line for aluminium + mixed crystals of the composition *f*, *AAl* the line of separation of pure aluminium from the melt.

The freezing-point curve, Fig. 78, thus divides the aluminium-magnesium alloys into the following groups.

Domains of Existence.

AlAd	Al + molten material.
ABhf	mixed crystals of Al_3Mg_4 + Al.
BgC	Al_3Mg_4 + molten material.
MgCk	Mg + molten material.
dAfe	Al + mixed crystals with 35 per cent. Mg.
gCih	Al_3Mg_4 + eutectic Mg,Al_3Mg_4.
Ckli	Mg + eutectic Mg,Al_3Mg_4.

Microscopic investigation shows, in agreement with the freezing-point curve, the following composition of the different alloys. From 0 to 35 per cent. primary separated crystals occur consisting of mixed crystals *A* surrounded by aluminium.

At about 30 per cent. magnesium the first separated aluminium crystals are scattered throughout the mass in beautiful dendritic forms.

Between 30 and 55 per cent. magnesium no crystalline structure is perceptible, but the section presents the uniform appearance characteristic of a conglomerate of mixed crystals.

Alloys with more than 55 per cent. magnesium show crystals of Al_3Mg_4 or Mg in a eutectic ground mass, according as the magnesium content is smaller or greater than that corresponding to its eutectic *C*.

Iron-Silicon.

The diagram, constructed according to the determinations of Guertler and Tammann,[1] of the iron-silicon alloys is reproduced in Fig. 79. The curve of the commencement of freezing, *FeABCDSi*, shows two maxima, corresponding to the compounds Fe_2Si and FeSi. Up to a content of $33\frac{1}{2}$ atoms per cent. of silicon the freezing is introduced by the formation of mixed crystals. Accordingly, the different "existence-domains" (Zustandsfelder) of the diagram are made up as follow.

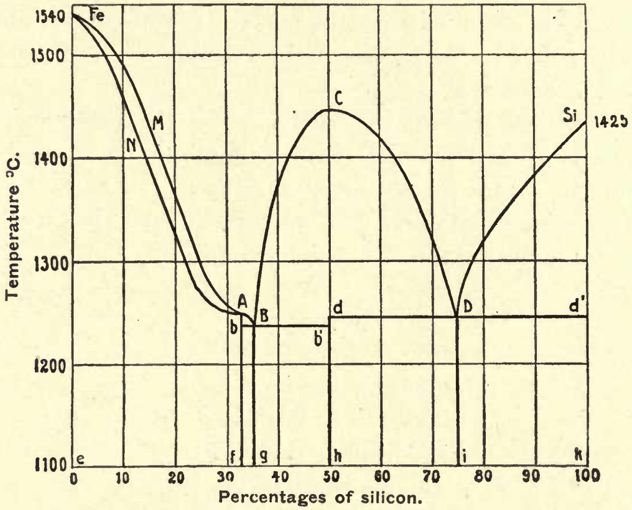

FIG. 79.—Freezing-point curve of the iron-silicon alloys (Guertler and Tammann).

Above *FeABCDSi* – molten material.

FeMAN – mixed crystals Fe,Fe_2Si + molten material.
ABb – Fe_2Si + molten material.
BCDdb' – FeSi + molten material.
DSid' – Si + molten material.

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[1] W. Guertler and G. Tammann, "Über die Verbindungen des Siliciums mit dem Eisen." *Zeitschr. f. anorg. Chemie*, 1905, Bd. 47, s. 163.

FeNbfe – mixed crystals Fe,Fe_2Si.
bBgf – Fe_2Si + eutectic *B* (Fe_2Si + FeSi).
Bb'hg – FeSi + eutectic *B*.
hdDi – FeSi + eutectic *D* (FeSi + Si).
iDd'k – Si + eutectic *D*.

Aluminium-Copper.

The freezing-point curve of the aluminium-copper alloys had already forced Le Chatelier[1] and Gautier[2] to the conclusion that several compounds of definite composition occur in the series, a fact which was confirmed by the microscopic investigations of the former.

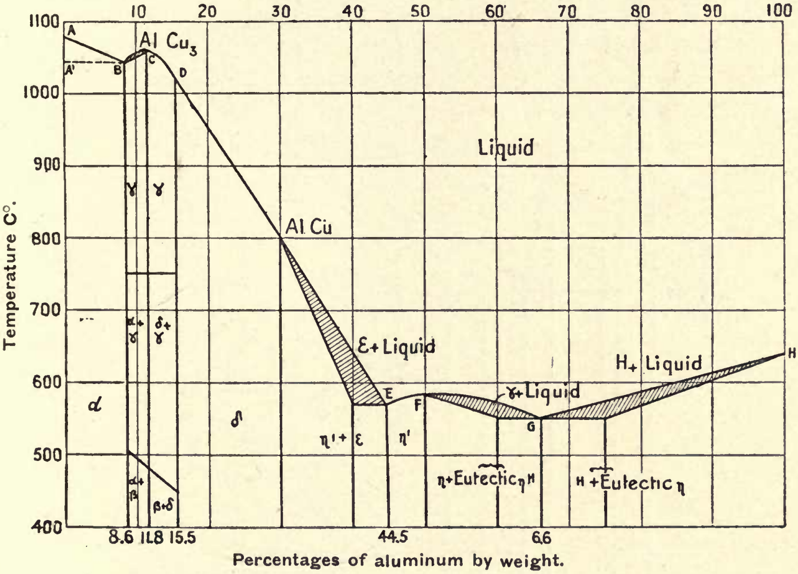

FIG. 80.—Diagram for the aluminium-copper alloys (Guillet).

Later, Guillet[3] endeavoured to establish the curve of complete

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[1] H. Le Chatelier, "Les alliages métalliques." *Revue générale des sciences*, 1895. "La technique de la métallographie microscopique." *Contribution à l'étude des alliages*, Paris, 1901, p. 421.

[2] Gautier, see p. 60, footnote 1.

[3] L. Guillet, "Étude théorique et industrielle des alliages de cuivre et d'aluminium." *Revue de métallurgie*, 1905, p. 595.

solidification along with that of the commencement of freezing. His results are reproduced in Fig. 80.

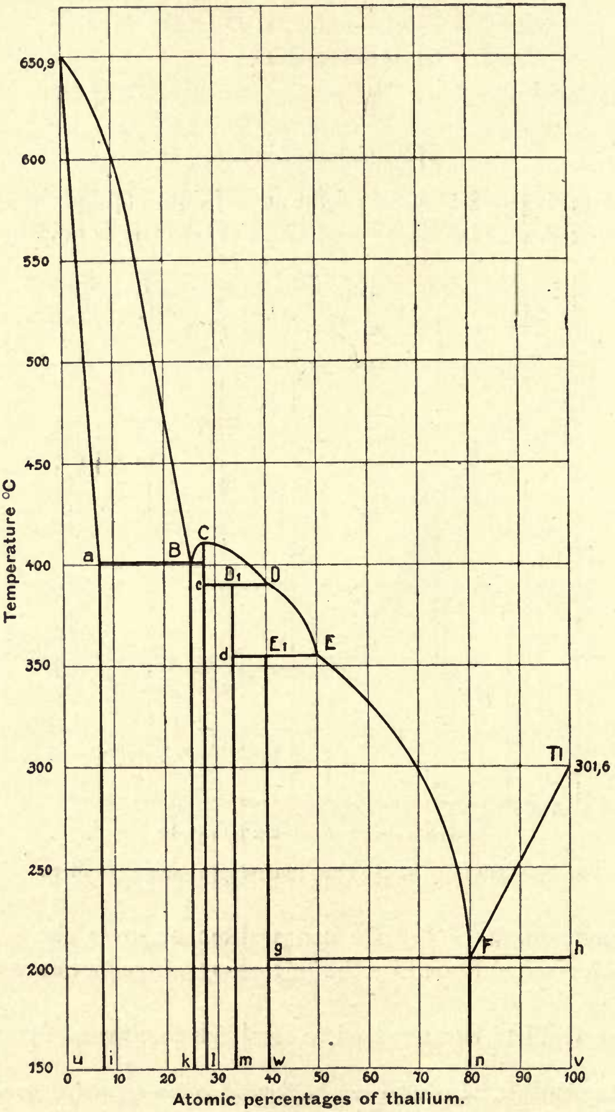

FIG. 81.—Diagram for the magnesium-thallium alloys (Grube).

Guillet affirms that alloys between *A* and *B* possess only one freezing-point. They yield therefore solid solutions from 0 up to 8 per cent. of aluminium. In structure these solid solutions appear as polyhedra, which are coloured yellow by a hydrochloric acid solution of ferric chloride (Heycock and Neville, see p. 112, footnote 3) or ammoniacal cuprous chloride solution. The structure is not changed by quenching at various temperatures; at the most there appear cleavage surfaces. These polyhedra are called constituent α by Guillet. Immediately the aluminium content exceeds 8 per cent., the dark-coloured β constituent appears surrounding the α-crystals. The former is either a compound $AlCu_3$ or a solid solution. If the alloys lying between B and D are quenched above their transition-point (750° C.) there appears the constituent γ, which is a solid solution with 8·6 to 15·5 per cent. of aluminium. Below this change-point the γ-solution decomposes into a mixture of γ-crystals and "limit-crystals" α and δ (see p. 44), with complete decomposition at a point lower still.

The δ-constituent, again, represents a solid solution with a content of from 15·5 to 30 per cent. of aluminium. The constituent ε seems to be identical with the compound AlCu, whilst the compound Al_2Cu corresponds to the constituent η. Guillet conjectures the further existence of a solid solution η' with 44·5 to 46 per cent. of aluminium. Finally the constituent χ consists either of pure aluminium or of a solid solution very poor in copper.

It is possible by chemical analysis to isolate the compound Al_2Cu only, not any of the others.

The alloys rich in copper and known as aluminium bronze are found of manifold use in the industries, whilst those richer in aluminium are often used for the casting of machine parts, in place of aluminium. Alloys between 11 and 94 per cent. of aluminium find no application.

Magnesium-Thallium.

The existence of the compounds Tl_3Mg_8, $TlMg_2$, Tl_2Mg_3 follows from the diagram of the magnesium-thallium alloys, according to Grube[1] (Fig. 81). The curve of the commencement of freezing shows a marked maximum at C and two concealed maxima corresponding to the kinks D and E. The phenomena of freezing may be read off from Fig. 81 without further remark.

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[1] G. Grube, "Über die Legierungen des Magnesiums mit Zinn und Thallium." *Zeitschrift für anorg. Chemie*, 1905, Bd. 46, s. 76.

Domains of Existence.

Above *Mg BCDEF Tl*—molten material.

MgBa – mixed crystals Mg + Tl_3Mg_8 + molten material,
BCDc – Tl_3Mg_8 + molten material,
D_1DEd – $TlMg_2$ + molten material,
E_1EFg – Tl_2Mg_3 + molten material,
FTlh – Tl + molten material.

Mgaiu – mixed crystals Mg + Tl_3Mg_8,
aBki – mixed crystals Mg + Tl_3Mg_8 + eutectic *B* (mixed crystals Mg + Tl_3Mg_8, Tl_3Mg_8),

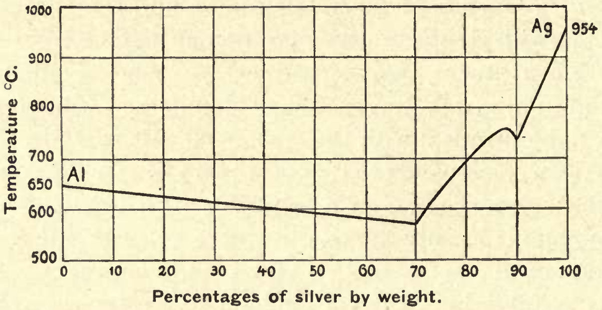

FIG. 82.—Freezing-point curve of aluminum-silver alloys (Gautier).

Bklc – Tl_3Mg_8 + eutectic *B*,
lcD_1m – Tl_3Mg_8 + $TlMg_2$,
mdE_1w – $TlMg_2$ + Tl_2Mg_3,
wgFn – $TlMg_2$ + eutectic *F* ($TlMg_2$,Tl),
nFhv – Tl + eutectic *F*.

Aluminium-Silver.

Fig. 82 shows the melting-point curve, drawn up by Gautier,[1] which points to the existence of a compound $AlAg_2$.

Later researches by Petrenko[2] have shown, however, that the system of the aluminium-silver alloys is more complicated than

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[1] Gautier, "Recherches sur la fusibilité des alliages métalliques." *Contribution à l'étude des alliages*, 1901.

[2] Petrenko, "Über Silber-Aluminiumlegierungen." *Zeitschrift f. anorganische Chemie*, 1905, Bd. 45, s. 49.

it appears from the researches of Gautier. Fig. 83 shows the diagram constructed by Petrenko. In it the line *AgDCFGAl* marks the commencement of freezing. At the point *D* the alloy freezes exactly like a chemical compound $AlAg_2$; it possesses only one arrest-point, and the frozen mass consists of homogeneous crystals. The freezing of alloys between *Ag* and *D* proceeds in such a way that mixed crystals *Agd* eventually separate from the composition *AgD; dD* does not correspond, however, as one would expect, to a eutectic, but to the freezing of the compound $AlAg_3$. This is the second case where the separating mixed crystals gradually approximate to the composition of a compound (see aluminium-magnesium). As the latter undergoes an

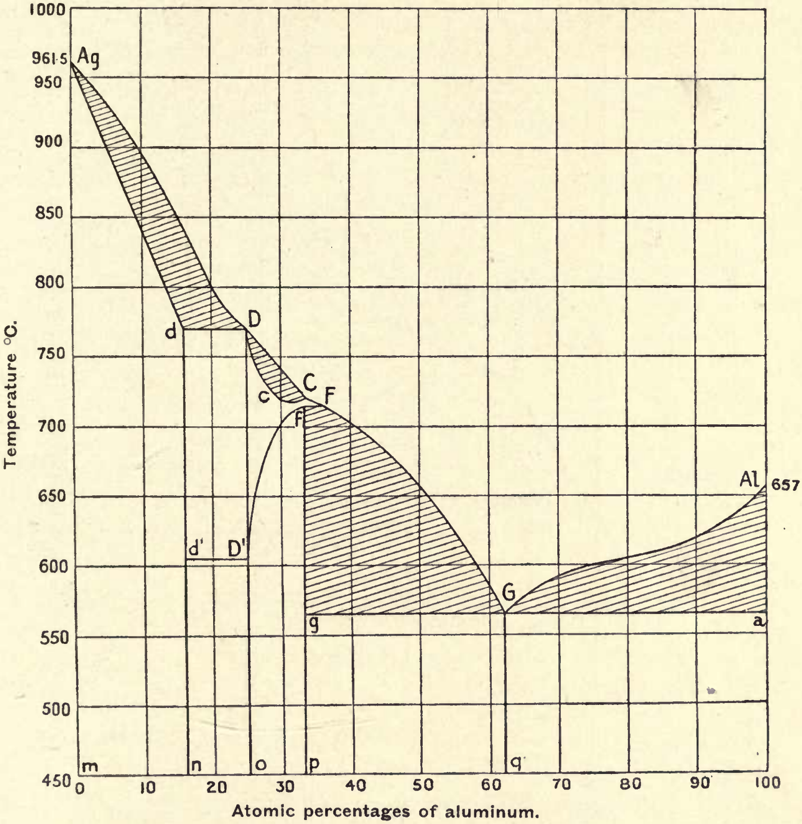

FIG. 83.—Diagram of the aluminium-silver alloys (Petrenko).

allotropic change at a temperature lying somewhat higher than 600° C., a horizontal line *d'D'* occurs in the diagram corresponding to this transformation. Further, the alloy *C* also, in respect of its freezing and structural characteristics, possesses the attributes of a chemical compound, which therefore is represented by the formula $AlAg_2$. As the two compounds $AlAg_2$ and $AlAg_3$ are able to form mixed crystals with one another, alloys between *D* and *C* freeze so that mixed crystals *DcC* separate from molten material of the composition *DC*. Moreover, $AlAg_2$ possesses a transition-point at about 718° C., consequently there appears a further arrest-point *f* after the complete freezing at the temperature C°. The position of the transition point *f* of the compound $AlAg_2$ will be influenced markedly by the isomorphous mixing with $AlAg_2$, so that in alloys between *D* and *C*,

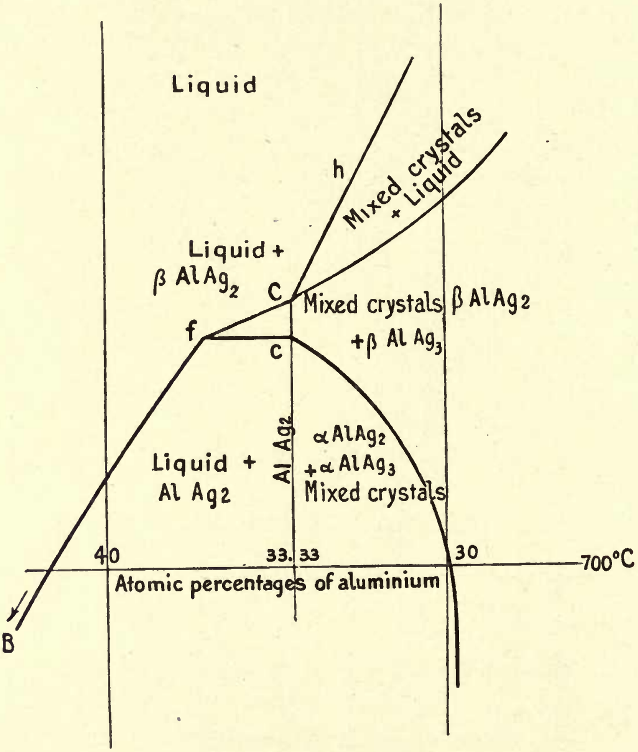

FIG. 84.

transformations of both compounds occur at a temperature corresponding to some such line as *D'f*. Fig. 84 reproduces a part of Fig. 83 more distinctly, and can be understood without further description. The further course of the freezing-point curve is simpler; *CF* corresponds to the separation, *fF* to the transformation of primary β-$\mathrm{AlAg_2}$ crystals; *FG* to the separation of primary $\alpha\mathrm{AlAg_2}$ crystals; *GAl* to that of aluminium, whilst *gGa* denotes the freezing of a eutectic $\alpha\mathrm{AlAg_2}$, *Al*.

Thus there are in the various domains of Fig. 83 the following phases in equilibrium:

AlGa : aluminium + molten material;
GFfg : α $\mathrm{AlAg_2}$ + molten material;
fFC : β $\mathrm{AlAg_2}$ + molten material;
CcD : mixed crystals (β $\mathrm{AlAg_2}$, β $\mathrm{AlAg_3}$) + molten material;
DdAg : mixed crystals (β $\mathrm{AlAg_3}$, Ag) + molten material;
arqG : aluminium + eutectic *G* (Al + α $\mathrm{AlAg_2}$);
qGgp : α $\mathrm{AlAg_2}$ + eutectic *G*;
pfD'o : mixed crystals (α $\mathrm{AlAg_2}$, α $\mathrm{AlAg_3}$);
fCcDD' : mixed crystals (β $\mathrm{AlAg_2}$, α $\mathrm{AlAg_3}$);
dDD'd' : β $\mathrm{AlAg_3}$ + saturated mixed crystals (Ag, β $\mathrm{AlAg_3}$);
d'D'on : α $\mathrm{AlAg_3}$ + saturated mixed crystals (Ag, β $\mathrm{AlAg_3}$);
Agdnm : mixed crystals Ag, β $\mathrm{AlAg_3}$.

Aluminium-Antimony.

From the freezing-point curve as determined by Gautier,[1] it follows that almost all the alloys of these two metals possess a higher melting-point than those of the pure metals. The maximum at 1048° C. corresponds to the compound SbAl, which has already been isolated by Wright.[2] In its further course the curve possesses a eutectic point and yet another maximum; it is possible that a second compound occurs here, which can crystallize isomorphously with aluminium, although closer investigations have not yet been made on the point.

The alloys which are rich in SbAl decompose in time into a powder, infusible at 1100° C. Whereas the corresponding

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[1] See p. 60, footnote 1.

[2] Wright, *Journal of the Chemical Society*, 1892, p. 493.

phenomena in the iron-aluminium alloys is a matter of an allotropic change, it is, in the aluminium-antimony alloys, a question of oxidation. If, for instance, the alloys are kept out of contact with air, they remain unchanged. The increase in weight of the decomposed alloys is a further proof of oxidation.

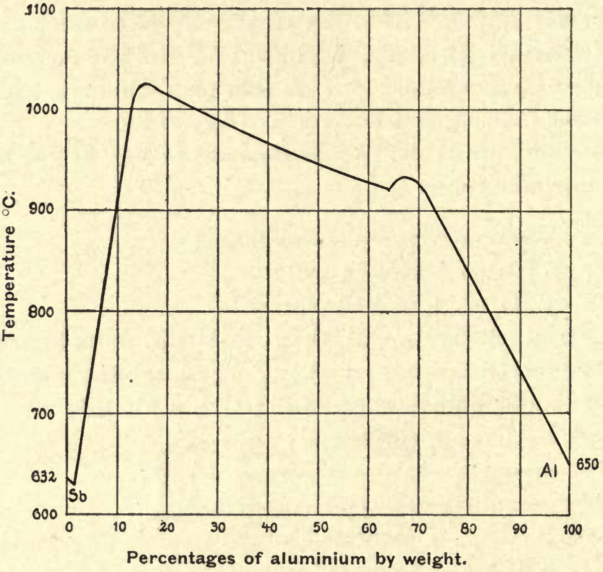

FIG. 85.—Freezing-point curve of the aluminium-antimony alloys (Gautier).

Gold-Tin.

The diagram, as worked out by Vogel, is reproduced in Fig. 86. From this it is apparent that by the addition of tin the temperature of the separation of primary gold sinks, and that rapidly from 1064° C. the melting-point of pure gold to 280° C., to rise again from this point to a maximum *C* at 418° C. Since gold can retain 5 per cent. of tin in solid solution, all gold-tin alloys with a tin content of 0 to 5 per cent. consist of homogeneous mixed crystals. Nevertheless a homogeneous structure is obtained under microscopic examination only when the pulpy mixture of gold and mixed crystals is allowed to cool for an inordinate length of time (some hours). The gold-tin compound corresponding to the maximum *C* possesses the formula AuSn, so that the constituents of the region *AuBCpm* can be deduced without further explanation. There exist

within *Aub'nm* – mixed crystals of gold and tin,
„ *AuBb'* – mixed crystals gold-tin + molten material,
„ *BCb''* – compound AuSn + molten material,

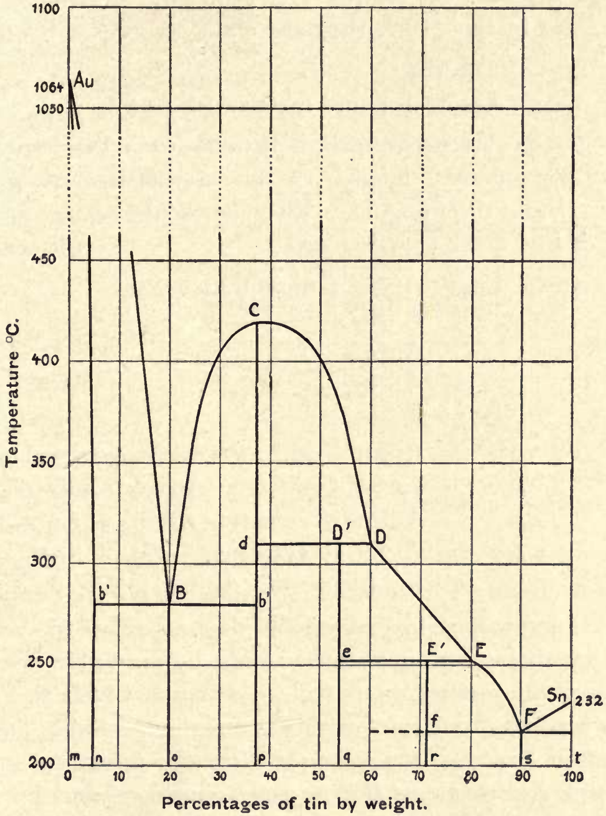

FIG. 86.—Freezing-point curve of gold-tin alloys (Vogel).

inside *b'Bon* – mixed crystals gold-tin + eutectic *B*, consisting of crystals of the compound AuSn + mixed crystals gold-tin with 5 per cent. Sn,
„ *Bb'po* – crystals AuSn + eutectic *B*.

The further course of the curve of separation of primary crystals shows more angular points at *DE'EF*.

The crystals separated out upon the branch *CD* correspond to the compound AuSn, those separated on *DE* to the compound $AuSn_2$.

Dd is a horizontal line upon which the following reaction takes place from left to right on cooling:

$$\text{AuSn} + \text{molten material} \rightleftarrows \text{AuSn}_2 \quad . \quad . \quad . \quad (1)$$

These crystals of $AuSn_2$ are primarily separated on the branch *DE*; in their turn they are changed at the temperature *eE* in the following way:

$$\text{AuSn}_2 + \text{liquid material} \rightarrow \text{AuSn}_4 \quad . \quad . \quad . \quad (2)$$

The crystals $AuSn_4$ are primarily deposited on the branch *EF*.

FSn corresponds, finally, to the appearance of pure tin crystals. From the foregoing, the constituents of the remaining regions of Fig. 86 can be deduced:

BCb″	corresponds to	AuSn + molten material,
CDd	"	AuSn + " "
DEeD′	"	$AuSn_2$ + " "
E′EFf	"	$AuSn_4$ + " "
FSnf″	"	Sn + " "
Bb″po	"	AuSn + eutectic (AuSn + mixed crystals),
dD′qp	"	AuSn + eutectic (AuSn + $AuSn_2$),
eE′rq	"	$AuSn_2$ + eutectic ($AuSn_2$ + $AuSn_4$),
fFsr	"	$AuSn_4$ + eutectic ($AuSn_4$ + Sn),
Ff″ts	"	Sn + eutectic ($AuSn_4$ + Sn).

The microscopic investigation, also prosecuted by Vogel,[1] shows that the system gold-tin presents a remarkable example of the changes described on p. 82, according to which the crystals already separated out react with the remaining mother-liquor.

It often happens, for example, that the primarily separated crystals of $AuSn_2$ along *DE* become enveloped by the crystals of $AuSn_4$ resulting from the reaction (2) at the temperature *eE*, and in this way their contact with the mother-liquor rich in tin is prevented, so that reaction (2) cannot proceed quantitatively.

Antimony-Silver.

It appears, from the freezing-point curve (Fig. 87) of the antimony-silver alloys according to the experiments of Heycock

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[1] Vogel, "Über Goldzinnlegierungen." *Zeitschrift. f. anorg. Chemie*, 1905, Bd. 46.

and Neville,[1] that the branch which corresponds to the primary separation of silver crystals from the melt, has a "kink" at *A*. This corresponds apparently to the compound Ag_3Sb. The eutectic alloy *E* contains 44·3 per cent. of antimony and freezes at a temperature of 486° C. Charpy,[2] who has investigated these alloys microscopically, ventures to conclude that the compound Ag_3Sb can form isomorphous mixed crystals with the silver. Dilute nitric acid is a suitable reagent for the development of the structure of alloys rich in antimony, whilst sulphuretted hydrogen and ammonia are used in the case of those alloys richer in silver. The former blackens the silver with formation of sulphide, the latter covers the antimony with a dark blue oxidation film.

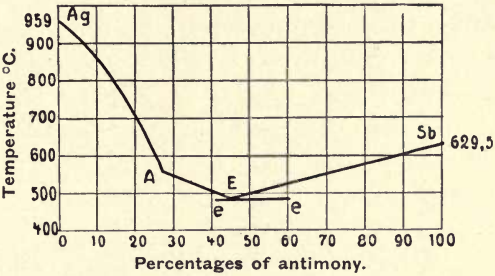

FIG. 87.—Freezing-point curve of silver-antimony alloys (Heycock and Neville).

Copper and Zinc.

(Brass.)

Next to the alloys of iron with carbon, the copper-zinc alloys are the most capable of assuming the greatest variety of working properties by virtue of suitable composition, thermal and mechanical treatment; indeed, there are many in the class of brasses whose compositions differ to no considerable extent from one another, which nevertheless present such great differences in tenacity, elasticity, and other properties, that they might be conjectured to be totally different metals.

The influences of cold-working, tempering, and annealing on the working properties and micro-structure have been determined by the work of Thurston[3] and Charpy.[4] Roberts-Austen[5] first

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[1] Heycock and Neville, "Freezing-Point Curves, etc." *Phil. Trans.* 189 A., 1897, p. 25.

[2] Charpy, "Étude microscopique des alliages métalliques." *Contribution à l'étude des alliages*, 1901.

[3] R. H. Thurston, "A Treatise on Brasses, Bronzes, and other Alloys." New York, Wiley and Sons. 1893.

[4] G. Charpy, "Recherches sur les alliages de cuivre et de zinc." *Contribution à l'étude des alliages*, 1901. Paris, Chamerot et Renouard.

[5] W. C. Roberts-Austen, "Fourth Report to the Alloys Research Committee." *Proc. Inst. Mech. Eng.*, 1897, p. 36.

drew up a complete freezing-point curve of the copper-zinc alloys.

The microscopic research pursued by Charpy concerned itself chiefly with the influence of cold-hammering and annealing on the structure. However interesting his results in this direction may be, his views upon the nature of the constituents can be brought into but incomplete accord with the Roberts-Austen diagram. The two investigators are agreed on this point only, that they assume the existence of isomorphous mixtures in the copper-zinc series, from which it follows that a considerable number of these alloys present a homogeneous crystalline structure under the microscope. According to the microscopic investigations of Le Chatelier,[1] moreover, the compounds CuZn, $CuZn_2$, $CuZn_3$, $CuZn_4$ appear to exist.

In the year 1904 the researches of Shepherd,[2] who drew up a complete freezing-point curve, brought further elucidation. These fully confirmed the conjecture concerning the existence of mixed crystals in the series, but not of compounds of definite chemical composition.

In Fig. 88 the line $ABCDEFG$ gives the temperature of the commencement of freezing, which is completed along the line $Ab_2b_1c_1Cd_1e_2e_1f_1F$. As in the case of the freezing of the copper-tin series (see p. 111), various crystal-types of solid solutions are formed, which will be designated α, β, γ, δ, ε, χ, η, and of which the domain of existence is limited.

As is apparent from the freezing-point curve, the phenomena of crystallization are merely a manifold repetition of Roozeboom's freezing-type IV, which was more particularly explained on p. 40. Upon the line AB, there begin to separate out α-mixed crystals of copper and zinc, the composition of which is given by the line Ab_2. Within the region ABb_2 α-mixed crystals and fluid melt exist side by side. After complete freezing according to Ab_2, the whole mass consists of homogeneous mixed crystals α, the zinc contents of which lie between o and the abscissa of b_2, Melts whose zinc content is higher than b_2 separate out α-crystals

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[1] Le Chatelier, "La technique de la métallographie microscopique." *Contribution à l'étude des alliages*, 1901, p. 439. Paris, Chamerot et Renouard.

[2] S. Shepherd, *Journal of Physical Chemistry*, VIII., 1904, pp. 421–434.

at first. When the temperature b_2b_1B is reached, the still fluid mass freezes to a conglomerate of *α*- and β-crystals. The latter, which were designated "limit-crystals" on p. 41, can undergo still further change below this temperature. An alloy with 33 per cent. of zinc, for instance, begins to precipitate at the temperature *m* mixed crystals *p*; whilst the mother-liquor passes through the composition *m* to *B*, the separated and still-separating *α*-crystal-conglomerate runs from *p* to b_2. At *n* an intimate mixture of *α*- and β-crystals of the composition b_2 and b_1 form from the remaining excess of mother-liquor, whereupon the freezing is at an end. At *o* the alloy enters into the domain of existence of *α*-crystals, that is, the β-crystals already separated react with the *α*-crystals according to the equation—

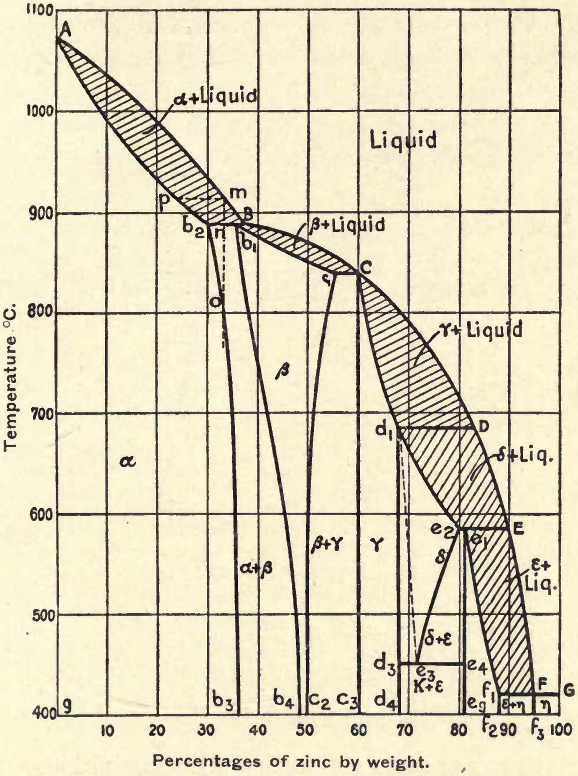

FIG. 88.—Diagram of the copper-zinc alloys (Shepherd).

$$\alpha\text{-crystals } b_2 + \beta\text{-crystals } b_1 = \alpha\text{-crystals } o.$$

Should this change proceed quantitatively, the whole mass consists of α-crystals.

The freezing of all melts between b_2 and b_1 takes place in this manner. Those lying between b_1 and B are transformed as follows. (See Fig. 89, which reproduces on a larger scale the part of Fig. 88 under consideration.) A melt containing about 37 per cent. of zinc begins to precipitate α-crystals with E per cent. of zinc at the temperature g. At the temperature r the separated mixed crystals possess the composition b_2, the corresponding molten material containing B per cent. of zinc. There now follows, at constant temperature, the transposition—

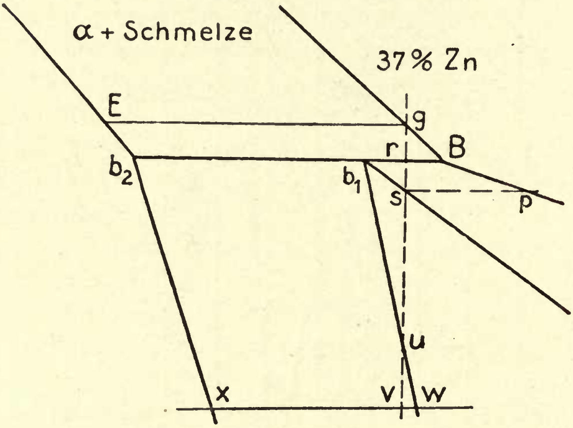

FIG. 89.—Detail of Fig. 88, enlarged.

$$\alpha\text{-mixed crystals } b_2 + \text{liquid material } B = \beta\text{-mixed crystals } b_1.$$

Afterwards the mass cools still further with separation of β-mixed crystals b_1s, which crystallize from a fluid mother-liquor Bp.

Below s the whole mass consists at first of β-mixed crystals down to the temperature u, where a second reaction takes place—

$$\beta\text{-mixed crystals} = \alpha\text{- } + \beta\text{-mixed crystals.}$$

So that, for instance, at v we have—

$$\beta\text{-mixed crystals } u = \alpha\text{-mixed crystals } x + \beta\text{-mixed crystals } w.$$

Similar changes take place in the alloys richer in zinc. Each enclosed field of Fig. 88 corresponds to the domain of existence of definite kinds of crystals which are indicated in that domain;

the bounding lines of these areas give the temperatures at which a conglomerate changes into its immediate neighbour.

The metallographic investigation of the slowly-cooled, as well as the quenched samples of metal, yielded complete agreement with the above statements. It must be constantly borne in mind, however, that the changes of the mixed crystals are progressive, and should the transformation or equalization of the composition be suppressed by accelerated cooling, many of the alloys can assume a heterogeneous appearance, when, according to the freezing-point curve, they should be homogeneous. By supplementary annealing at the corresponding temperatures, that is, maintenance of these temperatures for a longer time, the suppressed change can be subsequently completed.

Besides these kinds of brass which are composed of copper and zinc only, there are still a few special kinds used technically, of which we shall here give a short description from a work by L. Guillet.[1]

1. *Lead brass.* If lead is added to brass, the tenacity is diminished. Microscopic inspection shows, on the contrary, that the size of the crystal grains is reduced. Correspondingly the alloy becomes easier to hammer and to work. With a content of more than 5 per cent. of lead, this metal trickles out during hot working, whilst the structure of the alloy becomes heterogenous.

2. *Tin brass.* So long as the tin contents of a brass remain below 2·5 per cent., the metal is malleable whilst hot, and though the tenacity, elastic-limit, hardness, and particularly the brittleness are raised by the presence of this element, the extension and reduction of area are strongly diminished. Brass containing 0·3 to 1·5 per cent. of tin finds its chief sphere of employment in shipbuilding.

3. *Manganese Brass.*—This alloy, often spoken of as manganese bronze is employed in all cases where great tenacity is required, as for instance in screw-propellers, hydraulic-cylinders. It is used also in ship-building on account of its resistance to sea-water and its non-effect upon the compass.

4. *Aluminium Brass.*—Aluminium is added to molten alloys chiefly as a deoxidizing agent. A slight addition of aluminium,

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[1] L. Guillet, "Recherches sur les alliages de cuivre, laitons spéciaux, trempe des bronzes." *Bull. de la Soc. d'Enc. pour l'Ind. nat.*, January, 1905. *Revue de métallurgie*, February, 1906, p. 97.

like that of manganese, increases the resistance to tension; in consequence the sphere of employment of aluminium brass is much the same as that of manganese brass.

Antimony-Tin.

In Fig. 90 is reproduced the freezing-point curve of the antimony-tin alloys, drawn up according to the experiments of Reinders.[1] The curve of the commencement of freezing *SnCDESb* has apparently four branches, whose "kinks" lie at the temperatures 243°, 310°, and 430° C, with 8, 20, and 51 per cent. of antimony respectively. From the freezing-point curve it seems to follow that the two metals form two, perhaps also three, compounds with each other, of which two can form mixed crystals with the pure metals.

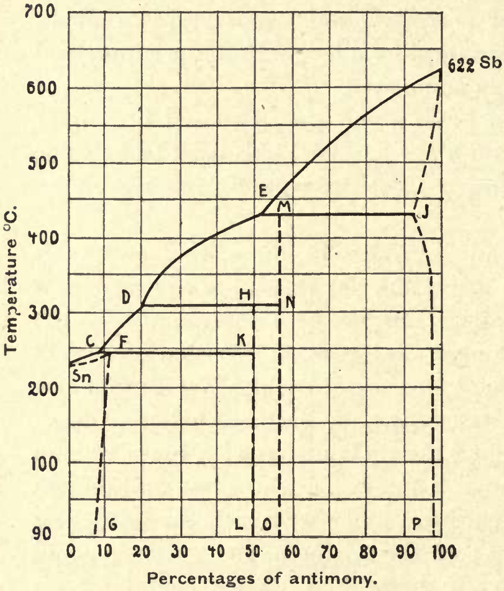

FIG. 90.—Freezing-point curve of the antimony-tin alloys (Reinders).

According to Charpy,[2] the metallographic investigation is easy if relief-polishing is combined with a mild action of hydrochloric acid. In the alloys rich in tin, large needles can be seen running through a magma in which tiny hard grains can be recognized. Judging from their appearance, these alloys consist of tin crystals in a eutectic.

An alloy with 10 per cent. of antimony shows white, hard, cubical crystals; dilute hydrochloric acid attacks only the mass which surrounds the crystals, and which proves also to be a

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[1] W. Reinders, "Über die Legierungen von Antimon und Zinn." *Zeitschrift für anorg. Chemie*, 1900, Bd. 25, p. 113.

[2] G. Charpy, see p. 55.

eutectic. With increasing antimony contents, the amount of these cubical crystals also increases, until at about 50 per cent. they form the sole constituent of the alloy. All the alloys between 45 and 55 per cent. exhibit a similar homogeneity, from which Charpy concludes that a compound with about 50 per cent. of antimony exists.

At a content of 60 per cent. and more, hard crystalline needles make their appearance on polishing, which, however, have an appearance similar to those more fully described under the antimony-bismuth alloys; that is, they represent isomorphous mixed crystals. They are best developed by nitric acid accompanied by an electric current. Charpy concludes, therefore, that tin and antimony can form a definite chemical compound SbSn with each other, which can form mixed crystals isomorphous with antimony.

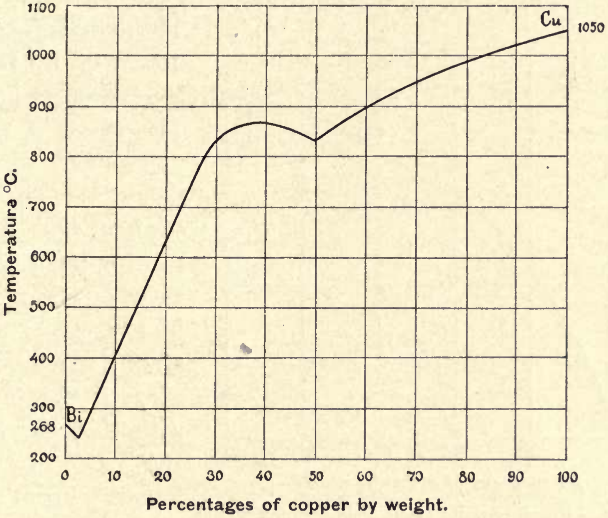

FIG. 91.—Freezing-point curve of the copper-bismuth alloys (Gautier).

Copper-Bismuth.

The shape of the freezing-point curve (Fig. 91), according to Gautier,[1] appears to indicate that a chemical compound exists; the corresponding eutectic mixtures with 2·8 and 37 per cent. of copper freeze at 243° C. and 885° C.

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[1] See p. 69, footnote 1.

Copper and Nickel.

The curve established by Gautier[1] (Fig. 92) shows two branches cutting at an angle. Gautier maintains that this is a eutectic point. The alloys, German-silver, etc., are copper-nickel alloys containing a certain amount of zinc.

Silver-Zinc.

Detailed investigations of the alloys of silver with zinc have been made by Gautier,[2] and particularly by Heycock and Neville.[3] The freezing-point curve drawn up by the latter is reproduced in Fig. 93. The curve of the commencement of freezing falls in an almost straight line from the melting-point of pure silver down to a content of 37·5 atoms per cent. of zinc, at a temperature of 710° C. Connected with this, the branches *AB*, *BC*, *CD*, *DZn* follow. From the form of this curve it may be surmised that the two metals form one or more chemical compounds with each other, the formulæ of which, however, cannot be deduced with certainty without further investigations. As the addition of small amounts of silver raises the freezing-point of zinc, it is assumed that one of the compounds forms mixed crystals with the zinc. The metallographic investigation of the various zinc-silver alloys, conducted by Charpy,[4] confirms this conclusion. Alloys with

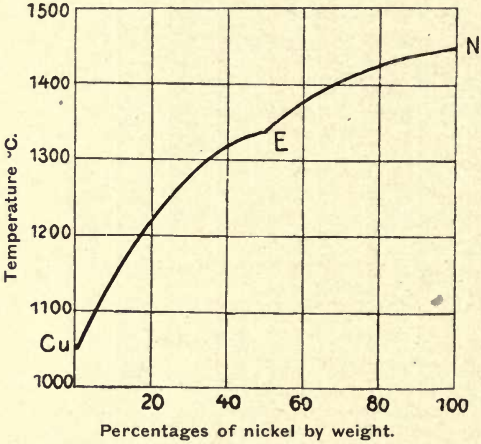

FIG. 92.—Freezing-point curve of the copper-nickel alloys (Gautier).

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[1] H. Gautier, "Recherches sur la fusibilité des alliages métalliques. *Contribution à l'étude des alliages.*

[2] Gautier, see page 60, footnote 1.

[3] Heycock and Neville, see p. 62, footnote 2.

[4] Charpy, see p. 61, footnote 4.

about 30 to 40 per cent. of zinc are extremely hard and are homogeneous. The alloys poor in zinc, as well as those rich in this metal, prove to be heterogeneous. Charpy recommends sulphuretted hydrogen as an etching medium for the alloys poor in zinc, and potash solution for the rich alloys.

Copper-Tin (*Bronzes*).

The investigations into this series of alloys (of so much industrial importance), which had already been undertaken by Behrens,[1] Thurston [2] and Le Chatelier,[3] established the fact that this system was extraordinarily complicated. Le Chatelier had drawn up a freezing-point curve, which consisted of three branches; the angles occurred in the neighbourhood of 3 and 72

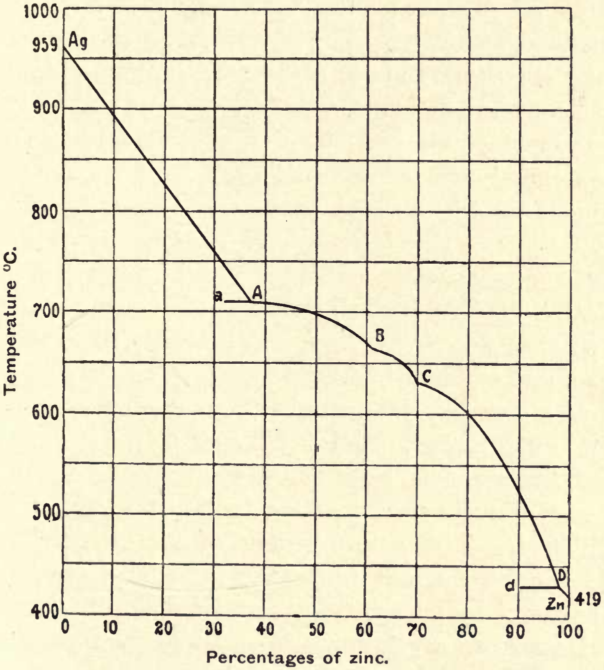

FIG. 93.—Freezing-point curve of the silver-zinc alloys (Heycock and Neville).

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[1] Behrens, "Das microskopische Gefüge der metalle und Legierungen."

[2] Thurston, "A Treatise on Brasses, Bronzes and other Alloys."

[3] Le Chatelier, "Les alliages métalliques." *Revue générale des sciences*, 1895, 1897.

per cent. of copper; the middle branch exhibited no maximum. The existence of a chemical compound of the formula $SnCu_3$ was accepted upon the foundation of chemical investigations by Le Chatelier,[1] measurements of the electric conductivity by Matthiessen, and determinations of the specific gravity and coefficient of extension by Riche and Crace-Calvert.

Later, researches into the phenomena of solidification and subsequent cooling of the alloys were repeated by Roberts-Austen [2] and Stansfield. The two observers drew up a somewhat complete freezing-point curve, which did not succeed, however, in explaining all the phenomena in a way free from objections. The microscopic investigations of Behrens and Charpy also did not make it possible to allot a place in the freezing-point curve to all the constituents found.

In 1903 Heycock and Neville[3] published their researches, which extended over the thermal as well as the metallographic behaviour of the whole series.

Fig. 94 gives the freezing-point curve drawn up by the two investigators. The curve of the beginning of freezing, *ABLCDEFGHIK* (liquidus) shows sudden changes of direction at the points *C,D,G,H,I.* Above it, the alloy consists of homogeneous liquid material, immediately below it a mixture of molten matter and solid crystal-masses. The more nearly the line of complete solidification, $AblcmdefE_2E_3H'H''K'$ (solidus), is approached, the more the mass of the solid crystals increases, until at the temperatures corresponding to this line, the whole mass has solidified. The determination of this latter line is not possible by the thermal method alone. The object is more easily achieved by quenching the samples at different temperatures. Now those crystals which had already separated before the moment of quenching are much larger than those which are formed during the rapid cooling. The separate points of the solidus-line can be determined fairly exactly in this way, excepting *m.* The exact course of the branch *Ab* is somewhat uncertain, as it is very difficult to obtain an equilibrium of the alloys

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[1] Le Chatelier, "Les alliages métalliques." *Revue générale des sciences,* 1895, 1897.

[2] Roberts-Austen, "Third and Fourth Report to the Alloys Research Committee." *Proc. Inst. Mech. Engineers,* 1895, 1897.

[3] C. T. Heycock and F. H. Neville, *Philosophical Transactions of the Royal Society of London,* (A) ccii., 1903 (pp. 1–69).

corresponding, that is to say, to effect the completion of all the changes appertaining to this interval. For the same reason the points *lcmdf* might lie several degress too low. Finally the line E_2E_3 which is here drawn vertically, must in reality exhibit

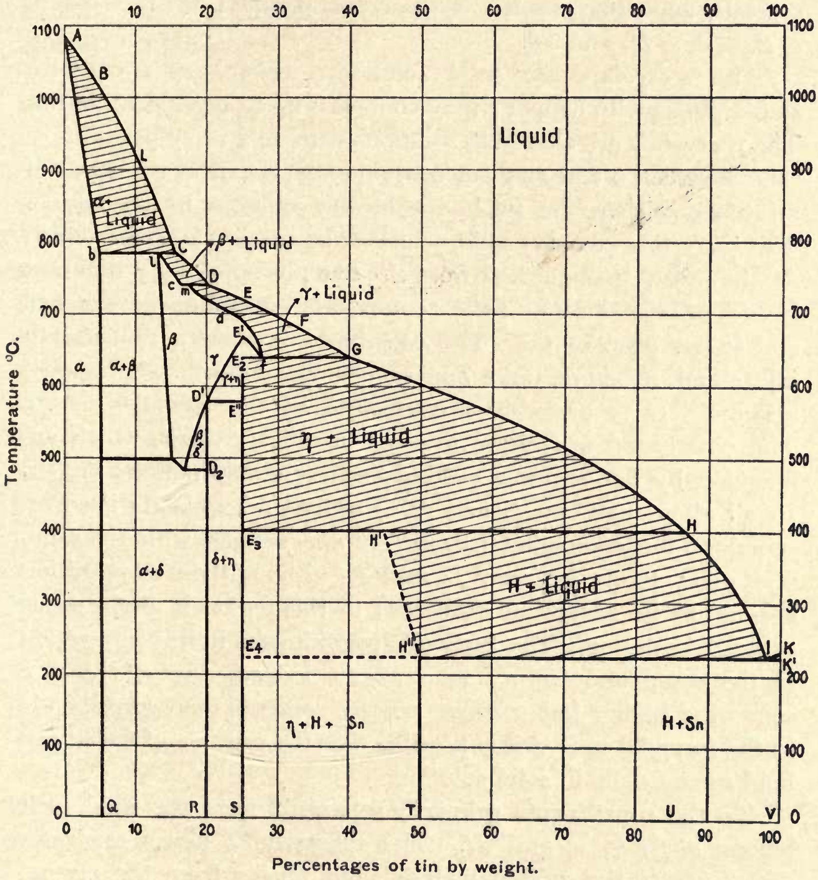

FIG. 94.—Diagram of the copper-tin alloys (Heycock and Neville).

a slight bend, and whereas H' is known with certainty, this is not the case with H''. As many of the changes proceed with extraordinary slowness, the cooling to the point of quenching was delayed so much (often twenty-four hours and more) that all the changes in structure could actually take place.

The area below the line of the commencement of freezing is divided by a system of lines into a number of closed fields, each of which corresponds to a definite structural arrangement.

In the cross-hatched areas, liquid material and mixed crystals exist in equilibruim with one another. The different types of crystals appearing in the system are denoted by the letters α, β, γ, δ, η, *H*, and *Sn.*

The α-crystals are solid solutions, which are apparently isomorphous with copper; they contain 0 up to 9 per cent. of tin. The β-crystals are also solid solutions with 22·5 to 27 per cent. of tin. Between 9 and 22·5 per cent., there is a gap in the series of mixtures, as there are no homogeneous solutions in this region. The γ-crystals are also solid solutions of copper and tin, which are, however, distinguished from the two preceding by a different system of crystallization; their composition fluctuates between 28 and 57 per cent. of tin. The constituent δ shows a remarkably crystalline structure, and appears to be uniform wherever it appears. It is probably a compound of the formula Cu_4Sn. The constituted η appears in large lamellar crystals, which are bounded by flat surfaces cutting each other at definite angles. In all alloys between *E* and *H*, η can be recognized; it corresponds to the compound Cu_3Sn. It appears also with the same crystalline forms between *D* and *E*, although its composition appears to be somewhat different; in this region it might occur as a solid solution. The body *H* approximates in its composition to the compound CuSn; its analysis, indeed, always shows a somewhat higher but constant copper contents than corresponds to the formula, so that it is possible that the crystals of CuSn can hold some Cu_3Sn in solid solution.

To the constituents primarily separated from the fluid melt belong α, β, γ, η, and *H.* The substance δ never separates directly from the molten material, but results from the mutual interaction of the solid solutions β and γ.

Exclusive of β and γ, all these constituents can exist under certain conditions at the ordinary temperature, and in consequence are found in unquenched pieces, whilst the two first-named can only occur in quenched materials.

Metallographic investigation confirms in all respects the views laid down above concerning the freezing and transformation phenomena of this system, which presents an interesting example of Roozeboom's views on the formation and transformation of mixed crystals.

At this point reference should be made to an interesting study by Heyn and Bauer,[1] in which the influence of oxygen upon the microstructure of bronzes was investigated, and the conclusion reached that the presence of oxygen causes the formation of stannic oxide.

II. THE TERNARY ALLOYS.

On page 51 it was shown how the composition of the ternary alloys is represented in a graphic manner. A method will now be mentioned by means of which the freezing-point curve of such mixtures can be laid before the eye comprehensively. The simplest method would consist in erecting perpendiculars to the surface of the paper at those points of the triangle which correspond to the alloys in question, and plotting the freezing and transition points on these perpendiculars. In this way a solid figure is obtained which, as such, is sufficiently plain to render a synoptic view possible. Its chief disadvantage consists in the fact that it can be shown but imperfectly in the flat.

Now use is made of the method in which, just as in Geodesy, horizontal planes are taken at different heights, and the lines of intersection with the surface projected upon the surface of the triangle. In this way there results a system of curves, the so-called isotherms. The method is not perfect, since, in order to obtain a clear diagram, only one system of isotherms, *e.g.* that of the surface of the commencement of freezing, can be plotted. For the lower lying surfaces, those corresponding therefore to eutectic crystallization and polymorphic changes, large numbers of isotherms must be constructed.

Lead-Bismuth-Tin.

Fig. 95 shows the chart of isotherms (dotted lines) of the surface of the commencement of freezing of the lead-bismuth-tin alloys as reproduced from the determinations of Charpy.[2] The

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[1] Heyn und Bauer, "Kupfer, Zinn und Sauerstoff." *Ztschft. f. anorg. Chemie*, 1905, Bd. 45, s. 52.

[2] G. Charpy, "Étude sur les alliages blancs dits antifriction." *Contribution à l'étude des alliages*, 1901, p. 200. Paris, Chamerot et Renouard.

triangle *Pb Sn Bi* is divided into three regions by the lines $G\varepsilon$, $H\varepsilon$, $I\varepsilon$, which correspond to the primary separation of one of the three pure components.

Let us next consider an alloy of the composition *A*. The point denoting this alloy lies in the region $BiG\varepsilon I$ on the isotherm 175°. At this temperature, therefore, pure bismuth commences to separate from the alloy. On this account the latter becomes poorer in bismuth, whilst the ratio $\frac{\text{weight of tin}}{\text{weight of lead}}$ remains constant.

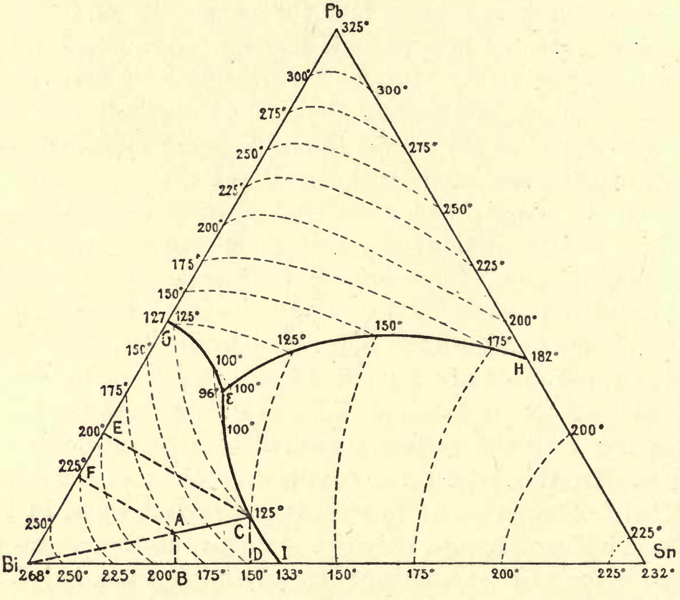

FIG. 95.—Isotherms of the surface of the commencement of freezing of the lead-bismuth-tin alloys (Charpy).

According to the explanations on p. 52, the tin content = *AF* per cent., the lead content = *AB* per cent. The proportion is therefore $\frac{AF}{AB}$.

Now in order that this ratio may remain constant, the composition of the alloy must be displaced by the progressive separation of bismuth along the line *BiAC*, since only in this case is the condition $\frac{AF}{AB}$ = constant fulfilled.

At the point *C* this straight line cuts the isotherm 125° and the line $I\varepsilon$ simultaneously. A eutectic mixture of bismuth and tin now separates out, the composition of the mixture is displaced along the line $I\varepsilon$, until finally the composition ε of the ternary eutectic lead-bismuth-tin is reached at 96° C. The latter consists of

32 per cent. lead.
15·5 „ „ tin.
51·5 „ „ bismuth.

An alloy of this composition freezes therefore at 96° C. to a ternary eutectic conglomerate.

The microscopic investigation of these ternary alloys, undertaken by Charpy, entirely supports this view of the course of freezing. For instance, alloy *A* shows after polishing and light etching with dilute hydrochloric acid large plates of metallic bismuth corresponding to the bismuth crystals separated out between 175° and 125°. The latter are surrounded by a layer which consists of an intimate mixture of bismuth and tin lamellæ, and corresponds to the binary bismuth-tin eutectic separating out between 125° and 96°.

A dark mass, which at a higher magnification shows tiny bright bismuth crystals, lamellæ of tin etched dark by the acid, and particles of lead bright with a film of lead chloride, fills up the remaining interspaces between the bismuth-tin eutectic. This is the ternary eutectic which freezes at ε. The cooling curve of alloy *A* shows three arrest-points, corresponding to the crystalization of bismuth, bismuth-tin eutectic, and bismuth-tin-lead eutectic.

The bearing metals.

The research by Charpy of the lead-tin-bismuth alloys can thus serve as an example of the way in which the ternary alloys can be investigated. Such systematic investigations would not only be very interesting, but also of direct applicability, inasmuch as these alloys find the widest use in machine construction. Latterly an enormous quantity of metals has come into the market under most curious names ; often enough the buyer is perplexed, for the declarations sent to him respecting the metal tell him little or nothing concerning its behaviour when used for bearings. For this reason it will be shown in what follows what properties an alloy must possess in order to withstand, as far as possible, the wear and tear of working.

Imagine a shaft, which runs in an accurately-machined bush. Between the shaft and the bush there is a thin layer of oil, so that in case the journal and bush fit one another mathematically, the nature of the bearing metal may be absolutely of no consequence. In practice such a fit cannot be obtained, particularly when a shaft is supported by several bearings. Moreover, the bearing metal wears away by use, probably on account of dust suspended in the lubricating oil, and always in the prevailing direction of rotation. In all cases it happens that the lubricant is forced out at certain points by the high bearing-pressure, and an immediate contact between journal and bearing metal induced. Now it will depend principally upon the nature of the latter whether the bush wears away in places or uniformly. If the bearing metal consists of a soft homogeneous substance, lead for example, the coefficient of friction is very high, and the danger arises of single particles of metal being torn off, and attaching themselves fast to (eating into) the journal, causing the temperature of the bearing to rise by the constant friction, so that the metal softens and is finally squeezed out by the pressure of the journal.

If, on the other hand, the bush is made of hard material, the coefficient of friction is certainly lowered, yet the friction is confined to a few points on account of the resistance of the metal, so that the danger of hot-running is again largely increased. Obviously a bearing metal consisting of hard grains surrounded by a soft plastic ground mass, acts to the greatest advantage. Should the bearing pressure, through some cause or other, become too high at any point, the grains would be pressed into the plastic mother-mass; in this way the form of the bush adapts itself exactly to that of the journal.

On the other hand, if soft grains lie in a hard mother matrix the former are quickly worn away, so that the pressure per unit of surface on the hard ground mass increases. As the latter is too hard to adapt itself exactly to the form of the journal, the danger of hot running is in this case also very great.

The white metals in general belong to the first class, the bronzes, on the other hand, belong to the second group. In the white metals, hard crystals of some compound or other lie in a plastic eutectic, whilst in the bronzes soft copper crystals are embedded in a hard eutectic.

Antimony-Copper-Tin.

In the alloys of antimony with tin, it is well known that at a content of from 10 to 40 per cent. of antimony, a compound exists of the formula SbSn, crystallizing in the cubic system. These crystals are hard, and on etching with hydrochloric acid, stand out brilliantly on a dark back-ground.

Between 5 and 50 per cent. of copper the copper-tin alloys contain a hard constituent $SnCu_3$ surrounded by a eutectic $Sn,SnCu_3$.

Since the crystals occurring in the antimony-copper-tin mixtures are identical with those described above, and no others have been proved to be present, we can assume that ternary compounds do not form and that the systems, at least those which are rich in tin, behave exactly as though they consisted of—

$$Sn,\ SnSb,\ SnCu_3.$$

A great number of different alloys have been investigated by Charpy[1] with respect to their resistance to compression. It appears from this, that the compound $SnCu_3$ imparts greater brittleness to the metal than the compound SnSb. The alloy which shows little brittleness with high resistance to compression has, according to Charpy, the composition—

Sn 83·33; Sb 11·11; Cu 5·55.

Moreover, the rate at which the alloy is cooled has a great influence upon the resistance to compression, as well as upon the size of the crystal grains of the contained compounds.

Antimony-Lead-Tin.

Of these three metals only the antimony and the tin form a compound, of the formula SbSn, which is able to yield a solid solution with the antimony. In consequence, the structure of the ternary alloy differs in appearance little or nothing from that of the binary system antimony-lead. The presence of the solid solution imparts the property, however, of higher resistance to

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[1] See p. 120, footnote 1.

compression to the alloys, so that they are more suitable as bearing metals than the binary alloys of antimony-lead. The following composition is worthy of recommendation—

Sn, 10 to 20 per cent.
Sb, 10 to 18 „
Pb, remainder.

Antimony-Copper-Lead.

As copper and lead, when melted together, separate into two layers, one rich in lead with little copper and the other rich in copper with little lead, liquation phenomena are very liable to appear in the ternary systems. It follows, therefore, that high copper and lead contents, occurring simultaneously, must be avoided in a bearing metal.

Antimony-Tin-Zinc.

As these alloys also do not appear to form a ternary compound with one another, as follows from Charpy's[1] microscopic investigations, three classes should be distinguished in these alloys, according to whether the constituent first crystallizing out is pure antimony, pure tin, or the antimony-zinc compound. The alloys most suitable for bearing metals are those belonging to the last class with about—

10 – 15 per cent. tin,
10 – 15 „ antimony,
80 – 70 „ zinc.

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[1] G. Charpy, "Étude sur les alliages blancs dits antifriction." *Contribution à l'etude des alliages*, 1901, p. 203. Paris, Chamerot et Renouard.

PRACTICAL MICROSCOPY OF METALS

PREPARATION OF THE SECTION.

The surface to be examined under the microscope must be perfectly flat, and, before etching, should not exhibit irregularities arising from external sources (scratches, etc.). During the grinding the hard constituents must be worn down uniformly with the soft ones. If this is not the case, *i.e.* if the softer parts are worked down more quickly, too strong a relief on the face of the section results, and it is impossible to obtain a uniformly sharp field under the microscope.

A small piece of the material to be examined is first of all procured, measuring about 1 × 1 × ½ cm. If the material is workable, the piece is cut off with a saw, filed flat with coarse and smooth files, and the edges and corners smoothed down, so as to prevent tearing the cloth in the subsequent operations. If the material is too hard to be worked with files (hardened steel, white iron), a fragment suitable for the purpose is broken off, and a surface is then ground on by a coarse and slowly-rotating emery wheel. In this operation it is important to keep the sample cool in order to prevent possible change of the structure by the heat developed (tempering of glass-hard steel, etc.). It is a good plan to have a vessel containing water near the emery wheel, and to dip the sample in it momentarily, about every ten seconds.

When the section has undergone its preliminary preparation in this way, various methods may be employed for the fine grinding, which differ from one another only in the manner and serial order in which the grinding materials are used (see footnotes pp. 122 and 124 for literature).

Two methods are more fully described below, the first one developed by Prof. Martens and the second by H. Le Chatelier.

1. *Method of Martens*—The piece of metal having been

prepared according to the above account by means of files or emery wheel, is freed by washing from any adhering grains of emery, and further ground on a vertically rotating wooden disc upon which emery paper is pasted. The "Hubert" brand is very suitable for this purpose in the grades 3, 2, 1 G, 1 M, 1 F, 0, 00.

The discs, which make about 400 revolutions per minute, must be perfectly flat; to prevent warping by moisture, they are built out of different pieces of wood glued over each other crosswise. When the emery paper on a disc is worn out, it is removed with a tool, the surface made smooth with sand paper, and a new sheet of emery paper fastened on with glue, filtered to prevent the formation of knots.

During the grinding the section is held so that the marks run in one direction. The grinding on any particular grade of emery must be continued until the scratches produced by the preceding one are completely effaced. To determine this the section is rotated each time so that the induced scratches are at right angles to the existing ones. When the latter are no longer discernible, the next finer grade of emery may be proceeded to.

When the section has been finally ground on 00 paper, the emery disc is replaced by a wooden one covered with cloth on which levigated jeweller's rouge is spread by means of a colouring brush. The piece is ground on this under constant rotation until the last scratches due to the 00 grade of emery are effaced, and the surface to be examined appears polished. No scratches ought, moreover, to be seen under the microscope. The time required for the complete preparation of a section varies somewhat with the hardness of the material, but it can be taken that 1½ to 2 hours constitutes the minimum attainable.

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[1] H. Behrens, "Das mikroskopische Gefüge der Metalle und Legierungen," 1894, pp. 7–10.

[2] F. Osmond, "Methode générale pour l'Analyse micrographique des aciers au Carbone." *Bulletin de la Société d'Encouragement pour l'industrie nationale*, 1895, May. *Contribution à l'étude des alliages*, 1901, Paris, Chamerot et Renouard, p. 278. Deutsch von L. Heurich. Verlog Knapp, Halle.

[3] H. Le Chatelier, "La technique de la métallographie microscopique." *Contribution à l'étude des alliages*, 1901, p. 421. Paris, Chamerot et Renouard. *Revue de métallurgie*, 1905, July, p. 528.

In many cases the desired object is attained more quickly by Le Chatelier's method.

The piece is prepared on files or emery wheel, and the surface first finely ground and then polished.

(*a*) The fine-grinding.

Small sheets (20 × 20 cm.) of coarse (Hubert 1 G) and fine (00) emery paper are cut out. With a ground-glass plate as a support, the surface of the section is rubbed to and fro on the 1 G paper until the scratches due to previous treatment are removed. The section is then passed on to 00 until no traces of 1 G are visible; this it mostly the case after 250 to 400 movements to and fro.

The operations now following are performed on cloth which is tightly stretched on an under-support of glass. Le Chatelier employs small boards for this purpose (Fig. 96). Round the ground plate glass *e*, over which the cloth (flannel) is stretched, there are spaces in the boards *c* into which fit strips of wood. The latter are for the purpose of stretching the cloth *f* and holding it fast. Two of these boards are prepared.

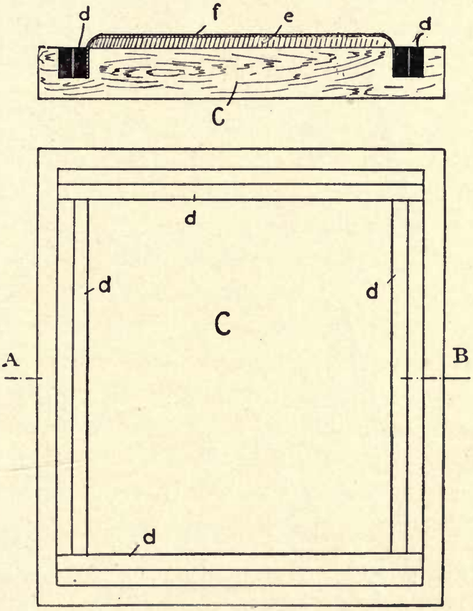

FIG. 96.—Board for grinding. Section on AB and plan.

The first is used for taking a coarse kind of emery. The material sold technically as "one minute" emery, which before use is passed through a fine sieve (1200 meshes per sq. cm.) is employed for this purpose. It is preserved in a flask tightly closed with an indiarubber plug. About 5 grams of this powder are placed on the cloth of the polishing board and rubbed over it with the finger, so that the emery penetrates the cloth and fills up the meshes. Some soap solution is then poured on so as to distribute the whole uniformly over a larger area. The soap solution is prepared by dissolving a pure soap (*e.g.* Venetian soap, toilette soap) in hot water and filtering the solution through a folded filter paper into a flask which is also carefully stoppered. After cooling, the solution should be syrupy. The section is rubbed to and

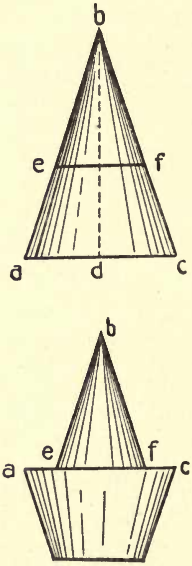

FIG. 97.—Cone for distribution of levigated emery.

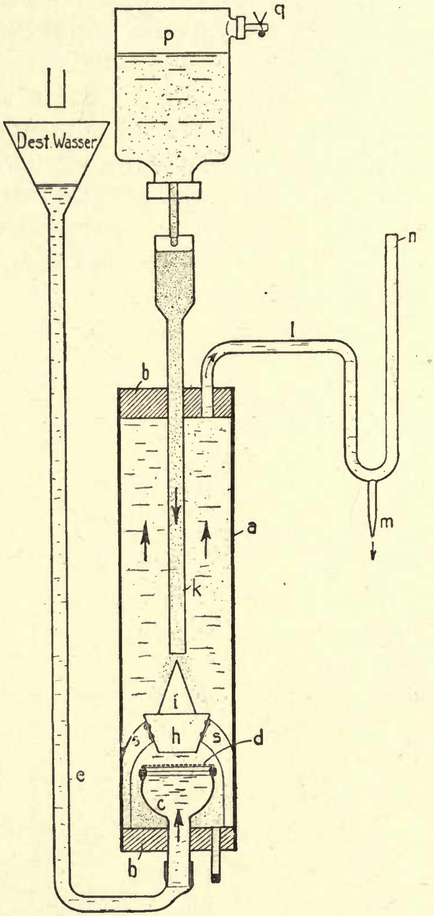

FIG. 98.—Levigation apparatus (Le Chatelier).

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[1] J. E. Stead, "Practical Metallography." *Proceedings Cleveland Institution of Engineers*, 1900, February. *The Metallographist*, III., p. 220.

[2] G. Charpy, "Étude microscopique des alliages métalliques." *Bulletin de la Société d'Encouragement pour l'Industrie nationale. The Metallographist*, I., p. 87.

fro on the cloth saturated with this emery mixture until the 00 scratches are obliterated.

The finer material, with which the cloth of the second board is saturated, is prepared as follows. Commercial emery (120 minutes' emery) is passed through a fine sieve (2600 meshes per sq. cm.), and the sieved material worked up in the following levigating apparatus (Fig. 98).

A glass tube *a* (about 40 cm. high and 50 mm. internal diameter) is closed above and below by indiarubber stoppers *b*. The lower stopper carries in one hole a small glass funnel *c*, the stem of which projects below, and the cone of which fits in the glass tube with a little play (1 to 2 mm.). The opening of the cone is closed with a wire gauze *d*. Distilled water, introduced by the indiarubber tube *e*, is distributed by the gauze, and in this way a uniform velocity of ascent is imparted to the water from the beginning. A little higher than the glass funnel a double cone *hi* of sheet copper is placed; this is prepared as follows. A cone *abc* (Fig. 97 lower part) is obtained in which $bd = 3ad$. At half the height the cone is cut into two pieces, so that a smaller cone and a frustrum are obtained. The frustrum is placed in the glass tube, the narrow part *ef* downwards, and on this (Fig. 97 lower part) the closed cone with the apex upwards, so that *ef* and *ac* shall lie in one plane. Through the middle of the upper rubber stopper a long glass tube *g* of 5 mm. internal diameter passes, which reaches to the apex of the cone and serves the purpose of delivering a constant stream of the emery. This slides down the sides of the cone and falls into the ascending stream of water which carries the finest particles with it. The coarser grains fall to the bottom and collect at the base of the apparatus round the funnel. The particles carried with the stream of water rise upwards and leave the apparatus by an **S**-shaped side tube *l*, which carries at the lower bend a drawn-out glass attachment with a small opening. In the vertical limb *n* of the exit tube the meniscus stands at a definite height, corresponding to a definite velocity of efflux. The most suitable velocity is determined experimentally; if, in subsequent experiments, it is desired to work under the same conditions, the entrance of water through the tap *o* is so regulated that the height of the meniscus *n* above the horizontal piece *l* is the same. The escaping water is collected in vessels of 2 to 3 litres capacity, and the suspended emery allowed to stand for 5 to 8 days, when it is found to have settled completely.

The apparatus is managed thus. The emery mentioned at the commencement (passed through a sieve of 2600 meshes per sq. cm.) is shaken up with water (50 grams emery powder, 250 grams distilled water), the mixture brought into the bottle *p*, and the latter closed with a perforated rubber plug carrying a small piece of glass tubing. The flow of the mixture is controlled by the screw clip *q*, so that it flows in drops into the wide upper part of the influx tube *r*. After the fine emery has settled and the supernatant water has been decanted, the residue is shaken up with a soap solution, which should be somewhat thinner than the one described above. The residues of all the vessels thus collected together are placed in one bottle, tightly closed.

The section, already roughly prepared on a coarse emery powder, is now ground further on the second board (the cloth of which is dressed with the emery-mud just mentioned), until only the fine hair-like scratches due to the latter can be discerned on the face of the section. The section is now ready for (*b*) the polishing.

This last operation, which does not demand more than about five minutes, supposing that the preceding operations have been carried out with the requisite care, is performed on a vertical disc which rotates with a velocity of 1700 revolutions per minute. Fig. 99 shows the scheme of such an arrangement, in which the polishing discs *ee* are screwed directly on the axle *c* of an electro-motor. The latter generates $\frac{1}{3}$ H.P. at 220 volts and 1·6 ampère, and makes 1700 revolutions per minute. A regulating resistance is fixed under the electro-motor. The discs themselves (*e*) are cast in brass, the hubs drawn out, screwed upon the axle of the motor, and turned off. In this way the exact perpendicularity of the plane of the disc to the axis of the motor is assured. To protect the discs from dust they are enclosed by a wooden box covered with sheet zinc, into which the axle passes through an opening made dust-tight with felting. Tightly closing doors give access to the discs. Flannel disc coverings *f* are used for receiving the polishing material, and they are stretched on the brass disc by means of a ring *g*.

Alumina serves as the polishing material and is prepared, according to Le Chatelier, as follows:—The purest precipitated alumina, from ammonia alum, is passed through a sieve of 2600 meshes per sq. cm., and 100 grams of it in 300 ccm. of distilled water are triturated in a mill for three hours. The whole is then poured into a litre flask, well shaken, and about 200 ccm. pipetted off into a flask closed with a caoutchouc stopper. To this are added 1800 ccm. of distilled water and 2 ccm. of concentrated nitric acid (s.g. 1·4), the mixture well shaken and allowed to settle; the settling is complete in a short time (about two hours). The clear supernatant liquid is syphoned off with an **S**-shaped syphon (Fig. 100); with careful manipulation, this is possible to the extent of $\frac{9}{10}$ of the total amount. The liquid drawn off is replaced by distilled water, the mixture well shaken several times and allowed to settle again, after which the wash water is again drawn off as before. This is repeated three or four times more. At last the supernatant liquid remains milky for a whole day, which

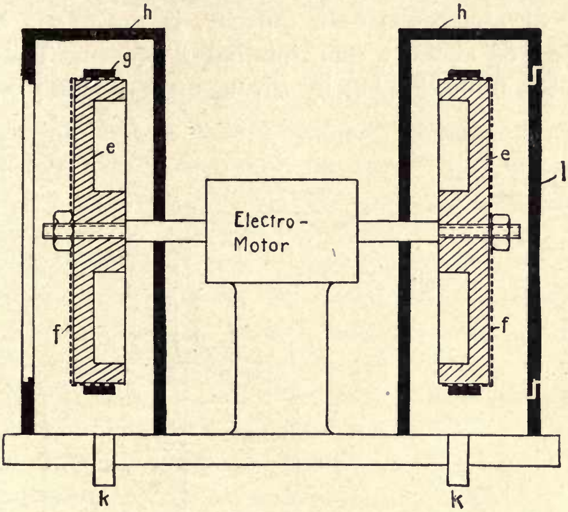

FIG. 99.—Motor for polishing.

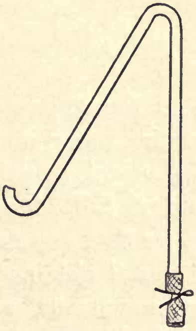

FIG. 100.

is an indication of the perfect removal of acid. Finally, distilled water is added for the last time up to about 2 litres, the mixture thoroughly shaken, and the alumina separated from the liquid in the following apparatus (Fig. 101). A pipette *a* of about 500 ccm. capacity, is drawn out below to an opening of about 3 mm. internal diameter. The alumina is prevented from clinging by giving an inclination of at least $\frac{1}{3}$ to the sloping sides of the tube. The piece *b* is connected to the water pump. The end (of the pipette) is dipped into the vessel containing the emulsified alumina, and the pipette sucked full, whereupon the opening *b* is closed with a screw tap so far that one drop runs out about every fifteen seconds. The material obtained during the first quarter of an hour is very heterogeneous, and still scratches the surface of the section markedly, so that it cannot be used. After the quarter of an hour has expired, the tap is closed and the alumina allowed to settle completely. After three hours the material is placed in the flask *A* (Fig. 102) provided with a spraying arrangement. Soap solution is added and the mixture diluted with distilled water. The material thus prepared is ready for use, and is

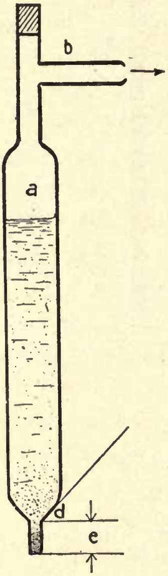

FIG. 101.

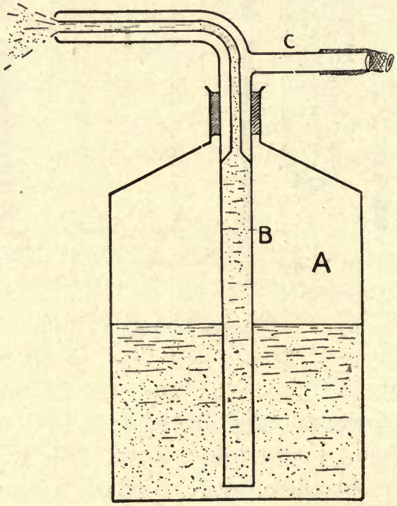

FIG. 102.—Sprayer for emulsified alumina.

suitable for steel and pig irons. The residue, which settles in from 3 to 24 hours, is treated similarly, and serves for polishing softer materials (iron, copper, etc.). The portion which still remains in suspension after 24 hours is too fine and is poured away.

The section which has undergone its previous preparation is now well polished on the disc, which is sprayed with one of the alumina emulsions described above. During the polishing, the section is slowly moved in the opposite direction to that of the disc's rotation, and so as to change the direction of grinding continually.

Cleanliness plays a very important part during the various operations in connection with the careful preparation of grinding and polishing materials. It is absolutely necessary that after using each grade of emery, the section piece and also the hands and nails of the operator should be washed with great care. A single pair of grains of a coarser kind of emery, if allowed to reach the cloth set apart for finer material, are able to retard the work to an extraordinary extent, and make the fine polishing appear illusory. If only about 1 per cent. (a scarcely weighable amount) of the finest emery powder reaches the polishing disc, a fine polish is altogether out of the question. Dust acts in a similar manner, and consequently the grinding boards as well as the polishing discs must be kept in cupboards free from dust. In this matter, the foresight to put the finer material above the coarser, and thus prevent destruction of the cloths by possible falling of small particles, must be exercised.

The two methods given above are selected from the large number of possible methods of polishing. By carefully carrying out all the operations, the second of the two methods achieves the desired result very quickly, as alumina alone is employed as the polishing medium. Le Chatelier has investigated other materials with respect to their applicability for this purpose, and classified them as follows:—

1. Alumina from ammonia alum.
2. Emery powder, levigated.
3. Chromic oxide from ammonium bichromate.
4. Ferric oxide from the oxalate.

Besides these, quite a number of economical products serve for the preliminary grinding, *e.g.* tripoli powder, etc. It is absolutely necessary, however, to employ in polishing only the most carefully prepared material. The softer the alloy to be polished, the finer must be the polishing powder employed; the different degrees of fineness are obtained as described for alumina.

Certain very soft alloys have the disagreeable property of "smearing" during the polishing; a thin film sticks to the surface of the section, and, in being torn away from the mother mass, produces a rough, torn surface, quite useless for microscopic examination. In such cases the least possible pressure must be exercised in holding the piece on its grinding support. Behrens[1] recommends the use of petroleum. Frequent moistening of the section with bone oil has also proved useful.

When the re-melting of the alloy under investigation is admissible, and it does not oxidize too much in the neighbourhood of its melting-point, the required flat face can be produced by pouring the molten metal upon another polished surface.

According to Ewing and Rosenhain,[2] the procedure with lead, tin, zinc, bismuth, cadmium, and their alloys consists in pouring the molten mass upon flat polished plate glass. By using a ground steel plate instead of glass, gold and silver as well as their alloys can be similarly treated.

Ground glass plates frequently break, however, by pouring molten metals upon them. Hannover[3] proposes, therefore, to make use of a freshly-cleaved plate of mica, the remaining procedure being that described above.

Another method consists in heating a piece of the metal under investigation in the reducing flame of a blow-pipe, and, at the moment of melting, pressing it out on a small plate of mica to complete solidification.

In the case of lead, a suitable sample can be obtained by merely pressing a freshly cut face upon a polished flat surface.

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[1] Behrens, "Das mikroskopische Gefüge der Metalle und Legierungen." Hamburg und Leipzig, 1894, s. 47.

[2] J. A. Ewing and W. Rosenhain, "Sur la structure cristalline des métaux." *Bulletin de la Société d'Encouragement pour l'Industrie nationale*, June, 1900, p. 877.

[3] H. J. Hannover, *Bulletin de la Société d'Encouragement pour l'Industrie nationale*, August, 1900, p. 210.

DEVELOPMENT OF THE STRUCTURE.

The polished surface of the section under investigation is seldom a perfect mirror. In very many cases, one can perceive under the microscope single tiny points, holes, etc.

The structure must first be rendered visible by suitable treatment, *i.e.* it must be developed. This is done by one of the methods described in the following, of which sometimes one and sometimes another gives the better result. To obtain the best representation of the structure, it is best to try various methods, in the choice of which one is guided by the practical accounts occurring so freely in the literature. It is necessary, however, above all, to adhere exactly to the written accounts, as it is possible, by slight deviations from them, to obtain results which may completely obscure the actual facts, and thus abnormally lengthen the apprenticeship of the learner.

Before the structure is exposed by one of the methods described below, it is necessary to make certain that the surface of the section is quite clean. Frequently dull places can be seen on it. Should this arise from any substance of a resinous or fatty character, it can be removed by means of a soft cloth moistened with xylol. If it cannot be removed either with water, or alcohol, or similar substances, it is due to the fact that the softer constituents have been worked down, whilst the harder ones remain in relief. The cause of this is to be found in the grinding operations. This frequently occurs if the operations performed on cloth (fine-grinding, polishing) have lasted too long, or if the cloth is too thick. If the grinding on the cloth-disc lasts longer than about five minutes, it may be assumed that the operations immediately preceding were faulty, and therefore the face of the section is spoilt, or that the emery powder was dusty or not uniform. Under the microscope it can then be seen that a strong relief occurs on the surface of the section, so that sharp focussing is impossible. In such a case the sample is re-ground, beginning at the paper 00.

For developing the structure, one of the following methods is employed, according to the material under investigation.

A. *Polishing in Relief.*

This operation consists in seeking to remove, by means of the finest possible polishing material, the softer and more easily wearable constituents more quickly than the harder ones. An elastic support (caoutchouc, parchment) is made use of, which can readily adapt itself to the irregularities of surface, and thus introduce the polishing material into the cavities.

A piece of parchment is stretched on a smooth planed piece of wood and the finest levigated rouge (obtained from iron oxalate) rubbed into it. It is then put under a powerful stream of water, which washes away all the ferric oxide which has not penetrated the pores of the parchment. It is perhaps best to scrub vigorously with a brush, so as to make certain that only the very finest grains remain behind. The prepared piece of parchment appears then only feebly reddened.

The polished section is then rubbed to and fro on the prepared parchment, the slightest pressure being exercised during the process. From time to time the operator assures himself of the progress of the work by examination under the microscope. The specimen is then rinsed in a powerful stream of water, and dried by means of an air syringe. Osmond[1] has employed the sulphates of barium and calcium in some cases, and these were also distributed over wet parchment.

The microphotographs (Figs. 132 and 138) of tool steel were taken from sections polished in relief.

B. *Heat-tinting.*

In many cases some constituents of a sectioned sample oxidise, on heating, more quickly than others. Behrens,[2] Martens,[3] and Stead[4] have made use of this behaviour with

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[1] F. Osmond, "Methode générale pour l'analyse micrographique des aciers au carbone." *Contribution à l'étude des alliages.* Paris, 1901. Chamerot et Renouard. German by L. Heurich. Knapp, Halle.

[2] H. Behrens, "Das microskopische Gefüge der Metalle und Legierungen." Hamburg und Leipzig, 1894, s. 13.

[3] Martens, "Stahl und Eisen," 1889.

[4] Stead, "Practical Metallography." *Proceedings of the Cleveland Institute of Engineers*, February, 1900. *The Metallographist*, III., p. 220. "Structure of Phosphoretic Pig Metals." *Proc. Clev. Inst. of Eng.*, February, 1900. *The Metallographist*, III., p. 261.

much success. For differentiating several constituents, *e.g.* carbides and phosphides, it is the only method that gives results of any value.

The completely polished section is heated to about 80°, rubbed with a soft piece of chamois leather and, without cooling, placed in an iron plate which is heated by a bunsen burner. The changes in the appearance of the surface are followed by the eye, and the sample is quenched in mercury as soon as the correct tint is reached. The introduction of moisture must be carefully guarded against, or spots will be developed which can only be removed by grinding and polishing anew.

The method demands a certain amount of practice, which is readily acquired by controlling the appearance of the section with the microscope, after the sample has been cooled in mercury.

The temperatures at which the thin films of oxide, upon the interference colours of which the method is based, form, is about 250° in the case of iron; they are largely influenced, however, by the chemical composition.

C. *Polish-attack.*

The work of polishing in relief (see A) is distinctly hastened by combining chemical with mechanical influences.

The polish-attack consists in treating the section exactly in the manner described under "polishing in relief," with the difference that the parchment is moistened with a solution of extract of liquorice,[1] ammonium nitrate, ammonia, etc., instead of with water. According to Osmond,[2] the safest solution to work with is—

2 grams ammonium nitrate,
100 ccm. water.

The processes described up to the present give by careful working good results, but they are in the generality of cases too tedious. The application of purely chemical methods comes into consideration in all those cases where different constituents

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[1] See footnote 1, page 132.

[2] F. Osmond and G. Cartaud, "New Reagents for the Micrographic Study of Carburized Irons." *The Metallographist*, III., p. 1.

of almost the same mineralogical hardness are to be distinguished from one another. According to the etching media employed, these constituents are differently coloured, so that it is possible to identify a particular one.

D. Etching.

The question of the manner in which different etching media act is not easy to answer. In many cases they dissolve one constituent more quickly than another, so that the latter appears in relief. Frequently they develop different colours on different constituents, a phenomenon which unfortunately occurs frequently also with one and the same constituent. Many deposit thin layers, consisting of a film of the oxide or one of the other metals, on some of the components, whilst others remain free from such. In by far the most cases, however, one is compelled to dispense with an exact knowledge of the reactions, and be contented with the actual results.

1. *Etching with concentrated nitric acid.*—This method is only applicable to such metals as remain passive to nitric acid—that is, to those upon which the action lasts only for a moment and then ceases. Such, therefore, are iron and its alloys.

The section is dipped into nitric acid (s.g. 1·4) and at once washed under a strong current of water. If one treatment proves under the microscope to be insufficient, the operation is repeated.

2. *Etching with dilute nitric acid.*—Solutions of different concentrations are in use; Roberts-Austen employs a solution of

1 ccm. HNO_3 conc. (s.g. 1·4)
in 800 ccm. ethyl alcohol.

Arnold recommends

1 ccm. HNO_3 (s.g. 1·20)
49 ccm. distilled water,

or

1 ccm. HNO_3 (s.g. 1·20)
199 ccm. distilled water,

or more strongly diluted solutions, according to the material under treatment.

The process consists in placing the section under investigation in a small dish with the solution, and allowing it to remain until the etching is sufficient; this can be assured by examination under the microscope.

It has been shown by recent work that a more uniform attack is obtained by using amyl alcohol or a mixture of different alcohols instead of water for the solvent. An exhaustive study of this was published by Kourbatoff[1] in 1905.

A slow and very uniform etching is obtained from a mixture of

4 ccm. nitric acid conc. (s.g. 1·4)
100 ccm. iso-amyl alcohol (b. pt. 127°–132° C.).

The attack often lasts for thirty minutes before the etching is completed.

Etching with nitric acid is of fairly general application to iron and its alloys in their ordinary as well as in their quenched state.

3. *Etching with picric acid.*—This reagent was introduced by the work of Ischevsky. He recommends the following mixture:

4 grams crystallized picric acid
100 ccm. ethyl alcohol.

By using amyl alcohol instead of ethyl alcohol, an extraordinary slow etching medium is obtained. It is of advantage to wash the excess of solution away with absolute alcohol after etching is complete, and then to wipe with a soft flannel cloth. The method is recommended for all the alloys of iron and carbon.

4. *Etching with hydrochloric acid.*—This method was studied by Martens and Heyn, in connection with quenched iron-carbon alloys.[2] A mixture of

1 ccm. hydrochloric acid (s.g. 1·19)
and 100 ccm. of absolute alcohol

is employed.

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[1] Kourbatoff, "Contribution à l'étude métallographique des aciers trempés." *Revue de métallurgie. Mémoires*, p. 169, March, 1905.

[2] E. Heyn, "I. Bericht über die mikroskopische Untersuchung der vom Sonderausschusz für Eisenlegierungen des Vereins zur Beförderung des Gewerbefleiszes hergestellten Legierungen." *Verhandlungen des Ver. z. Bef. d. Gewerbefleiszes*, 1904, Heft. IX., s. 355.

A more uniform etching is frequently obtained by the simultaneous use of a current of electricity. In this case a mixture of 1 ccm. concentrated hydrochloric acid (s.g. 1·19) with 500 ccm. of distilled water is employed.

5. *Etching with tincture of iodine.*—The iodine tincture of pharmacy is diluted with an equal volume of water. In etching it is best to bring a few drops of the solution upon the surface under investigation, and rub lightly with the finger so that the attack of the etching medium is uniformly distributed. The following solution also leads to the desired result:—

20 grams iodine
400 grams absolute alcohol.

6. *Etching with cuprammonium chloride.*—The solution consists of

12 grams cuprammonium chloride crystals
100 grams distilled water.

The copper which separates out is carefully rubbed away with a soft cloth.

7. *Etching with sodium picrate.*—To identify a particular constituent of many iron-carbon alloys, viz. cementite (see below), the etching is conducted as follows:—

Two grams of picric acid are dissolved in 100 ccm. of caustic soda solution (25 grams of the solid in 75 ccm. water), and the solution digested for half an hour on the water-bath. The supernatant solution is then poured off and is kept in a dark bottle, closed so as to be air-tight.

The process of etching a section consists in pouring a certain amount of the solution of sodium picrate into a test tube which is placed in a beaker of boiling water, and when it has attained the temperature of the bath, introducing the section. The etching is generally sufficiently strong in from 5 to 10 minutes; the section is washed with water, and the operation repeated if necessary.

The process appears to be cumbersome, yet it is the only safe one for the recognition of iron carbide.

8. *Etching with molten calcium chloride.*—To determine the structure of iron and steel at high temperatures, Saniter[1]

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[1] E. H. Saniter, "Carbon and Iron." *The Journal of the Iron and Steel Institute*, August, 1897. *The Metallographist*, I., p. 72.

employs molten calcium chloride for etching. The polished section is placed in molten calcium chloride heated to bright redness in a platinum crucible, and submerged by shaking. After the piece of metal has reached the temperature of the molten mass it is heated for another 15 seconds, and the whole then quickly cooled by quenching in cold water. By dissolving away the salt, the section is extracted and is then dried in alcohol.

9. *Etching with the simultaneous application of an electric current.*—The section under treatment, according to Le Chatelier,[1] is fastened to the positive pole of a battery; for instance, it is held tightly with pinchers which have been wired firmly to the positive electrode of a cell. A piece of sheet lead is taken for the negative electrode. The whole is dipped into a 10 per cent. solution of ammonium chloride or sulphate, and a current of from 0·001 to 0·01 ampères per square centimeter is passed through. A few minutes suffice in most cases to make the structure appear.[2] The following arrangement is given by Charpy[3] specially for investigating brass. The polished surface is carefully cleansed from grease by means of benzene and alcohol applied with a brush of badger hairs. The section is then immersed for a few minutes in a warm solution of potash and then washed with hot water.

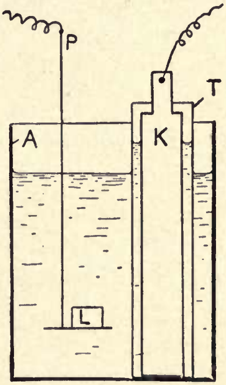

FIG. 103.

It is then placed on a small platinum support *P* (Fig. 103) which is immersed in a vessel containing diluted sulphuric acid (1 : 10). The vessel also contains a porous cell, *T*, holding a saturated solution of copper sulphate and a strip of sheet copper *K*. A Daniell element is thus obtained, the zinc of which is furnished by the alloy L under examination. The sample

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[1] H. Le Chatelier, "Sur la métallographie microscopique." *Bulletin de la Société d'Encouragement pour l'industrie nationale*, 1896, April. *Contribution à l'étude des alliages*, Paris, 1901, p. 67. Chamerot et Renouard.

[2] "The Crystallization of Iron and Steel," by J. W. Mellor. Longmans, Green and Co., 39, Paternoster Row, London, 1905.

[3] "Metallography," by A. H. Hiorns.

dissolves very slowly under these conditions, the zinc somewhat more quickly than the copper. Since a small amount of copper frequently precipitates as a powder, it is disposed of at intervals by brushing the surface with a soft brush. The method is suited to all zinc-copper alloys with less than 50 per cent. of zinc, exclusive of pure copper.

10. *Etching with concentrated potash.*—This method, which is particularly suitable for zinc-copper alloys containing more than 50 per cent. of zinc, and for which it gives very uniform results, consists in treating the alloy with a hot solution of caustic potash, saturated in the cold.

11. *Etching with ammonia.*—A solution of ammonia, not too concentrated (s.g. about 0·93), gives good results with samples of copper after an attack of about two hours.

THE MICROSCOPE.

The idea of employing the microscope for the examination of polished metallic surfaces dates back to the English savant Dr. Sorby and to Prof. Martens, the worthy chief of the mechanico-technical research institute at Berlin. To the latter we are indebted for a microscopic installation which will be described later, and which has proved particularly suitable for these investigations.

The microscope serves the purpose of producing either an enlarged image of the object to the eye of the observer or upon the photographic plate. This is first brought about by means of a system of lenses, called the objective, producing a real image of the object, which, as needs be, can be further enlarged by a second system of lenses, called the eye-piece.

In subjective observation it is well known that the magnification depends entirely on the angle of vision under which the object or its image appears to the eye at the distance of distinct vision (about 250 millimetres). The "magnification" of the objective alone is found by dividing the number 250 by the focal length of the objective. It is therefore

$$V = \frac{250}{f} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where V is the linear magnification, and f the focal length of the objective in millimetres.

From formula (1) it follows at once that the attainable magnification of the objective alone depends only on the focal length of the objective. A suitable magnification can therefore be obtained, given a sufficiently small focal length. As, however, the radius and with it the field of view of the lens diminish with the focal length, a limit is fixed to this magnification.

As explained already at the commencement, the eye-piece has for its object the enlargement of the image produced by the objective. The newer objectives, *e.g.* Zeiss' compensating and projection oculars, are provided with numbers 2, 4, 6, etc., which give the number of times which they (the oculars) magnify the image produced by the objective. The total enlargement is thus obtained by multiplying the value given by formula (1) by the ocular number. This is therefore

$$V = \frac{250}{f} \cdot n \qquad . \ . \ . \ . \ . \ . \ . \qquad (2)$$

In this formula

V denotes the total magnification.
f „ the focal length of the object in millimetres.
n „ the magnifying power of the eye-piece, as given by its number.

Thus, for instance, objective 3 and eye-piece 18 give a total magnifying power of $\frac{250}{3} . 18 = 1500$.

There is also a limit set to this magnification. Since the eye-piece serves the purpose solely of enlarging the image produced by the objective, it can only make it more conveniently visible without making it richer in detail. The available magnification, on this account, is that which is sufficient to make the image, with a given objective, distinctly visible at a distance of 250 millimetres. To obtain in a specific case an image richer in detail, one can therefore only employ a stronger objective.

Since the perfection of the picture produced by a microscope is dependent in the highest degree on the image developed by the objective, the latter must be as free as possible from imperfections of representation. These are induced by the spherical and chromatic aberration of the system.

Spherical aberration consists in this, that a pencil of parallel rays, after its passage through the lens, is not brought together to a single point, the focus. This is because the surfaces of the lenses, as can easily be seen from a geometrical construction, ultimately consist of sections of the cone. If the fault is eliminated by a suitable combination of single lenses, the corrected objective so obtained is said to be aplanatic.

Chromatic aberration is induced by the different deflections of the individual colours of the spectrum, so that instead of one only, there are several differently coloured images in different planes, produced by the objective. If two of these planes coincide, the resulting system is called achromatic. If, however, three different coloured images coincide, an apochromatic system of lenses is obtained. Such a one was first constructed in 1886 from the calculations of Prof. Abbe, of the firm of C. Zeiss, Jena. Whilst for ordinary observations achromatic objectives suffice, the more perfect apochromatics are absolutely essential for more precise work, such as microphotography.

As already stated above, the eye-piece serves the purpose of enlarging the real image of the object produced by the objective. By a suitable construction of the eye-piece it is therefore possible to compensate certain errors of the objective image. From this, the necessity arises of always employing the eye-piece belonging to a given objective, if the greatest possible perfection of the picture is to be obtained. Thus with apochromatic objectives the corresponding compensating or projection eye-pieces must be used, whilst with achromatic objectives Huyghenian eye-pieces are to be employed. As a more extended treatment of the construction of the parts of the microscope would exceed the scope of this small work, only an introduction to their application will be given, such as can be found in the excellent works of Martens[1] and Heyn[2] as well as in the catalogues of Zeiss.

On account of the opacity of the objects under investigation, it is impossible to apply the method of illumination which is used in mineralogical and petrographical observations. This

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[1] A. Martens, "Die mikrophotographische Ausrüstung der Kgl. mech.-techn. Versuchsanstalt." *Mitteilungen aus den Kgl. techn. Versuchsanstalten in Berlin*, 1891, H. 6, s. 278.

[2] A. Martens and E. Heyn, "Über die Mikrophotographie im auffallenden Licht und über die mikrophotographischen Einrichtungen der Kgl. mech.-techn. Versuchsanstalt in Charlottenburg." *Mitteilungen aus der Kgl. techn. Versuchsanstalt*, 1899, s. 73.

consists in passing the light straight through the objective, so that observations are made by transmitted light, as shown schematically in Fig. 104. In this diagram *A* represents the objective of the microscope, *B* the object under examination, *C* a mirror which deflects the ray of light *de* falling on it in the direction of the optical axis *ef* of the objective. In the case of metals and similar opaque objects, light reflected by the object must be employed; that is to say, the light proceeding from an external source must be directed on the object by special contrivances. From this illuminated object rays of light proceed which, after traversing the objective of the microscope, are collected in a real image. This is either made visible to the eye by means of the ocular, or recorded on a photographic plate. A complete equipment for the microscopy of metals consists, therefore, of the illuminating arrangement, the microscope, and the photographic apparatus.

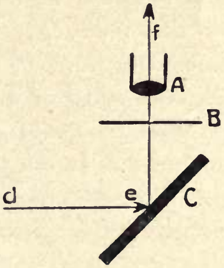

FIG. 104.—Illuminated by transmitted light.

The illumination arrangement.—The purpose of this is the illumination of the object in such a way as to obtain from the objective, at the magnification chosen, its utmost powers of resolution. Without further discussion it follows that the intensity of the light, *i.e.* the amount of light concentrated on each unit of surface of the object, must increase with the square of the linear magnification, if the brightness of the image is to remain constant. The following sources of light are to be taken into consideration: diffused daylight, sunlight, limelight, electric incandescent and arc lights, incandescent gas light, Nernst and mercury lamps, etc. The suitability of the various methods of illumination will be dealt with later.

Provided the linear magnification is no greater than about 5, diffused daylight is used, in which case an irregular illumination due to shadows must be guarded against.

In by far the most cases, however, the light must first be concentrated to a point, and from this directed upon the object. The concentration is effected by definite combination of lenses, which are arranged on the so-called optical bench. To explain the action of such a combination, let us first consider the simple case in which the source of light consists of a luminous point, *e.g.* the electric arc. Let *F* in Fig. 105 denote the arc, which is placed at the principal focus of the lens-system *A*. The diverging pencil of light proceeding from the arc consists, after passing through *A*, of parallel rays which, by a second single lens *C*, are reunited at its principal focus, F^1, to form a real image of the point *F*. To absorb the heat-rays proceeding simultaneously from *F*, at least partially, the so-called water-chamber *B*, consisting of a vessel whose walls are constituted by plane parallel pieces of glass, is introduced between the lens-systems *A* and *C*. If only rays of a definite wave length are to be used, *i.e.* monochromatic light, more absorption vessels, called light-filters, must be inserted in the path of the light. These are vessels of the same construction as the water-chamber, containing the correspondingly coloured liquids instead of water.

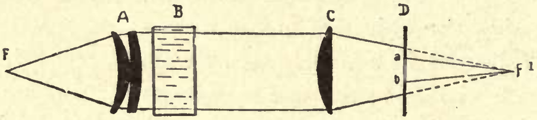

FIG. 105.—Path of light-rays on the optical bench.

The following, according to Marktanner-Turneretscher,[1] are the most useful monochromatic light-filters.

(*a*) Green light-filters.

1. *The Zettnow filter.*—Concentrated solutions of this, according to Zettnow's instructions, are prepared as follows: 160 grams of pure copper nitrate and 14 grams of pure chromic acid are dissolved in water and made up to 250 cc., and solutions of about 1 cm. thickness are employed.

2. *Eder's light-filter* is a mixture of indigo-sulphuric acid with strong picric acid.

(*b*) Blue light-filter.

3. *Ammoniacal copper solution.*—Ten grams of finely powdered copper sulphate are dissolved in 40 grams of ammonia solution of specific gravity 0·96.

4. *Febling's solution.*—which is prepared as follows: 10 grams

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[1] G. Marktanner-Turneretscher, "Die mikrophotographie als Hilfsmittel naturwissenschaftlicher Forschung," 1890, s. 23. *Verlag von W. Knapp, Halle a S. Zentralblatt f. Bakteriol. und Parasitenkunde,* 1888, *II. Jahrg.*, Bd. IV., s. 51.

of copper sulphate are dissolved in 75 ccm. of distilled water, also 30 grams of caustic potash and 40 grams of sodium potassium tartrate in 75 ccm., of distilled water. The two solutions are filtered and finally mixed together. As a considerable amount of the chemically active rays are absorbed by this solution, it is only used in those cases which require a short exposure.

(*c*) Yellow light-filter.

5. *Potassium bichromate filter.*—This consists of a saturated solution of potassium bichromate in distilled water.

Light-filters made up of coloured glass are more convenient to use than vessels filled with correspondingly coloured liquids.

In order to cut out the edges of the light pencil, a diaphragm, *D*, is placed in the path of the rays, the internal aperture of which, *ab*, can be made smaller or larger according to requirements. The iris diaphragm, which is easily movable, is particularly serviceable, and can be made to serve as a receptacle for the coloured light-filters at the same time.

The arrangement for illumination sketched in Fig. 105 possesses the advantage that, with feeble sources of light, too much light is absorbed, on account of the considerable thickness of the lenses. In such cases a single lens of small thickness is advantageously employed; with petroleum or incandescent gas light, for example, such a condensing lens serves better than the system described above.

Of the large number of microscopes employed in the microscopy of metals, only two constructions will be described here, viz. those of Martens and Le Chatelier.

1. *Martens' Microscope and Stand.*

Fig. 106[1] shows the construction of this stand as supplied by the firm of C. Zeiss of Jena. The objective *A* is screwed either directly or with the interpolation of a vertical illuminator, to be described later, into the front cover *C*, which is fixed in the outer tube *E* by means of a screw thread. The eye-piece *B* fits into the inner tube *F*, which slides to and fro in a

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[1] A. Schüller, "Die metallographische Einrichtung des eisenhüttenmännischen Instituts an der Kgl. Techn. Hochschule zu Aachen." *Metallurgie*, I., s. 333.

guiding flange of the cover *D*. The extent of this displacement can be read from a millimeter scale on the casing of *F*. The outer tube *E* carries a rack, *H*, underneath, which moves in the guide *G* by means of the pinion *I*. *G* is connected with the foot-piece *K*, the lower part of which, *L*, consists of a flat plate. Four screws, of which Fig. 106 shows only two, bind the plate to the table *M*.

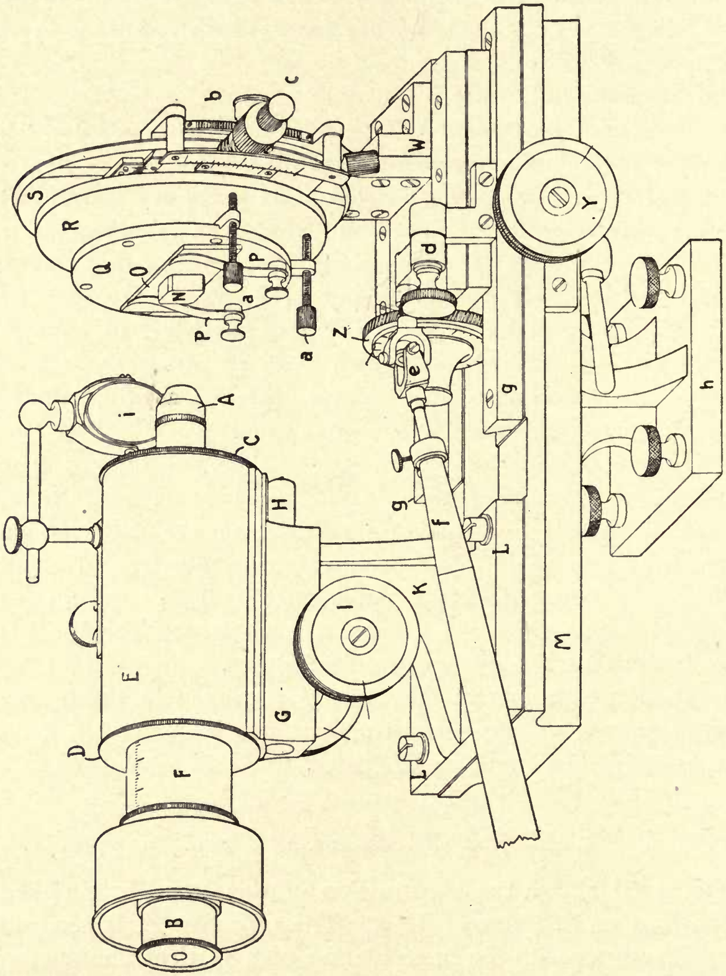

FIG. 106.—Microscope and stand (Martens').

The object *N*, which is stuck to a small piece of glass or cardboard by a mixture of equal parts of beeswax and sealing-wax, is pressed upon a round plate, *Q*, by the springs *P*, *P*. As a general rule, the surface of the small piece of metal *N* under examination will not be perpendicular to the optical axis of the microscope. On this account the plate *Q* is fastened to the upper part of the object table in such a way that, within certain limits, it can assume any chosen position and thus secure the possibility of adjusting the surface under examination exactly at right angles to the optical axis of the microscope. Fig. 107 shows diagramatically the construction of this combination in a vertical median section through the staging. The middle point of the plate *Q* is made fast to the head of a screw, *T*. By the introduction of a nut, *V*, and a spring, *U*, *Q* can be pressed more or less tightly against a second disc, *R*. Lastly, this is connected to *S* by means of a piece not reproduced in Fig. 107, and *S* is in connection with the grooves of the table by means of the angular piece *W*. The change of position of the plate *Q* is brought about as follows. On its circumference there are two screws, *a*, *a*, and a pin, *X*; by screwing the former in or out, the plate *Q* can be made to assume any desired position round the point of contact of *X* and *R* as a pivot. The adjustment is easily accomplished, as one of the screws *a* lies on the horizontal, and the other on the vertical, diameter of the plate *Q*. The plates *R* and *S* are bored out at the centre, so that the spindle *T* possesses sufficient play. In order that the object may also be moved in all possible directions perpendicular to the optical axis, the plate *R* and the one with its connecting piece (not shown in Fig. 107) can also be displaced horizontally and vertically by means of a rack and pinion. For deflecting the rays of light upon the object, the outer tube *E* carries definite contrivances, so that it is an advantage to be able to separate or bring together the object and the objective without changing the position of the latter. On this account the object table is made to move in the direction of the optical axis by means of the pinion *Y*. For the exact focussing of the object the micrometer screw *z* is used, and on it a scale permits one to

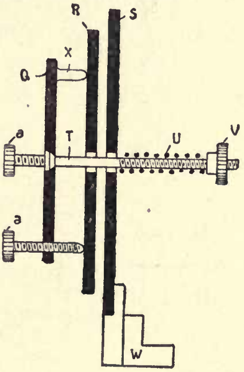

FIG. 107.—Scheme of the stage of the Martens' microscope stand.

read, to 0·005 mm., the displacement of the object along the optical axis. The micrometer screw can be moved either directly with the hand or by means of a small pinion on a movable arm, *d*, in connection with a universal joint *e*. The latter is connected with a bar, *f*, and can thus be moved from a distance. Two pieces, *g*, *g*, serve for the guidance of the table slides. Through the agency of a strong bed-plate, *M*, the whole rests on the square piece *h*, which is fastened to the foot-plate with four screws. This also is composed of slides and guides, so that the whole stand can be moved when considerable displacements of the entire apparatus have to be undertaken.

According to whether the object is to be directly or obliquely illuminated, so the contrivances which are connected to the microscope stand vary. The desired end is reached by employing a mirror, a plane parallel glass, or a vertical illuminator. Figs. 108 to 110 show diagrammatically the manner of their action; *A* represents the objective, *B* the outer tube, and *C* the inner tube with the eye-piece. It will be assumed that the surface of the object *D* under investigation is always set perpendicularly to the optical axis of the microscope.

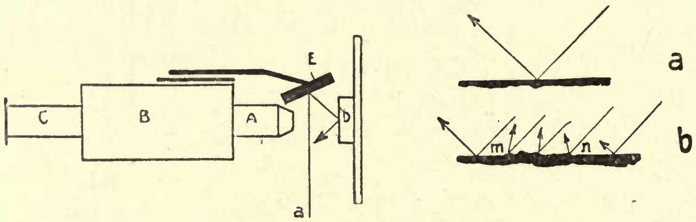

FIG. 108.—Oblique illumination by mirror.

(*a*) Illumination by means of a mirror (Fig. 108).

The incident pencil of light from *a*, perpendicular to the optical axis, falls on the mirror *E*, and is reflected by it upon the object which is thus illuminated obliquely. If the illuminated surface is perfectly polished, all the rays will be reflected obliquely, and no light at all will reach the objective, so that the surface appears dark (Fig. 108*a*). If, on the contrary, there are imperfectly polished portions of the surface, as indicated in Fig. 108*b* between *m* and *n*, the light at these points will be diffusively reflected. A part of the rays will in this way reach the objective, and hence the unpolished parts appear bright on a dark ground. In Fig. 108, *E* represents the illuminating mirror, and it is evident that it must be capable of assuming the most varied positions; this is provided for by means of slides and a universal joint.

(*b*) Illumination by means of plane parallel glass (Fig. 109).

Plane parallel glass is applicable to the direct as well as to the oblique illumination of the object. The arrangement for direct illumination is shown in Fig. 109. Between objective and object a disc *F* of thin and evenly ground glass is introduced, and supported like the mirror *E* in Fig. 108. Part of the light rays coming from *a* after striking the disc are deflected towards *D*, and another portion proceed uninterruptedly in a straight line (shown dotted). The deflected rays impinge upon the object *D*, are reflected back again by it, and again fall on the plane glass *F*. A portion is again deflected, whilst the remainder, amounting to about a fourth of the original amount of light, reaches the objective *A*. It is evident, without further explanation, that if the glass *F* is inclined at an angle of 45° to the optical axis of the microscope the object is directly illuminated, whereas if at any other angle it will be obliquely illuminated. The effect of direct illumination on the appearance of the object follows from Figs. 109*a* and 109*b*. If the surface is perfectly polished, as in Fig. 109*a*, all the incident rays are reflected in the direction of the optical axis and the surface appears bright. Unpolished places, *e.g.* *m*, *n* in Fig. 109*b* reflect the light irregularly, so that part of the rays are lost.

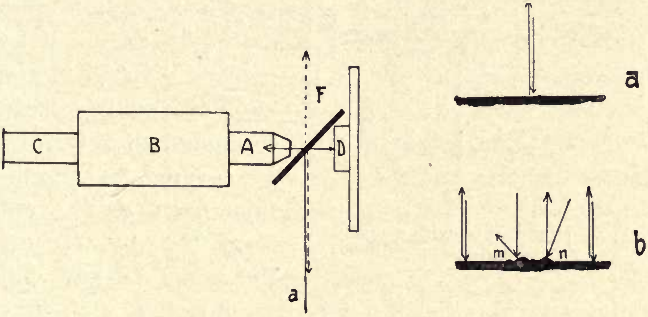

FIG. 109.—Illumination by means of plane parallel glass.

Such places thus appear dark on a bright ground, and therefore exactly the reverse of what occurs in oblique illumination.

From Fig. 109 it follows that this method of illumination is only applicable when the distance between object and objective is large enough to permit the introduction of the plane glass, that is to say, in the case of small magnifications.

Moreover, this method possesses the drawback that the images are only clear enough when the thickness of the plane glass reflector does not exceed to any extent that of the ordinary cover slip, as Heyn[1] has shown experimentally.

(*c*) Illumination by means of a vertical illuminator.

Fig. 110 shows diagrammatically the action of the vertical illuminator. This consists essentially of a glass prism *G* for total reflection, the extreme edge of which reaches only to the optical axis of the microscope, so that one-half of the objective is covered. The incident rays from *a* are reflected from the hypothenuse of the prism *G* and deflected along the optical axis, through the objective, and upon the object. In front of the aperture of the vertical illuminator a small iris diaphragm is placed, which cuts down the incident pencil of light to the requisite size. Further, between the prism of the illuminator and the objective there is a slit which permits the insertion of small diaphragms. These serve the purpose of absorbing rays of light reflected by the surfaces of the objective lenses.

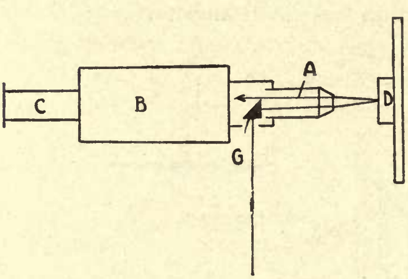

FIG. 110.—Illumination with a vertical illuminator.

Manipulation of the Martens' Microscope Stand.

The piece of metal having been fastened to a glass or cardboard slip with a mixture of equal parts of beeswax and sealing-wax, is clamped on the stage as shown in Fig. 106, and by moving the set screws *aa*, is adjusted nearly perpendicular

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[1] See page 140, footnote 2.

to the optical axis of the microscope. This is easily accomplished by inserting a low-power apochromatic objective (about 16 mm. focal length) in the outer tube, and bringing it about 1 mm. from the object. By observations taken in two perpendicular directions, it is easily seen whether the edges of the objective and the surface to be examined are parallel to one another.

If micro-planars (which are used without eye-pieces and mostly for producing comprehensive images) are employed for the exposure, the covers *C* and *D* (Fig. 106) of the outer tube are screwed off. The objective itself fits into a special adapting-tube, which is fastened in the outer tube by means of a screw thread, in place of the cover *D*. The mirror or plane glass *i* is then so adjusted that the axis of the cone of light impinges on its centre. The exact adjustment of the object is effected by turning the pinion *Y*, which actuates the object-table. The most favourable arrangement of the objective-diaphragms of the mirror or plane glass reflector respectively must be tested by the appearance of the image on the ground glass screen of the photographic camera described below. The magnification is best measured by a direct comparison of the dimensions of object and image. Table 1 shows the various attainable magnifications.

TABLE 1.

MAGNIFICATIONS OF THE MICRO-PLANARS FOR 50, 100, AND 150 CMS. DISTANCE BETWEEN OBJECTIVE AND SCREEN.

Distance of screen from objective in cm.	Focal length of objective in mm.					
	100	75	70	50	35	20
50	4	5·7	6	9	13	24
100	9	12	13	19	28	49
150	14	19	20	29	42	74

For producing larger magnifications, apochromatic objectives are employed in connection with projection or compensating eye-pieces. The illumination is then generally effected in most cases (and always in the more powerful combinations) by the vertical illuminator. Both covers *C* and *D* (Fig. 106) of the outer tube are screwed in, *C* furnished with the vertical illuminator and this with its objective. On the amount of the latter, the particular length of tube is given with the Zeiss objectives, at which the objective works most suitably. An objective of 16 mm., for example, requires a length of tube of 184 mm., that is to say, the distance between the collar of the objective screw and the extreme edge of the inner tube *F* must be 184 mm. These distances are indicated on the tube *F* in millimetres for the case in which the objective is screwed into the cover C. without an intermediate piece, as in Fig. 106. If a vertical illuminator of 22 mm. is inserted between the objective and the cover, this amount must evidently be deducted from the indicated length of tube. In the assumed case the inner tube *F* must, therefore, be pushed so far into the cover *D* that the edge of the latter stands at the number 184 – 22 = 162.

Then the tube *E* is so far moved by means of the pinion *I* that the aperture of the vertical illuminator lies in the axis of the optical bench. This is effected practically by closing the iris-diaphragm of the vertical illuminator almost completely as well as the diaphragm *D* (Fig. 105). Thereupon, with a correct position of the lens C, an image of the source of light appears in the aperture of the vertical illuminator; *E* is then moved until this image appears exactly in the centre. After this, the surface to be examined must be adjusted at right angles to the optical axis. This is first of all done roughly by sighting, as described above, along the edges of the object. For exact adjustment one proceeds as follows: The stand is set up with a somewhat stronger objective (about 4 mm. focal length) and a medium eye-piece (say, compensating eye-piece No. 6). Whilst the observer looks through the eye-piece, the object is cautiously approached by turning *Y* until it appears in the field of view. By means of the fine adjustment *eZ* the middle of the field is brought sharply into focus. If now the object is exactly at right angles to the optical axis of the microscope, the whole circle of view will appear uniformily sharp and will also remain so if by means of the pinions *c* and *b* a parallel displacement is imparted to the plate. If, on the other hand, the surface to be examined is inclined to the optical axis, this displacement will cause the image to appear blurred. From the direction in which *e* must be rotated to produce a sharp focus again, it is easily seen how the screws *aa* must be turned in order to adjust the object exactly perpendicular to the optical axis.

Certain objectives, the so-called immersion lenses, are brought into contact with the object by means of an immersion fluid, generally cedar-wood oil. To effect this, a drop of a Canada balsam solution in xylol is placed on the object, and a thin cover slip then placed over it. The latter is then provided with a thin film of cedar-wood oil, and the stage is cautiously approached until the objective dips in the oil. Then looking through the eye-piece, the stage is moved until the image is seen. The exact focussing is done by means of the pinion *eZ*. Since the distance between the edge of the objective and the object is so small in the case of these powerful lenses (see table 2), the greatest care has to be exercised in moving the stage, for a slight blow imparted to the edge of the objective by the cover glass might loosen the front lens. Objective and object are cleaned after use with xylene. In most cases no deleterious effect on the surface of the section under examination is to be apprehended from the immersion liquid, so that the cover glass may be dispensed with, and a drop of the immersion fluid can be placed directly between object and objective.

In using different objectives, the most suitable positions of the individual diaphragms must be determined by trial, in which one is guided by the rule of never illuminating more of the field of view than one intends to photograph. In this way the harmful effect of reflected light can most readily be prevented.

Projection and compensating eye-pieces are used with apochromatic objectives, the latter of these when very high magnifications are attempted.

It is of great importance that a decisive opinion of the capabilities of the individual objectives be obtained, in order to be certain of the magnifications at which the best results can be obtained with the different glasses. The determination of the magnification in photographic exposures is accomplished by putting a so-called object micrometer on the stage in the place of the object. This consists of a very thin glass slip upon which have been etched 100 divisions about 0·10 mm. distant from one another. The image of the micrometer is then obtained on the screen and the distance between the separate divisions measured, from which the linear magnification at once follows. Table 2 gives a series of magnifications obtainable with apochromatics. Experiment must in most cases decide which is the best magnification to employ, as the nature of the object, comprehensiveness of the image produced, etc., exercise a considerable influence.

TABLE 2.

APOCHROMATIC 16.

Proj. eye-piece P_2		Proj. eye-piece P_4		Comp. eye piece K_2		Comp. eye-piece K_4		Comp. eye-piece K_6	
Dist.[1]	L.M.[2]	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.
16	22	17	50	16	28	16	60	16	86
18	25	35·5	100	33	50	30·5	100	20	100
37	50	54·5	150	52·5	75	49	150	45	200
56	75	73·5	200	71·5	100	68	200	70	300
75	100	93	250	91·5	125	86·5	250	95	400
94	125	112	300	111	150	105	300	120	500
112·5	150	131	350	130·5	175	123·5	350	145	600

APOCHROMATIC 8.

Proj. eye-piece P_2		Proj. eye-piece P_4		Comp. eye-piece K_2		Comp. eye-piece K_4		Comp. eye-piece K_6	
Dist.	L.M.	Dist.	L.M.	Dist.	L M.	Dist.	L.M.	Dist.	L.M.
20	50	20	100	16	56	33	200	16	160
40	100	40	200	34	100	52	300	22	200
60	150	61	300	54	150	71	400	47	400
80	200	82	400	74	200	91	500	73	600
100	250	103	500	95	250	110	600	99	800
120	300	124	600	115	300	130	700	124	1000
140	350	146	700	135	350	150	800	150	1200

APOCHROMATIC 4.

Proj. eye-piece P_2		Proj. eye-piece P_4		Comp. eye-piece K_2		Comp. eye-piece K_4		Comp eye-piece K_6	
Dist.	L.M.	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.
20	100	22	200	16	100	16	200	24	400
44	200	45	400	37	200	37	400	40	600
68	300	68	600	60	300	60	600	55	800
91	400	92	800	82	400	82	800	71	1000
115	500	115	1000	105	500	105	1000	87	1200
138	600	138	1200	127	600	127	1200	102	1400
150	650	150	1300	150	700	150	1400	118	1600

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[1] Dist. = Distance between ground glass screen and eye-piece.

[2] L.M. = Linear magnification.

APOCHROMATIC 3.

Proj. eye-piece P_2		Proj. eye-piece P_4		Comp. eye-piece K_2		Comp. eye-piece K_4		Comp. eye-piece K_6	
Dist.	L.M.	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.	Dist.	L.M.
27	200	28	400	24	200	24	400	24	600
42	300	43	600	39	300	39	600	44	1000
56	400	58	800	53	400	53	800	64	1400
70	500	72	1000	68	500	68	1000	84	1800
85	600	87	1200	82	600	82	1200	104	2200
99	700	102	1400	98	700	98	1400	124	2600
113	800	117	1600	112	800	112	1600	—	—
128	900	131	1800	127	900	127	1800	—	—
142	1000	146	2000	142	1000	142	2000	—	—

2. *Le Chatelier's Microscope Stand.*

The microscope stand of Le Chatelier differs from that of Martens in that the optical axis of the objective is set vertically instead of horizontally. Fig. 111 *abc* shows the construction scheme of this apparatus. The incident light rays coming through the illumination tube *T*, strike a prism, *F*, which reflects them vertically upwards. The object *D* is placed on a table pierced in the centre, which is fixed once for all at right angles to the optical axis and can be moved by the coarse and fine adjustments *B* and *E*. The light returning from the object impinges on a prism, *G*, placed lower down, and is then reflected by it either towards the front into the eye-piece *C* (see Fig. 111 *c*, horizontal section) or into the photographic camera. For this purpose the prism *G* can be rotated round a vertical axis. Although the manipulation of this installation appears to be simpler than that of Martens, particularly because the adjustment of the object for parallelism is done away with, its applicability is more limited than the other on account of its construction.

For observing the progress of etching and other metallographic work, the ball-jointed microscope stand introduced by Martens, as shown in Fig. 112, can be employed with advantage. The construction is extremely simple and adapted for rapid and certain work under direct illumination. The less costly achromatic objectives are recommended for employment with this equipment, as they are quite good enough for the purpose.

Photographic Apparatus.—For taking microphotographs, a camera capable of movement along the optical axis of the eye-piece is set up. Very extensible apparatus is recommended, as greater freedom is permitted in this case in the selection of the magnification.

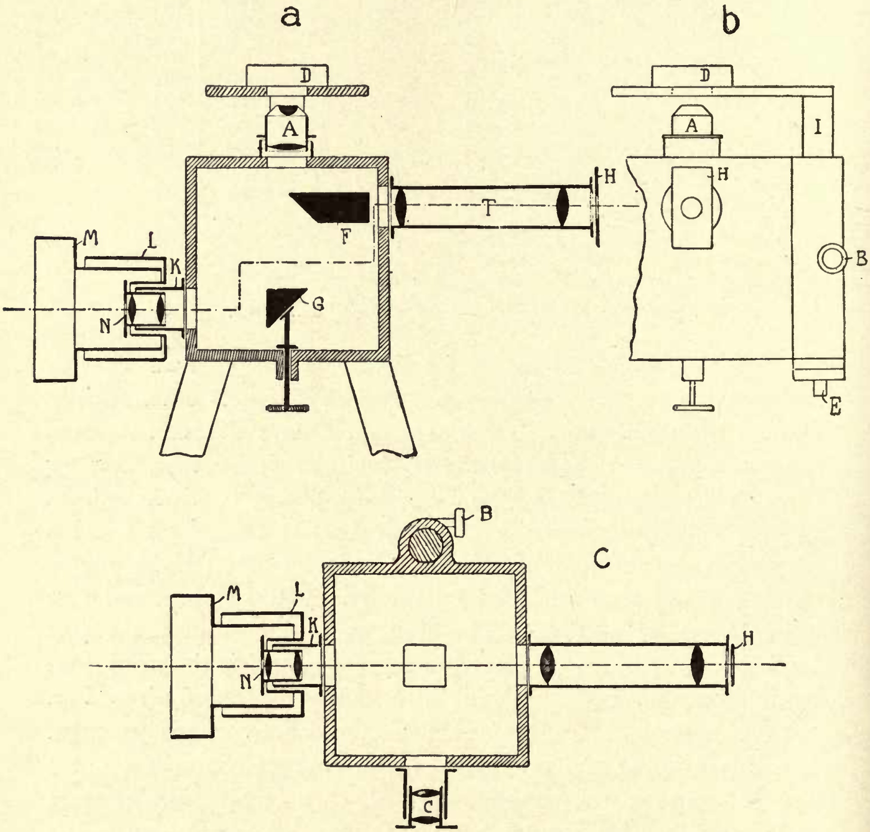

FIG. 111.—Scheme of Le Chatelier's microscope.
(a) Vertical section; (b) side elevation; (c) horizontal section.

Camera and microscope are connected with each other so as to be light-tight, as shown in Figs. 111 *a* and *b*. The tube-piece *M* is fastened to the camera, whilst *L* is made to slide on the tube *K* of the microscope. *L* is covered internally with black cloth, so that in the arrangement sketched no light can penetrate into the camera from the outside.

THE TECHNIQUE OF PHOTOGRAPHY.

The method of work described below presents an example by which good results can be obtained. It corresponds *in toto* to the procedure adopted in the metallurgical institute of the Technical High School at Aachen. Good results naturally follow from a corresponding manipulation of materials other than those specified.

Choice of Photographic Plates.—With exposures at small magnifications (less than 100 linear diameters) and with rather strong illumination of the object, any good dry plate can be used. It is advisable to employ the less sensitive materials when the source of light is very strong, particularly the electric arc. With high magnifications it is desirable, if possible, to use monochromatic light, as mentioned earlier; the insertion of the yellowish-green filter is absolutely necessary in exposing with the powerful apochromatics of 4, 3, and 2 mm. focal length, unless the mercury light is preferred. In these cases orthochromatic plates are the best to use for the exposure, as they are very sensitive to coloured light.

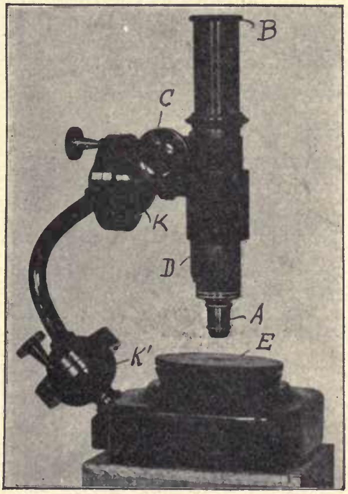

FIG. 112.—Ball-jointed microscope (Martens).

The Exposure.—As the intensity of the illumination of the object depends on the most varied circumstances and frequently alters with the same source of light, it is an advantage to find out the correct time of exposure by a preliminary experiment. A kind of sliding box is best used for this purpose, which is arranged so that the photographic plate can be made to slide behind a narrow slit. Thus, of the same part of the object a series of narrow exposures can be made in juxtaposition and of varying durations of illumination. The exposed plate is developed for 10 minutes, then fixed, and the time suitable for the final exposure selected from the appearance of the separate strips of the picture.

Production of the Negative.

Development of the Negative.—After the plate has been exposed, the still invisible "latent" picture must be developed. Development consists in subjecting the plate to the action of certain chemical substances which deprive the bromide of silver existing on the plate of bromine, and thus precipitate metallic silver. As this reaction occurs first and most strongly at those parts of the plate which have been most brightly illuminated, the plate appears black at these places, whilst the unexposed silver bromide remains intact.

The developer consists, as a rule, of a mixture of a reducing substance with an alkali.

For microphotographic purposes the following metol-adurol mixture has proved excellent :—

Water	1000	c.cm.
Metol	10	grams.
Adurol	50	„
Sodium sulphite (cryst.)	300	„
Potassium carbonate	250	„
Potassium bromide	1–2	„

The metol and adurol are dissolved together before the sulphite. One part of the solution is used with from 10 to 15 parts of distilled water. The temperature of the bath should not exceed 18° to 19° C. In preparing other developers, such as hydroquinone, glycine, pyrogallol, etc., the instructions for use must be referred to.

It is possible to judge, from the progress of the development, whether the time exposure was correctly chosen. It can be observed that the high lights, *i.e.* the places where the effect of the light is most marked, appear first of all. If the developer penetrates deeply into the film at the same time that the surface development shows up, density is obtained. If surface development and density are obtained together, the typical picture of normal development results, as should always be the case with correctly exposed plates. Trifling errors of exposure can at this stage be set right in many cases by suitable alterations to the developing liquid. If the plate is over-exposed, the image appears too quickly at all points, and the developer has no time to penetrate the film and blacken the high lights sufficiently. To prevent this, the dilution of the developer and the addition of a few drops of a solution of potassium bromide of the following composition are recommended:—

Potassium bromide (cryst.) . .	10 grams.
Distilled water	100 c.cm.

The same result can be obtained by the addition of a small amount of old developing solution.

If the plate was under-exposed, some of the following solution is added:—

Potassium carbonate (cryst.) . .	10 grams.
Distilled water	100 c.cm.

To trace the progress of the development, the plate is held now and then against a ruby-red light for a moment, so as to control the density of the exposed parts of the plate by looking through it. As a general rule the time of development should not exceed 10 minutes.

Fixing the negative.—After the development is finished, the portions of the plate which were not illuminated, and which therefore contain unreduced silver bromide, must be freed from it; this takes place in the fixing. The fixing-bath consists of a solution of sodium thiosulphate (hyposulphite of soda).

The following acid fixing bath can be advantageously employed for the plates. Fifty grams of sodium sulphite crystals are dissolved in 1000 c.cm. of water, and then 15 grams of citric acid. After this has dissolved, 200 grams of sodium thiosulphate are dissolved in the solution.

The plates, washed free from the greater part of the still adhering developer, are allowed to remain in the fixing-bath until milky-looking patches are no longer visible on the back. They are then washed for an hour in running water and dried in the air.

Hardening the negative.—Although the gelatine film of good plates should remain fast on the glass on the edges, it happens at times, and particularly with warm baths, that the film becomes rather loose and crinkled round the edges. To prevent damage to the picture, the plate, previously washed, is placed in a saturated solution of alum in distilled water for 10 minutes. It is then washed in running water for 10 minutes longer.

Intensification of the Negative.—It is not advisable, as a rule, to undertake subsequent changes in the appearance of the negative; rather, should a correctly exposed and developed picture be taken afresh. Nevertheless the operator may be called upon to strengthen a negative which is too weak, either because of too short an exposure or of development; that is to say, he must subsequently deposit a metallic film on the places which have been exposed and have not a sufficiently strong coating of silver. This is done by placing the thoroughly washed plate in a bath of the following composition:—

Distilled water	100 c.cm.
Mercuric chloride	2 grams.
Potassium bromide . . .	2 grams.

The plate is allowed to remain in this solution until the picture becomes white through and through with a precipitate of mercurous chloride. After washing thoroughly in running water, the whitened image is blackened by placing the plate in a solution of ammonia of the following composition:—

Ammonia (s.g. 0·91)	1 c.cm.
Distilled water	10 ,,

When the image has become quite black, owing to the formation of mercurammopium chloride, the plate is removed from the solution and washed in running water for 2 or 3 hours.

Reduction of the Negative.—If a uniform obscuring film appears, in consequence of over-exposure or protracted development, a part of the silver film is removed by treatment of the plate with a reducing solution:

Distilled water	100 c.cm.	Solution I.
Sodium thiosulphate . .	10 grams.	
Potassium ferricyanide .	1 gram,	Solution II.
Distilled water	10 c.cm.	

For use, 5 to 10 cc. of Solution II. are added to 100 c.cm. of Solution I., and the plate is treated until the desired appearance is produced.

It also frequently happens that individual places on the picture are perfectly opaque on account of abnormal density, whilst the middle tones are right. In this case a persulphate reducer of the following composition is recommended :—

Water	100 c.cm.
Ammonium persulphate . .	2 grams.

In every case the plate, after reduction, must be thoroughly washed.

Clearing the Negative.—It sometimes happens, and notably after long developments, that the film becomes somewhat stained by the developer. In order to clean such a negative, the fixed and well-washed plate is placed in the following solution :—

Thiocarbamide	20 grams.
Citric acid	10 grams.
Distilled water	1000 c.cm.

The clearing is complete after several minutes.

Production of the Positive.

Copying.—Just as it is impossible to obtain a good positive from a bad plate, so can a bad picture frequently be obtained by improper copying. Of prime importance is the choice of a suitable paper, which at first sight would appear by no means easy on account of the great number of these manufactured articles. As a general rule glossy papers are more suitable for reproducing microphotographs than matt papers.

Papers requiring no development possess the advantage of permitting the progress of copying to be followed. The copying process of two typical papers will be described here, a gelatine and a collodio-silver paper, as the commercial brands generally belong to one or other of these classes. In the case of gelatine papers, and Aristo paper in particular (for which the following procedure holds good), the sensitive silver chloride is suspended in a vehicle of gelatine on the paper. By exposure to light, the silver chloride is decomposed with liberation of silver. The image is copied somewhat darker than the final positive is intended to be, as it fades slightly in the subsequent operations.

Collodio-silver papers differ from the above in that the silver chloride is suspended in an emulsion of pyroxylin. These are more convenient in use than the gelatine papers, since the film is not so sensitive to the influence of water as the gelatine of the former, which swells up. In order to obtain pictures exhibiting rich contrast from flat negatives, papers showing different shades of colour in the emulsion are recommended. The colour is obliterated in the subsequent operations.

Fixing and Toning the Positive.—The fixing of the positive, like that of the negative consists in dissolving away the chloride of silver which has not been exposed to the light by means of sodium thiosulphate. In the simultaneous or subsequent toning process the separated silver is more or less completely replaced by gold. Fixing and toning can either be done in separate baths, or simultaneously in a combined toning and fixing bath. The first method, as a rule, gives pictures of greater durability.

Method of Separate Baths for Gelatine Paper.—The prints, after having been washed with water several times in a darkened room are placed in a toning bath of the following composition:—

Sodium-gold chloride solution (1 g. of the salt in 50 c.cm. water)	20 c.cm.
Distilled water	280 c.cm.
Powdered chalk	20 grams.

This mixture is set aside for a time, shaken, and filtered. When the yellow tints of the pictures have disappeared, the prints are washed and then placed in a bath of alum, consisting of:

Alum (cryst.)	10 grams.
Distilled water	200 c.cm.

When, after about ten minutes, the film has become hardened, the prints are again washed, and then brought into the fixing bath. This has the following composition:—

Sodium thiosulphate	10 grams.
Distilled water	200 c.cm.

Fixing is complete in about a quarter of an hour, and the prints are then washed for several hours in running water. After thoroughly washing them, they are squeegeed with the film side downwards on a carefully cleaned piece of plate glass, in order to impart a glossy appearance. When perfectly dry the brilliantly polished prints are easily detached.

Method of Separate Baths for Collodio-silver Papers.—The prints, which have been somewhat over-copied, are washed with water and then toned in the following bath:—

Distilled water	1000 c.cm.
Alum crystals	6 grams.
Citric Acid	6 „
Ammonium thiocyanate	24 „
Potassium-gold chloride solution (1 gram of the salt in 100 c.cm. water) . .	50 c.cm.

After washing, the prints are fixed in :

Sodium thiosulphate	10 grams.
Distilled water	100 c.cm.

The prints are then well washed. Collodio-silver papers are not suitable for the production of a glossy appearance on a polished surface.

Method of Mixed Baths.—The simultaneous toning and fixing of gelatine as well as collodio-silver prints can be carried out in the following combined bath:—

Distilled water	2000 c.cm.
Sodium thiosulphate	500 grams.
Ammonium thiocyanate	50 „
Alum crystals	15 „
Citric acid crystals	15 „
Lead acetate	20 „
Lead nitrate	20 „

The alum, citric acid, lead acetate, and nitrate are each dissolved separately in small portions of the total amount of the water, and then added to the main solution. The bath is first used three or four days after making, when it has cleared. For use, about 100 c.cm. of the solution are mixed with 6 c.cm. of a gold solution of the following composition:—

Potassium-gold chloride	1 gram.
Distilled water	100 c.cm.

If it is desired to obtain quickly a very durable positive from a plate, silver bromide papers, accompanied by development, are advantageously employed. They certainly work somewhat hard as a rule, nevertheless one can obtain, from normal negatives, prints equally as serviceable as those from silver chloride papers.

The paper, placed in a dark slide, is exposed for about 10 seconds at a distance of about half a metre from an ordinary gas flame, and is then developed in the metol-adurol bath which was employed for the negative. The more quickly the development proceeds, the purer the black tones. After washing in water, the prints are fixed for 15 minutes in the following bath:—

Sodium thiosulphate	200 grams.
Distilled water	1000 c.cm.

and then washed for 2 hours. They are then hardened for 2 or 3 minutes in—

Potash alum	6 grams.
Distilled water	100 c.cm.

After washing again for about 15 minutes the prints are taken out to be dried. A highly glossed surface can be imparted to this paper also by squeegeeing on plate glass or an enamelled disc.

THE SPECIAL METALLOGRAPHY OF IRON AND ITS ALLOYS

The most important alloys of iron are those with carbon; this element exercises by far the greatest influence on the useful properties of the metal. This influence can be intensified or lowered by the presence of other elements—a fact of which advantage is taken in the so-called ternary and quaternary alloys. These are materials of particularly pronounced properties, such as are used for tool steels and machine parts requiring great strength.

As in the case of the alloys previously dealt with, the freezing-point diagram of the iron-carbon alloys will first of all be dealt with. The first work on this point was produced by Osmond[1] in 1888 in relation to an earlier work on the structure of steel.[2]

As the works of Osmond are classical, in connection with the nomenclature, they will be briefly discussed so far as concerns our present purpose. The materials investigated by him possessed the following composition:—

No.	Method of Production.	Composition.				
		C	Si	S	P	Mn
1	electrolytic	0·08	0·08	0·08	0·08	0·08
2	forged	0·16	0·01	0·02	0·03	0·11
3	„	0·29	0·06	0·06	0·05	0·27
4	„	0·57	0·08	0·02	0·05	0·23
5	„	1·25	0·19	0·02	0·02	0·10
6	cast	4·10	0·22	0·04	0·02	0·12

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[1] Osmond, "Transformation du fer et du carbone dans les fers, les aciers et les fontes blanches." Libraire militaire, L. Baudouin et Co., Paris, 1887. Abstracted: *Annales des Mines*, 1888. Série 8, tome XIV. *Journal of the Iron and Steel Institute*, 1890, No. I.

[2] Osmond et Werth, "Théorie cellulaire des propriétés de l'acier." *Annales des Mines*, 1885. Série 8, tome VIII. pp. 5–85.

Osmond's results, stated briefly, are as follows :—

1. Pure iron has two critical points, one at 855° C., which Osmond designated Ar_3, and the other at 750° C., the point Ar_2.

2. The second sample, with 0·16 per cent. of carbon, has three arrest-points :

Ar_3 at 845° C.,
Ar_2 at 755° C.,
Ar_1 at 680° C.

3. At a carbon content of 0·29 per cent., the two upper points Ar_3 and Ar_2 fall together ; there are therefore only two :

$Ar_{3,2}$ at 780° C.,
Ar_1 at 680° C.

4. With higher carbon contents all the three critical points coincide, so that samples 5 and 6 have only one :

$Ar_{3,2,1}$ at 720° C. and 695° C. respectively.

Osmond established these critical points by allowing the strongly heated samples to cool down, and thus determining the cooling curves. On reheating corresponding accelerations occur, although they fall at higher temperatures than the points of retardation Ar. To distinguish the points occurring on heating from the former, Osmond designates them Ac.

It was not possible from the first experiments to draw up a complete diagram of the iron-carbon alloys ; in particular, the determinations of the melting-points were wanting.

In the fourth and fifth Reports of the Alloys Research Committee, Roberts-Austen[1] submitted a complete freezing and transformation diagram. His methods and results have formed a foundation for subsequent experimental control and theoretical developments. The materials with which Roberts-Austen dealt were the purest electrolytic iron, cemented steel, and Siemens-Martin steel. His results were embodied in the diagram of Fig. 113, which contains the freezing points as well as the critical points occurring during the cooling down of all alloys up to about 5 per cent. of carbon. The chemical

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[1] W. C. Roberts-Austen, "Fifth Report of the Alloys Research Committee." *Proceedings of the Institution of Mechanical Engineers*, 1899. *The Metallographist*, vol. II. July, p. 186.

composition of the material employed by him is given in the following table:—

No.	C	Si	S	P	Mn	As
1	1·800	0·008	0·032	0·054	0·391	Trace
2	—	—	—	—	—	—
3	1·740	0·006	0·037	0·046	0·380	Trace
4	1·451	0·006	0·029	0·023	0·340	0·004
5	1·461	0·007	0·038	0·025	0·340	0·002
6	1·234	Trace	0·030	0·013	0·327	0·004
7	1·161	"	0·030	0·016	0·290	Trace
8	0·927	"	0·025	0·013	0·293	0·004
9	0·912	"	0·036	0·010	0·236	Trace
10	0·871	"	0·040	0·008	0·270	0·002
11	0·690	"	0·038	0·009	0·220	0·004
12	0·540	"	0·032	0·006	0·280	Trace
13	0·434	"	0·030	0·009	0·270	"
14	0·342	"	0·032	0·006	0·270	0·003
15	0·160	"	0·037	0·008	0·240	Trace
16	0·145	"	0·041	0·006	0·250	"
17	0·102	"	0·037	0·008	0·230	"
18	—	—	—	—	—	—
19	0·070	Trace	0·035	0·008	0·244	Trace
20	—	—	—	—	—	—
21	0·097	Trace	0·030	0·007	0·220	0·004
22	—	—	—	—	—	—
23	0·108	Trace	0·033	0·005	0·240	Trace
24	0·101	"	0·034	0·004	0·217	"
25	0·078	"	0·033	0·007	0·217	"

The materials of higher carbon contents were prepared by carbonizing in the electric furnace.

A great similarity can be seen in Fig. 113 to the freezing-point curve of salt and water (see p. 32). The line *ABD* represents the commencement of freezing of all the alloys from 0 up to 5 per cent. of carbon, and *aC* represents the end points of the freezing of these alloys. Corresponding to the freezing-curve of the salt-water system, we have therefore:

Along *AB*—freezing out of one component, the iron.

Along *BD*—freezing out of the second component, the carbon as graphite.

Along *aC*—freezing of the eutectic mixture, iron-graphite.

Concerning the separation of the iron, Roberts-Austen remarks: "There is, however, the following difference between ice and iron; on account of its high fusion point, the latter retains a certain amount of carbon. There exists, therefore, a solid solution of iron and carbon, on which account further complications ensue when the iron has cooled down to the temperature at which it can no longer hold carbon in solution."

These changes on cooling will now be considered for the whole series of iron-carbon alloys, commencing with pure iron. Immediately after solidification (at 1600° C. according to Roberts-Austen), pure iron is a non-magnetic metal which possesses the property of holding carbon in solid solution, the amount of which rises with the temperature. At 1000° C. the saturated solution contains about 1·5 per cent. of carbon, at about 700° C. only 0·90 per cent.

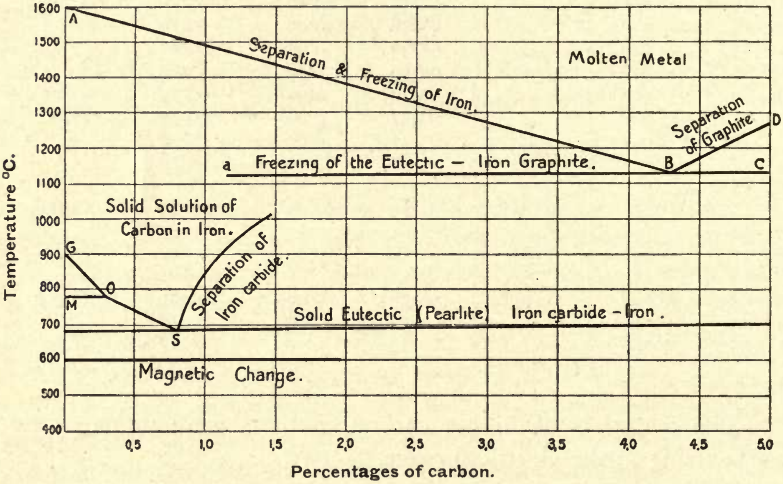

FIG. 113.—Diagram of the Iron-carbon Alloys (Roberts-Austen).

This modification of iron, γ-iron, is stable down to 880° or Ar_3 (in Fig. 113, *G*), at which temperature it changes into β-iron with development of heat. β-iron is also non-magnetic, but the amount of carbon which it can hold in solid solution is far less, possibly nil. Just as the fusion-point of iron is lowered by the presence of carbon, so also the position of Ar_3 changes with increasing carbon contents. When, by further cooling, the point Ar_2 is reached (*M* in Fig. 113), 780° in the case of pure iron, the β-iron changes into *a*-iron. This is magnetic and possesses no solubility for carbon. As a micrographic constituent it is called ferrite.

A molten alloy with 0·2 per cent. of carbon would behave as follows on cooling. The freezing-point falls lower than 1600° C., at about 1550°, because of the dissolved carbon. As at the temperature 1130° C., corresponding to the eutectic line *aC*, γ-iron can retain as much as 1·5 per cent. of carbon in solution, no eutectic of iron-graphite forms, but the mass remains as a homogeneous solid solution down to the Ar_3 point. At this point part of the iron crystallizes out as β-iron, to form ferrite subsequently. The remainder becomes richer in carbon, and consequently remains in the γ-condition. This phenomenon corresponds exactly to the separation of ice from salt solutions. A solution containing 5 per cent. of salt is liquid down to a temperature of about $-3°$ C. (see Fig. 25 on p. 32). At this point a portion of the water separates as ice, that is to say, the excess part of the water changes from one modification (the liquid) into the other (the solid), whilst the residue still remains in the liquid condition.

The carbonless β-iron which first separates changes into α-iron at 780°. The position of this point cannot be affected by the presence of carbon, for it represents only a change of the already separated iron. In Fig. 113 the line *MO* therefore runs horizontally, whilst *GO* sinks with increasing carbon contents. At the point *O* in which the lines *MO* and *GO* cut each other, the separated iron, in the opinion of several authors, changes at once into β and α successively, that is, Ar_3 and Ar_2 coincide. Moreover, it is not necessary to assume that β-iron must first be formed during the transformation of γ into α-iron; for just as it is possible in certain cases to change a solid directly into a gas (sublimation) without first changing to the liquid condition, so the allotropic transformation of γ directly into α-iron cannot be regarded as particularly exceptional.

By the further cooling of the alloy containing 0·2 per cent. of carbon, the phenomena are almost identical with those of the salt-water system. In proportion to the separation of β-iron, the remaining solid molten mass becomes richer in carbon, whilst the transformation temperature Ar_3 simultaneously sinks. When so much iron has separated that the remaining mass contains 0·9 per cent. of carbon, the lowest temperature is reached at which γ-iron can exist. In the salt-water analogue this means: the greater the amount of ice crystallizing from the solution, the richer the mother-liquor becomes in salt. The change-point of water to ice falls in a corresponding degree, until the lowest temperature is reached at which water can exist as a fluid. This is called the "eutectic temperature," and the mother-liquor solidifying at it is called the "eutectic mixture." The iron-carbon system similarly possesses such a eutectic temperature, at which the solid solution existing up to then changes into a eutectic mixture which is designated pearlite.

This eutectic does not consist of juxtaposed particles of iron and carbon, but of iron and iron carbide of the formula Fe_3C.

To this phenomenon there is also an analogue in salt solutions, viz. in the ferric chloride-water series (see p. 34). A solution which contains 1 molecule of ferric chloride in 100 molecules of water deposits pure ice at first, and thereby becomes richer in the salt, until at a temperature of $-55°$ C. the eutectic ice-ferric chloride, $12H_2O$, freezes out. If the original solution is hyper-eutectic, that is to say, if it contains more ferric chloride than corresponds to the eutectic mixture, it deposits the hydrate first and the eutectic afterwards at $-55°$ C.

Just as the ferric chloride is combined as hydrate with its solvent, present in large excess, so also is the carbon combined with the iron as carbide. The eutectic mixture, the pearlite, consists therefore of juxtaposed particles of iron and iron carbide. Micrographically the pure iron is called ferrite, the eutectic pearlite; the iron carbide, Fe_3C, is called cementite.

By cooling further, the alloy under consideration with 0·2 per cent. of carbon suffers no further change; it is found on microscopic investigation to consist of ferrite and pearlite (see p. 191, Fig. 133). All hypo-eutectic steels exhibit a similar structure up to 0·9 per cent. of carbon, the composition of the eutectic mixture. At this composition $Ar_{3,2}$ and Ar_1 coincide in the point $Ar_{3,2,1}$ (S in Fig. 113).

If the carbon contents exceed 0·9 per cent., the carbide separates out first as free cementite, whilst pearlite again forms at the eutectic temperature.

If the transition point Ar_1, at which the reaction—

solid solution → pearlite

takes place, is suppressed, the solid solution can remain as such at the ordinary temperature, and appears in the structure of the alloy as a definite constituent called martensite.

In 1900 Bakhuis Roozeboom[1] published his views on the iron-carbon alloys, which he had formulated according to the laws of the Phase Rule. The importance of the bearing of the latter on the study of metallic alloys, and particularly of those under present consideration, had been recognized by Le Chatelier[2] in the same year.

The merit of Roozeboom's work consists chiefly in the fact that in the diagram (Fig. 114) he took into consideration the fact already observed by Roberts-Austen, viz. that from the fluid melt it is not pure iron but a solid solution of iron with carbon which crystallizes out, and that this crystallization proceeds according to the laws explained in the general part. Thus the freezing of all alloys which can hold carbon in solid solution (according to Carpenter and Keeling's experiments, up to 2 per cent. of carbon) would proceed as follows:—

An alloy containing, *e.g.* 1·5 per cent. of carbon begins to deposit mixed crystals at *c*, the carbon contents of which are smaller than those of the excess liquid. The manner of the freezing of mixed crystals of two substances has already been demonstrated (see p. 38). If *a* is the extremity of the eutectic line, that is, the point whose abscissa gives the highest carbon contents which the mixed crystals can contain at that temperature, the line *Aa* will correspond to the line *CgD* in the diagram on p. 38. In other words, at the temperature of the commencement of freezing *c*, mixed crystals separate containing *a' b* per cent. of carbon, the point *b* being the point of intersection of the line *Aa* with a horizontal line drawn through *c*. On further cooling, the mother mass becomes richer in carbon simultaneously with the separating crystals. At the temperature *e* the carbon of the mother mass is equal to *if*, and that of the mixed crystals *id*. At the beginning of freezing, mixed crystals containing *a'b* per cent. of carbon had separated. If the cooling proceeds slowly enough, these mixed crystals will take up carbon from the mother mass, so that at the temperature *e*, for instance, the whole will consist of mixed crystals containing *id* per cent.

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[1] B. Roozeboom, "Eisen und Stahl vom Standpunkte der Phasenlehre." *Zeitschrift für Physikalische Chemie*, Bd. xxxiv., 1900. *The Metallographist.* Vol. 3, p. 293. *Contribution à l'étude des alliages.*

[2] Le Chatelier, "Application de la loi des phases aux alliages et aux roches." *Comptes rendus.* Vol. 130, p. 85 (1900).

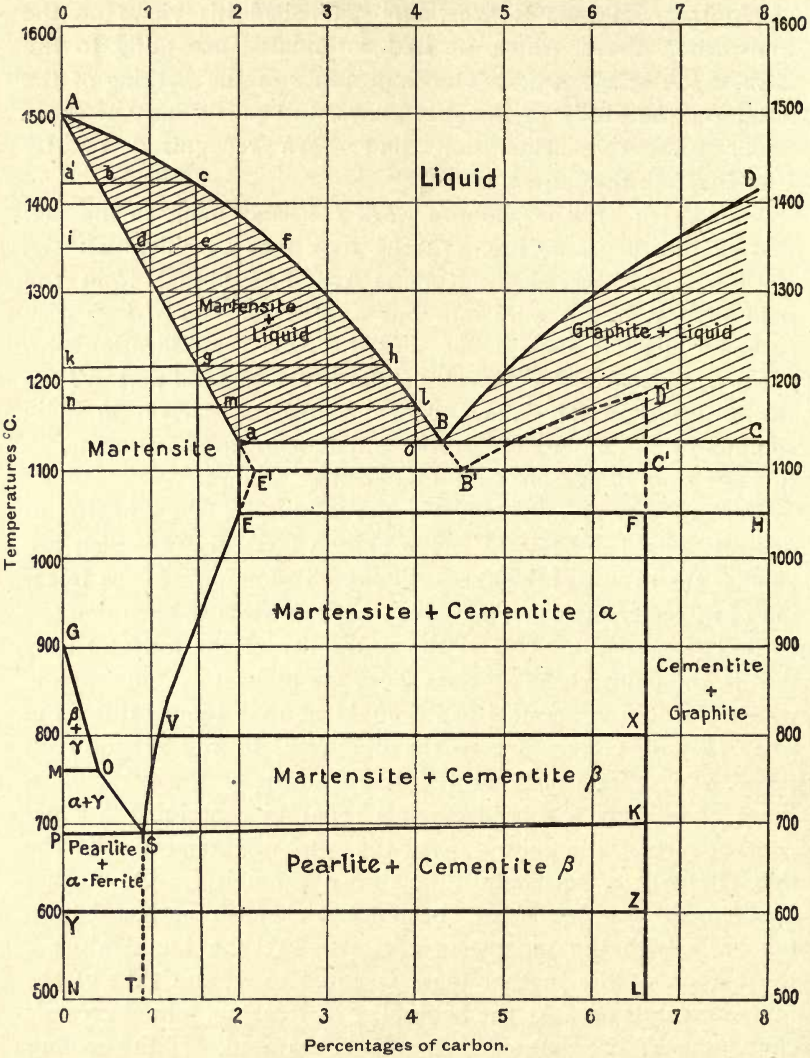

FIG. 114.—Diagram of the iron-carbon alloys (Bakhuis Roozeboom); the temperatures have been corrected by Carpenter and Keeling's figures.

of carbon and a mother mass containing *if* per cent. The amount of the mixed crystals can be calculated from the equation—

$$\frac{\text{amount of mixed crystals}}{\text{amount of mother liquor}} = \frac{ef}{ed}$$

which has been already proved on an earlier occasion (see p. 39).

At the point g the vertical line through the 1·5 abscissa cuts the line Aa, that is, the freezing is finished. The crystals last separated contained kg per cent. of carbon, and the excess of mother liquor remaining at the same time kh per cent.; the excess serves to enrich the previously separated crystals up to kg per cent., so that at the temperature g the whole mass consists of homogeneous mixed crystals containing $kg = 1{\cdot}5$ per cent. of carbon.

To explain the phenomena of freezing of iron-carbon alloys of higher carbon contents, Roozeboom made the assumption proved later to be untenable by the work of Heyn,[1] Wüst,[2] Charpy,[3] and Benedicks,[4] that the formation of cementite at about 1000° C. from the eutectic graphite-martensite[5] (which separates at 1130 C.) occurs according to the reaction

Graphite + martensite = iron carbide.

The formation of graphitic iron would thus be explained, according to Roozeboom, by the suppression of this reaction, whereas white iron would result by its completion. If this were correct, very slowly cooled pig-iron should always be white, since sufficient time would thus be allowed for the above reaction to occur. The experiments of Wust[6] have undoubtedly proved, however, that pure, highly carbonized iron, after slow cooling, is always graphitic, whereas white iron, *i.e.* iron containing combined carbon, results from rapid cooling. As a matter of fact, iron-carbon alloys behave in a manner exactly the opposite of Roozeboom's statement of the matter, and later experiments of the author[7] go to show that from highly carbonized melts the

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[1] Heyn, "Labile und metastabile Gleichgewichte in Eisen-Kohlenstofflegierungen, *Zeitschrift für Elektrochemie*, 1904. S. 591.

[2] F. Wüst, "Beiträge zur Keuntnis der Eisen-Kohlenstofflegierungen höheren Kohlenstoffgehaltes," *Metallurgie* III. H. 1. S. 1.

[3] Charpy, "Le diagramme de l'equilibre des alliages fer-carbone." *Comptes rendus*, 1906.

[4] Benedicks, "Über das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff," *Metallurgie*, 1906. Bd. III. S. 303.

[5] "Martensite" here denotes either "mixed crystals" or "solid solution."

[6] Wüst, *loc. cit.*

[7] Goerens, "Über den augenblicklichen Stand unserer Keuntnisse der Eisenkohlenstofflegierungen." *Metallurgie*, 1806, Bd. 3. 175. 1907, Bd. 4 137, 170.

carbide always separates out at first, and then by exceedingly slow cooling decomposes into graphite and iron.

In consideration of this disagreement between the Roozeboom reaction and the actual behaviour of iron-carbon alloys, Benedicks projected the diagram reproduced in Fig. 122. This depends upon the distinction between a stable and a metastable system of iron-carbon, a distinction which had been already recognized earlier by Charpy and Grenet,[1] as well as by Heyn. According to this, the freezing of all iron-carbon alloys up to 2 per cent. proceeds in the manner described above by Roozeboom. After solidification they consist of a homogeneous solid solution of carbon (apparently of iron carbide) in γ-iron. If the carbon contents are higher, then, in the case of the metastable system occurring mostly by rapid cooling, a eutectic of iron carbide-mixed crystals appears along with the mixed crystals. The amount of the eutectic increases with the carbon contents, and at 4·3 per cent. of carbon the whole metallic mass consists of it. If the carbon rises still further, increasing amounts of free iron carbide appear with the eutectic. The freezing of the metastable eutectic cementite-mixed crystals proceeds at 1130° C., corresponding to the horizontal line *E'B'C'*.

If the cooling proceeds slowly enough, the stable system may eventuate, that is to say, a eutectic of graphite + solid solution is formed. The eutectic horizontal of the stable system is *aBC* at a very slightly higher temperature than *E'B'C'*. As convincing proof of the existence of the horizontal *EFH*, *VX*, *YZ* (Fig. 114), in the pure system iron-carbon is wanting; Benedicks deletes them from his diagram.

Immediately after complete solidification we have therefore the following :—

A. In stable systems :

1. Alloys containing from 0 up to 2 per cent. of carbon consist of homogeneous mixed crystals.
2. Alloys containing from 2 to 4·3 per cent. of carbon consist of saturated mixed crystals and increasing amounts of the eutectic graphite-mixed crystals.

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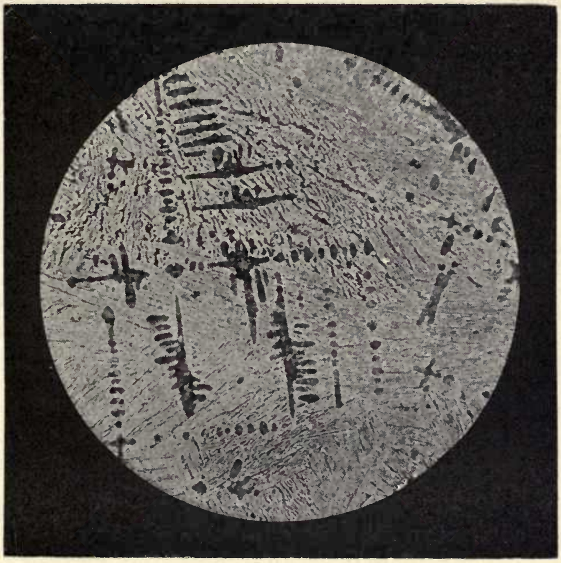
[1] Charpy and Grenet, "Sur l'equilibre des systemes fer-carbone." *Bulletin de la Societé d'Encouragement pour l'Industrie Nationale*, 1902, vol. 102, p. 398.



× 50.

FIG. 115.—The dark "pine-tree" shaped constituent consists of primary mixed crystals; the ground mass is the eutectic of mixed crystals and carbide.

× 750.

FIG. 116.—The same material as in Fig. 115 more highly magnified.

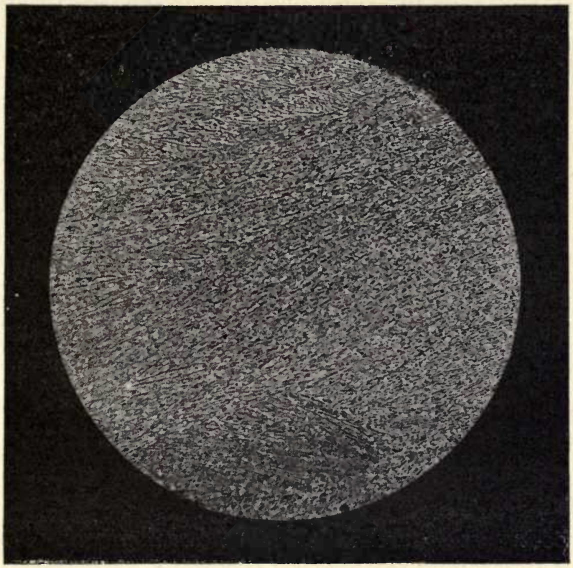
3. Alloys containing more than 4·3 per cent. of carbon consist of a network of graphite, the meshes of which are filled with the eutectic. As this network is due to graphite separating along the line *BD*, it can only be present under defined cooling conditions, since it rises through the liquid mass by virtue of its low specific gravity, and floats on the surface of the bath as "kish."

B. In undercooled systems:

1. Alloys containing from 0 up to 2 per cent. of carbon consist of homogeneous mixed crystals.
2. Alloys containing from 2 to 4·3 per cent. of carbon consist of saturated mixed crystals and increasing amounts of the eutectic cementite-mixed crystals. The former occur as crystal skeletons ("pine-tree" shaped) belonging to the crystal-system of iron. Figs. 115 and 116 show such dark crystals in a fine eutectic of cementite-martensite. It is seen from an examination of Fig. 116 that the "pine-tree" crystals, which, being a solid solution, should really exhibit a homogeneous structure, are built up of light and dark constituents. We shall see later, in considering the individual structural constituents, that by quenching most carefully, an incipient alteration of the solid solution cannot generally be prevented, and that a portion almost invariably decomposes with formation of troostite. At the eutectic percentage *B′* these mixed crystals completely disappear, and the material consists of eutectic only (Figs. 117 and 118).
3. Alloys containing more than 4·3 per cent of carbon exhibit independent crystals of cementite, separated along the line *B′D′*, surrounded by the eutectic (Figs. 119 and 120).

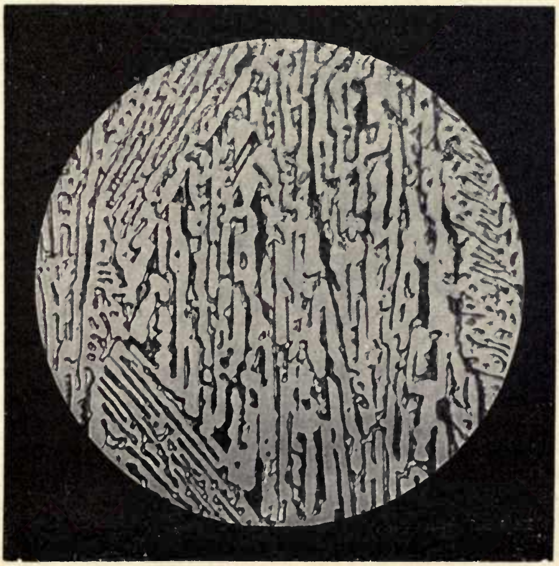
Changes in iron-carbon alloys (*containing more than* 2 *per cent. of carbon after freezing*).

When the temperature falls, after freezing is complete, the solubility of iron carbide and carbon in iron fall off according to the lines *E′S* and *aE* respectively. Correspondingly, cementite must separate with falling temperature, or carbon itself if the



× 50.

FIG. 117.—Eutectic pig-iron (corresponding to point B′ in Fig. 114) Mixed crystals (dark), cementite (bright).



× 750.

FIG. 118.—The same material as in Fig. 117 more highly magnified.

cooling is exceedingly slow. As at 690° the change from γ to α-iron takes place, the solubility becomes zero or very nearly zero, and at this temperature the solid solution martensite decomposes according to the equation :

$$\text{Martensite} = \text{ferrite} + \text{cementite (pearlite).}$$

a reaction accompanied by a notable development of heat.

According to Carpenter and Keeling's researches, an evolution of heat may be also observed at 800° C. in all the alloys. Supposing that this really corresponds to an internal change, which Osmond[1] doubts, the line VX (Fig. 114) can only indicate a change of one modification of cementite into another. Roozeboom designates these α-cementite and β-cementite. As exact experimental evidence of these points is wanting, however, these changes must only be considered as possible, not as established.

On cooling still further, a feeble development of heat also occurs at about 600° C., which, according to Roozeboom, is to be attributed to the iron. (Compare Osmond's view of this, footnote below.)

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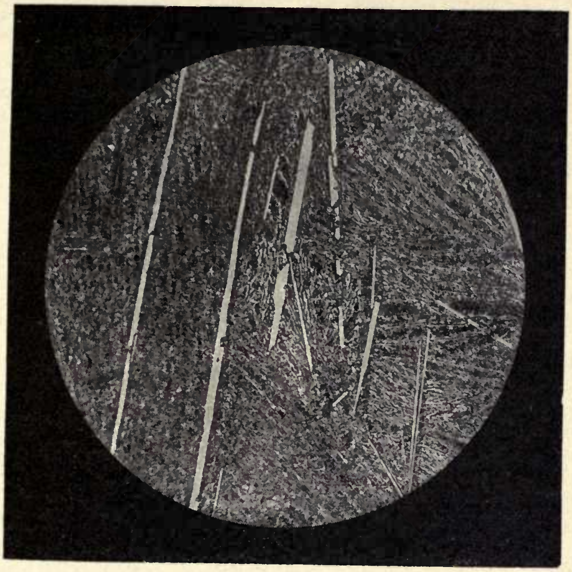
[1] In the discussion of Carpenter and Keeling's work, Osmond says : "In the alloys containing from 0·8 to 4·5 per cent. of carbon, the point Ar_3, which Messrs. Carpenter and Keeling have rediscovered, and which, although small, is nearly always present, might well be due to some accidental cause. Steels heated in air (and it would be the same in any other medium) are superficially decarburized, and surround themselves with a skin of variable carbon contents. If this is so, and it would be easily proved by micrographic analysis, this slight surface skin will possess its own distinct critical points, and if the recording apparatus is sufficiently delicate, the presence of an abnormal point Ar_3 in eutectic and hypereutectic steels becomes readily explicable." With respect to the point occurring about 600° C., found by Carpenter and Keeling, Osmond expresses himself, in the same place, as follows: "The carbon induces the appearance of the point Ar_1, *the recalescence;* whilst the metal either gives out heat, or maintains itself at constant temperature, the surrounding objects begin to cool, so that, once the period of recalescence is over, the metal, now in a relatively cool environment, begins to cool at an accelerated pace, which ultimately yields place to the normal rate of cooling. This might be the cause, in alloys containing sufficient carbon, of the point designated Ar_0, which I have frequently observed in my own curves, without, in view of the foregoing explanation, attaching any importance to it."



× 50.

FIG. 119.—Bright needles of cementite in a dark eutectic.

× 750.

FIG. 120.—Same as Fig. 119, more strongly magnified.

Changes, after solidification, in mixtures containing less than 2 per cent. of carbon.

When solidification of these alloys has become complete at temperatures indicated by the line *Aa*, the whole mass consists of homogeneous mixed crystals, martensite, containing from 0 up to 2 per cent. of carbon.

1. Mixed crystals containing 0·85 to 2 per cent. carbon.

At 1000° C. the mixed crystals can hold 2 per cent. of carbon in solid solution. As the temperature falls, the solubility diminishes until it amounts to 0·85 per cent. only at 700° C. During the cooling from 1000° C. to 700° C., therefore, all alloys containing more than 0·85 per cent. of carbon must deposit it as carbide (cementite). The temperatures at which this separation occurs are indicated by the line *ES*. Finally, at 700° C., the remaining 0·85 per cent. of carbon falls out as cementite, pearlite thus resulting from the martensite.

2. Mixed crystals containing 0 to 0·85 per cent. carbon.

All the changes which these alloys undergo stand in close relationship to the transformations of the iron itself.

Fig. 121 shows, on a larger scale, the corresponding portion of Fig. 114. Roozeboom's opinions of the meaning of this diagram are in perfect agreement with those of Roberts-Austen (see p. 166). Accordingly, we have in Fig. 114:

GO, the separation of β-iron from martensite.

MO, transformation of β-iron, separated at *GO*, into α-iron.

OS, separation of α-iron from martensite.

PS, formation of pearlite; that is decomposition of martensite into α-iron and cementite.

This applies to the case in which β-, as well as α-iron, can hold no carbon in solution. It is possible, and a work of C. Benedicks[1] makes it appear probable, that β-iron, at least, can retain a small quantity of carbon in solid solution. In that case, the transformations into β- and α-iron would proceed somewhat as depicted in Fig. 121.

By cooling along the line *GO*, a solid solution of β-iron in carbon would separate instead of carbonless β-iron. As in the

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[1] C. Benedicks, *Recherches physiques et physico-chimiques.*

freezing out of mixed crystals of two substances, the carbon content of these β-iron-carbon-mixed crystals is smaller than that of the γ-iron-mixed crystals out of which they form. Similarly, if the abscissa of o′ represents the saturation point of β-iron, the carbon contents of these β-mixed crystals are given by drawing a horizontal through the point *a*, cutting *GO′* in *b* when *bc* will represent the carbon contained by the mixed crystals which first begin to separate. The subsequent course of the freezing is absolutely identical with that of the alloys containing 2 per cent. of carbon.

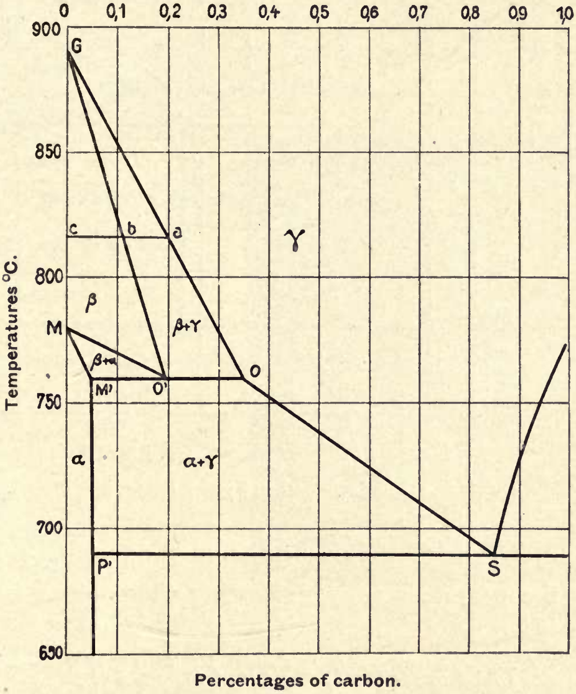


FIG. 121.

On the supposition that α-iron is able to retain 0·05 per cent. of carbon in solid solution, the separation of mixed crystals of α-iron with carbon would proceed in a similar manner.

The system containing iron-carbide, as mentioned above, must be regarded as under-cooled. Practical experience teaches that this under-cooling can be overcome by annealing for a long time. The microphotograph 145 on p. 199 shows a white iron containing traces only of silicon. After annealing for 50 hours in vacuo at 980° C., it presented the appearance shown in the photograph 146 on p. 199. The black particles of carbon (temper-carbon) are surrounded by light areas of ferrite; in these places the stable condition of equilibrium has been attained, whilst in the pearlite masses separating these areas from each other this is not so.

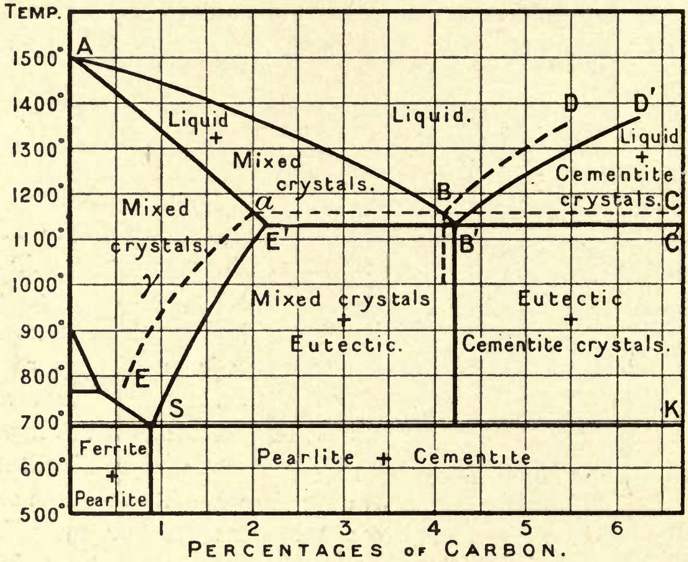


FIG. 122.—The Iron-Carbon System (Benedicks').

The Constituents of Iron-Carbon Alloys.

In the freezing diagram of iron-carbon alloys (Fig. 114, p. 170), the following structural constituents were distinguished:—

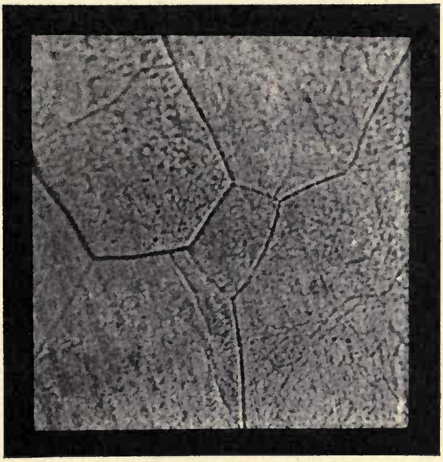
1. Carbon-free iron, ferrite.
2. Iron-carbide, Fe_3C, cementite, and its eutectic mixture with 1, pearlite.
3. Solid solution of carbon in iron, martensite.
4. Carbon in the form of graphite, or temper-carbon.

The properties of these different constituents will now be studied and described, so that they may be recognized metallographically.

Ferrite.

Ferrite is α-iron, chemically pure or, at any rate, free from carbon. By polishing in relief, or by joint polishing and etching. it is resolved into grains, the surfaces of which appear roughened after long treatment. Fig. 123 shows such an appearance at 500 diameters. By treating with tincture of iodine or picric acid, ferrite is similarly altered.

The effect of nitric acid is very characteristic. At first the grains are uniformly attacked, but according to the orientation of the small secondary crystals of which they are composed, at varying rates. Under the microscope it can be seen that some grains are in relief, others are depressed, so that the junction lines are sharply marked. The individual grains are, for the most part, bounded by lines more or less straight, which however, have no crystalline orientation. Their formation is explained by conceiving that during solidification centres of crystallization form, proceeding from which the crystal conglomerate grows until it encounters the mass of the next, forming in this way irregular polyhedra. It follows from this that the boundary lines of the ferrite grains bear no relation to the crystalline system of the iron; such a grain is therefore regarded as an allotrimorphic iron crystal, as its geometrical form does not correspond with its internal symmetry. On the other hand, there are idiomorphic crystals in which the external corresponds to the internal symmetry, such as, for example, is the case in the so-called "pine-tree" crystals of iron.



× 500.

FIG. 123.—Ferrite.
The individual grains are enclosed by an irregular polygonal boundary line. Each crystal grain is roughened by the treatment with picric acid.

After longer treatment with nitric acid, the different grains begin to take on a colour. The coloration is dependent upon the strength of the acid, and alters with the time. If a concentration of 2 c.cm. of concentrated nitric acid in 1000 c.cm. of water is employed, some of the grains are coloured yellow to brown, and others remain colourless. These tints cannot be removed by gentle rubbing with a very soft piece of leather. If the sample be treated with a stronger acid (about 2 c.cm. nitric acid in 100 c.cm. water), similar appearances to those of heat-tinting in the air can be observed. The individual grains are coloured successively yellow, brown, purple, and blue, although these films are not very stable, and can be wiped off. In explanation of these phenomena, Osmond[1] remarks that the attack of nitric acid takes place in two stages. First of all a thin film of oxide or of some other compound forms, the colour of which alters with its thickness. Simultaneously the nitric acid tends to dissolve this compound. If the solution proceeds just as quickly as the formation of the film, that particular grain remains colourless. In other cases, the film will run through the whole colour scale, and with a velocity dependent upon the difference between the speed of its formation and that of the smaller solubility of the oxide.

The internal structure of these individual ferrite grains is elucidated by a protracted attack of various reagents. The most suitable for this purpose, according to Heyn,[2] Osmond,[3] Stead,[4] and Andrews,[5] are cuprammonium chloride solution, dilute nitric acid, and a warm 20 per cent. sulphuric acid solution, followed by a bath of dilute nitric acid.

The investigations of Tschernoff,[6] Gautier,[7] Martens,[8] Fulton,[9]

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[1] Osmond, "Méthode générale pour l'analyse micrographique des aciers au carbone." *Contribution à l'étude des alliages*, 1901, p. 285. Paris: Chamerot et Renouard. German by L. Heurich. Published by W. Knapp, Halle a. S.

[2] Heyn, *Mitteilungen aus den k. techn. Versuchsanstulten*, 1898, s. 310, bis 331.

[3] Osmond, *Méthode générale* . . .

[4] Stead, *Journal of the Iron and Steel Institute*, 1898, I. p. 145.

[5] Andrews, *Engineering*, LX., 1895, p. 88.

[6] Tschernoff, *Proceedings Institution Mechanical Engineers*, January, 1880, p. 152.

[7] Gautier, *Bulletin de la Société Minéralogique*, vol. II. p. 210. 1879.

[8] Martens, *Stahl und Eisen*, February, 1887.

[9] Fulton, *Metallurgy of Steel*, p. 148.

but particularly the searching work of Osmond[1] and Cartaud,[2] have proved that the three modifications of iron crystallize in the regular system. The proof of this was obtained by the latter investigators by reducing ferric chloride in a current of hydrogen at temperatures corresponding to the different allotropic forms. The crystals obtained in this way were examined microscopically; stated briefly, Osmond's results were as follow.

Gamma-iron occurs in all combinations of the cube with the octahedron. Beta- and alpha-iron crystallize in cubes and are isomorphous; they can form mixed crystals with each other, as the arrest point Ar_2 indicates. This is not confined to a definite temperature, but to an interval of temperature, during which the β-crystals form mixed crystals at first with a little α-iron. This increases gradually until the whole mass consists of α-iron only. Similarly the other changes occurring at this arrest-point, *e.g.* of magnetic properties, are not sudden but gradual, as Le Chatelier has observed.

Gamma-iron is not isomorphous either with β-iron or with α-iron. The change of γ- into the β- modification takes place suddenly, in accordance with the fact that Ar_3 is not distributed over an interval, but occurs at a definite temperature.

A further difference between the various modifications of iron consists in their behaviour towards carbon. Benedicks is of opinion that a metallographic distinction between α- and β-iron in particular has been established, and that the latter has been proved capable of retaining up to 0·27 per cent. of carbon in solid solution. Roozeboom had previously expressed the same conjecture, but sufficient experimental support is wanting to allow one to regard this solid solution, which Benedicks designates ferronite, as a structural element.

Ferrite constitutes the chief constituent of all kinds of iron poor in carbon. As it can hold fairly large amounts of silicon, phosphorus, and manganese in solid solution, the very soft slagless ingot-irons of commerce consist of ferrite which may frequently contain such products of deoxidation. Bar iron, on the contrary, always contains slag inclusions, by which the iron

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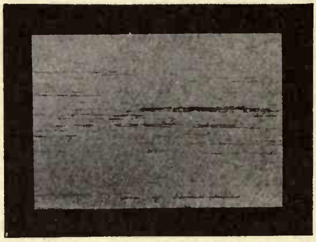
[1] Osmond, "On the Crystallography of Iron," *Annales des Mines* January, 1900. The *Metallographist*, III. pp. 181–275.

[2] Osmond and G. Cartaud, "On the Crystallography of Iron." *Annales des Mines*, August, 1900. The *Metallurgist*, IV. pp. 119, 236.

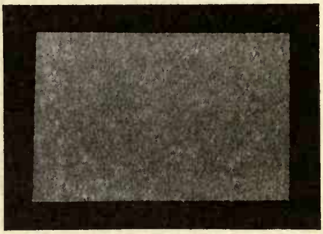
is traversed in the form of threads. At small magnifications, bar iron exhibits black streaks in the direction of rolling, whilst ingot iron is free from these, as appears from Figs. 124 and 125. Fig. 126 shows the ferrite of forged iron, resolved by etching into grains. Under high magnification, it can be seen that the slag is composed of several constituents (see Figs. 127, 128).



× 5.

FIG. 124.—Forged iron.

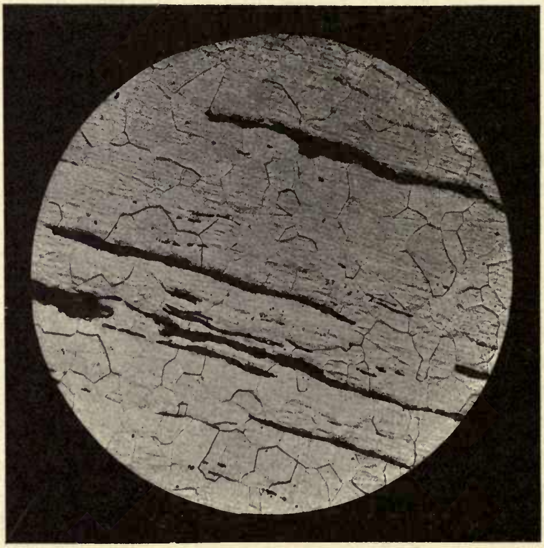
Section parallel to the direction of rolling. Dark slag inclusions surrounded by a mother mass of ferrite.



× 5.

FIG. 125.—Ingot iron.

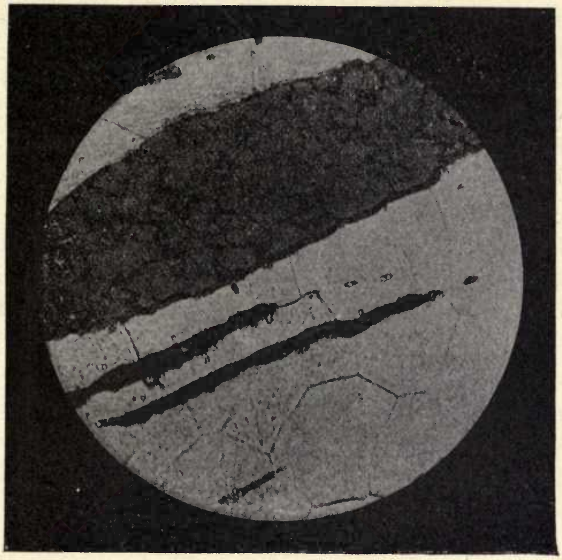
Section parallel to the direction of rolling, free from slag inclusions.



× 50.

FIG. 126.—Forged iron.

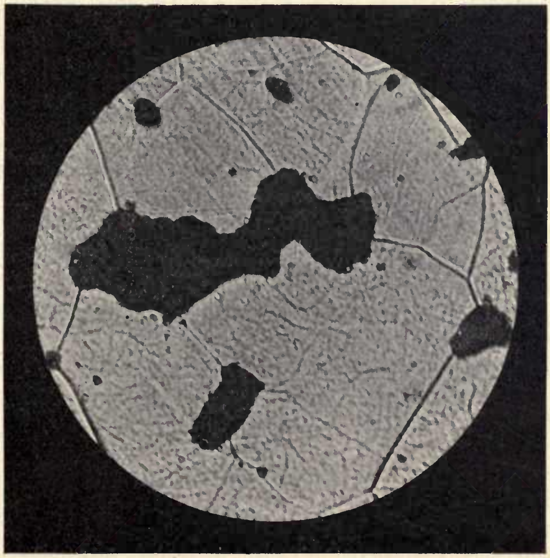
Same as Fig. 124. The ferrite is resolved into grains by etching with HNO_3.



× 500.

FIG. 127.—Forged iron.

Section in the direction of rolling. Shows the longitudinal sections of the slag fibres. Light and dark areas can be recognized in these, a proof of the fact that in slags, just as in alloys, decomposition of the solidifying mass takes place.



× 500.

FIG. 128.—Forged iron.

Section perpendicular to direction of rolling. Shows cross-sections of the slag fibres.

Cementite.

Cementite is an iron carbide of the formula Fe_3C. This was first proved in 1885 by the work of Abel and Deering,[1] which established the fact that after dissolving slowly cooled steels in dilute acids, a residue remained whose composition corresponded sufficiently closely to the formula Fe_3C. The experiments were repeated later by Müller,[2] Osmond and Werth,[3] Arnold and Read,[4] Benedicks,[5] Mylius, Förster and Schöne,[6] and Moissan,[7] and the conclusions of Abel and Deering were substantiated. In all these experiments carefully annealed and very slowly cooled samples of steel were employed, yet in the best examples it was found impossible to separate the total amount of the contained carbon in the form of carbide. According to Arnold and Read, the carbon obtained as carbide amounted to from 72 to 94·9 per cent. of the total amount present. In slowly annealed pig irons, the difference amounts to more than this, as appears from later experiments by Wüst. On the other hand, the composition of the separated carbide does not always correspond to the formula Fe_3C, representing 6·67 per cent. of carbon. According to Campbell and Kennedy's[8] experiments this amount fluctuates, in highly carbonized alloys, between 6·67 and 9·67 per cent. The latter figure corresponds to the formula Fe_2C. Benedicks also is of opinion that the existence of this carbide Fe_2C must be admitted as the result of his own researches. The variable carbon contents of the iron carbide separated by dilute acids would be unconvincingly explained

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[1] Abel and Deering, *Proc. of the Institute of Mechanical Engineers*, 1885, p. 30.

[2] Müller, "Grundzüge einer Theorie des Stahls." *Stahl und Eisen*, 1888, s. 291.

[3] Osmond and Werth, *Annales des Mines*, 1885. II.

[4] Arnold and Read, "The Chemical Relations of Carbon and Iron," *Journal of the Chemical Society*, 1894, vol. LXV. p. 788.

[5] C. Benedicks, *Recherches physiques et physico-chemiques des aciers au carbone.*

[6] Mylius, Förster, und Schöne, *Zeitschr. f. anorg. Chemie*, Bd. XIII. (1896), s. 38.

[7] Moissan, *Comptes rendus*, 122, p. 421.

[8] Campbell and Kennedy, "Probable existence of a new carbide of iron, Fe_2C." *Journal of the Iron and Steel Institute*, 1902, vol. II. *The Metallographist*, VI. p. 139.

by the supposition that a varying mixture of both carbides occurs in steel. On the other hand, the ease with which the carbide decomposes must be taken into consideration. As is well known, it is separated as free cementite by cooling highly heated steels, containing more than 0·9 per cent. of carbon, and mixed with ferrite in the form of pearlite by cooling further to Ar_1. Whereas the thicker cell walls of free cementite may easily withstand a feeble oxidizing attack, the fine lamellæ of the pearlite, which are often less than 0·001 mm. in thickness, present a very large surface to this attack. In this way a certain amount of the cementite will be decomposed with separation of carbon, and the residue thus becomes enriched by this element without its being necessary to assume the existence of Fe_2C.

As a micro-constituent cementite can always be recognized on account of its hardness; according to Müller[1] this amounts to 6 on Moh's scale, and is therefore greater than that of a hardened steel needle.

As is evident from its genesis, cementite can occur independently as such, as well as in the form of a structural constituent of the eutectic ferrite-cementite (pearlite). Both kinds of cementite, as one would expect, are perfectly identical chemically, as is undoubtedly proved by the analysis of Ledebur.[2] Although, in separating iron carbide by dilute acids or by Weyl's[3] method, two constituents can frequently be distinguished in the residue, one lustrous and the other dull, the existence of two carbides is not to be concluded from this, because the different varieties, the compact and the finely lamellated, may easily produce such a difference in appearance.

In developing the structure cementite, on account of its hardness and resistance, remains in relief, colourless and glistening. It is only by etching with sodium picrate[4] that it is coloured brown to brownish-black, whilst the remaining constituents are unattacked. This method is consequently very valuable to determine cementite with certainty in doubtful

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[1] Müller, *Stahl and Eisen*, VIII., 1898, s. 292.

[2] Ledebur, *Ibid.*, Bd. VIII. s. 742; Bd. XI. s. 294.

[3] Weyl, *Journal Chem. Soc.*, August, 1894, Bd. LXV. p. 788.

[4] See p. 136.

cases. Le Chatelier[1] has called attention to a peculiar property; if the thickness of the cementite lamellæ is less than 0·001 mm. sodium picrate has no effect on them. If, therefore, the pearlite is very fine, it remains uncoloured, a phenomenon for which a satisfactory explanation is not yet forthcoming.


× 1500.

FIG. 129.—Forged iron containing 0·024 per cent. of carbon. Lamellæ of cementite surrounded by ferrite.

Figure 129 shows a cementite plate in an iron containing rather more than 0·02 per cent. of carbon; the surrounding matrix is ferrite. This occurrence of free cementite is a striking proof of the fact that *a*-iron, ferrite, cannot hold carbon in solid solution.

Pearlite.

Being a eutectic, pearlite is an intimate mechanical mixture of cementite and ferrite; as such it always appears, if the cooling of the sample under investigation proceeds slowly enough to permit the spacial separation of the two constituents. Figs. 130, 131, and 132 clearly show this characteristic appearance of the so-called lamellar pearlite. If the cooling is unduly prolonged, or if a sample exhibiting lamellar pearlite is annealed for a longer time below 700° C., the spacial separation of the cementite and ferrite is completed in such a way that the cementite forms independent globules set in


× 750.

FIG. 130.—Hypo-eutectic steel. Lamellar pearlite + ferrite.

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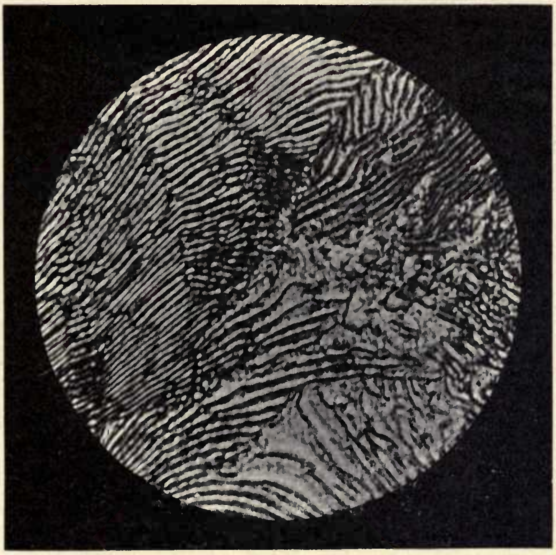
[1] Le Chatelier, "Examen métallographique des fers, aciers et fontes." *Rapport de la Section de métallurgie du congrès internationale de Liège*, 1905, Tome I. p. 269.

a ground mass of ferrite. To this appearance the name granular pearlite has frequently been given. Fig. 133 shows that phenomenon in pig-iron which was annealed for a long time below 700° C. This alteration of the pearlite, due to controlled annealing, explains the phenomenon long considered as mysterious, of structurally free cementite along with structurally free ferrite, which had been noted by various investigators.[1] The simultaneous occurrence of free ferrite and free cementite had been regarded as out of the question, because the formation of the eutectic pearlite must take place first in hypo- as well as in hyper-eutectic alloys. Sauveur, in particular, was emphatic on the point that ferrite-pearlite and pearlite-cementite, but never ferrite-cementite, could be observed. The point was overlooked, however, that at the moment of the formation of pearlite, the ferrite and cementite are spacially separated; should the sample be subjected to a temperature below that of the eutectic formation, or to other operations, such as annealing or mechanical work, it is possible for the different plates of cementite to



× 750.
FIG. 131.—Eutectic steel. Lamellar pearlite.

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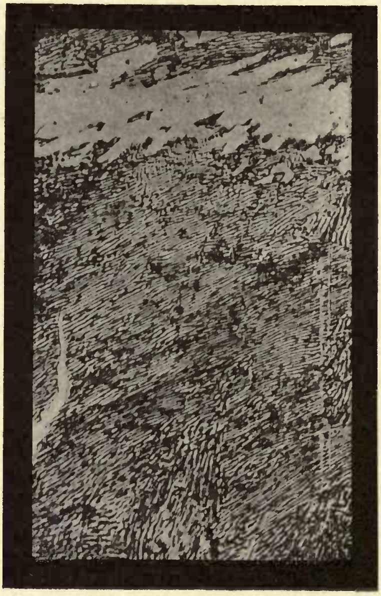
[1] Lange, *Metallographist*, vol. VI. p. 9.

unite in one larger complex. Osmond avers that the independent existence of cementite with ferrite is the last stage of equilibrium of the reaction martensite → pearlite, which will be referred to below, and he called this the stage of structural equilibrium.

To the unaided eye, pearlite has the lustre of mother of pearl on its surface, as its name implies. Sorby[1] had designated it the "pearly constituent." The same causes which produce the characteristic play of colours in mother of pearl operate in this case also. In both cases, tiny juxtaposed lamellæ act like a grating, and the interference phenomena thus created produce the particular light effect studied and explained by Fresnel.



× 500.

FIG. 132.—Hyper-eutectic steel.
Free cementite surrounded by lamellar pearlite.

Now, according to the rate of cooling, the separate cementite lamellæ of the pearlite become separated more or less; the

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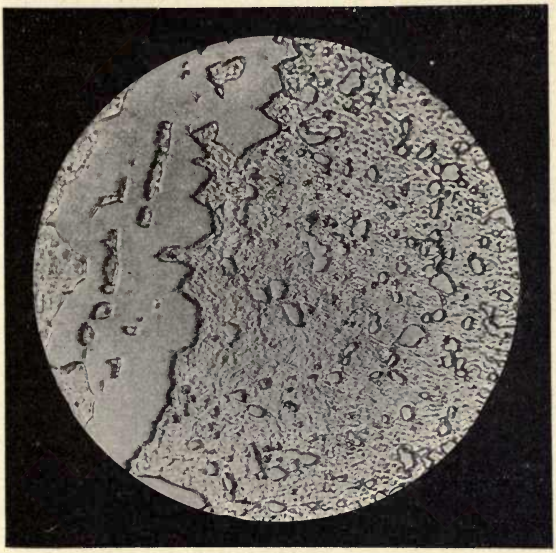
[1] Sorby, "On Microscopic Photographs of Various Kinds of Iron and Steel." *Brit. Ass. Report*, 1864, II. p. 189.

quicker the cooling the more closely they come together, until finally the most powerful microscope is unable to render the individual plates recognizable. Simultaneously the property of being coloured by the polish attack, or by tincture of iodine becomes accentuated in the pearlite areas. Osmond has given the name



× 750.

FIG. 133.—White pig-iron.
Massive cementite and granular pearlite (mixture of cementite globules in a matrix of ferrite.)

Sorbite

to this new constituent, in honour of the father of metallography. Osmond[1] describes sorbite as that constituent in which chemical equilibrium has not been attained. That is to say, if the solid solution of carbon in iron changes at the eutectic temperature into pearlite (spacially separated cementite and ferrite), chemical equilibrium is reached as soon as the separation is complete, but, if, from any cause, this change does not proceed quantitatively, and a portion of the cementite still remains in solution, the

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[1] Osmond, *Revue de métallurgie*, 1904.

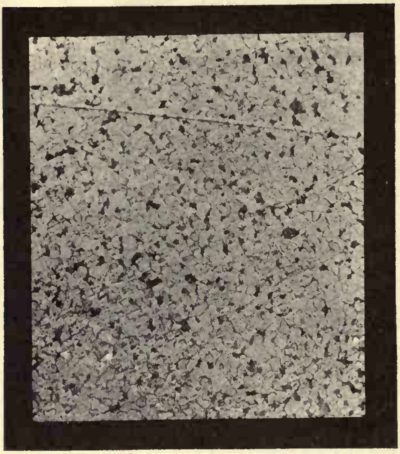
chemical equilibrium is imperfect and sorbite appears. The process therefore runs as follows :—

Sorbite : incomplete chemical, incomplete structural equilibrium.

Lamellar pearlite : perfect chemical, incomplete structural equilibrium.

Granular pearlite—independent cementite with independent ferrite : perfect chemical and structural equilibrium.

Pearlite and sorbite (sorbitic-pearlite), together with ferrite, constitute the whole mass of structural steels. After a short etching these exhibit, at low magnifications, a network of ferrite grains, separated by a number of pearlite or sorbite areas proportional to the carbon contents of the material. Figs. 134 and 135, at 50 and 1500 linear diameters respectively, show a specimen of ingot iron containing 0·08 per cent. of carbon. In worked material the pearlite-sorbite areas are always indefinitely scattered, as in Fig. 134. In cast alloys, but particularly in cemented material, the pearlite is peculiarly arranged, as appears from Fig. 136. On account of the crystalline character of the ferrite, the orientation of the cleavage faces determines the form in which the pearlite separates. Fig. 137 shows almost pure sorbite. The more highly carbonized alloys, up to a content of about 1·8 per cent. of carbon, find their chief employment as tool steels. Fig. 138 represents such a steel, with 1·6 per cent. of carbon, in the annealed state.



× 50.

FIG. 134.—Ingot iron 0·08 per cent. of C. Etched for two minutes in picric acid. The light ground-mass is ferrite, the dark areas pearlite (and sorbite.)

Iron alloys containing more than about 1·8 per cent. of carbon are called pig-irons. Those whose total carbon is present in the combined condition are called white-irons. Fig. 139 at 50 diameters, and Fig. 140 at 500 show the structure of one

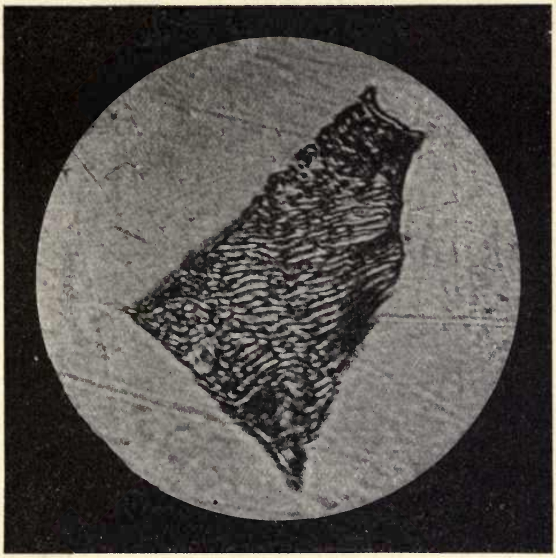
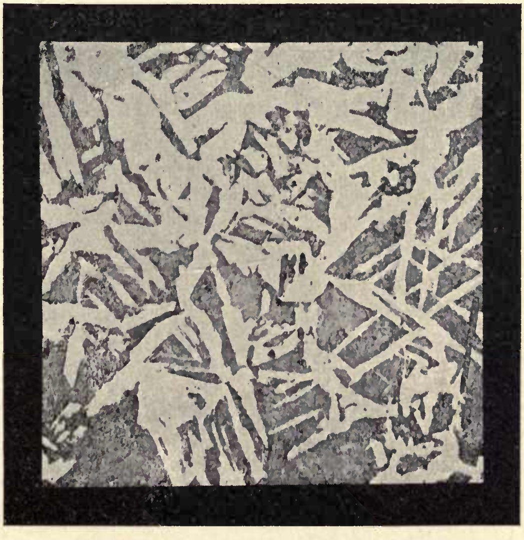


FIG. 135.—Same material as Fig. 134.
A single island of pearlite (× 1500) surrounded by ferrite.



×100.

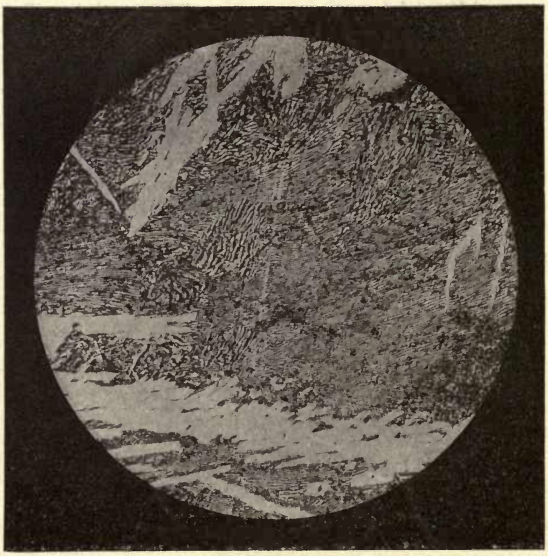
FIG. 136.—Cemented steel.

Sorbite, arranged so as to make the crystalline orientation of the ferrite apparent. The characteristic triangular structure of the regular system can be clearly distinguished. Besides ferrite (white) and pearite (dark) there are several small slag inclusions.

×100.

FIG. 137.—Cemented steel.

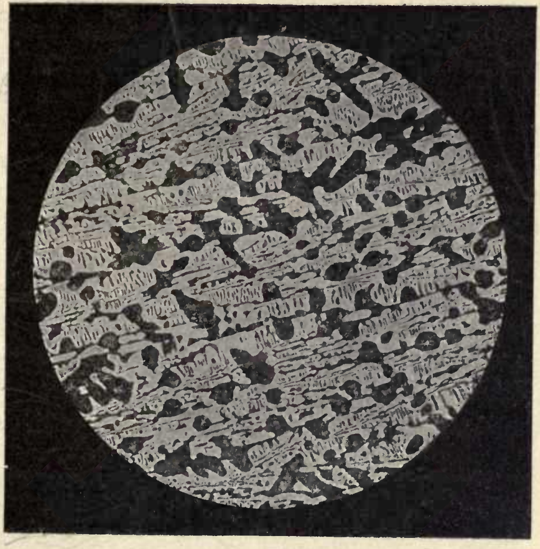
Sorbite. Near the top, bright ferrite. The same material as that of Fig. 136. The photograph is taken near the edge, where the material is richer in carbon. A few slag inclusions.



×400.

FIG. 138.—Tool steel (annealed).

Bright cementite, embedded in pearlite.



× 50.

FIG. 139.—White pig-iron.
Pearlite dark, cementite bright.

× 500.

FIG. 140.—White pig-iron.
Bright cementite in ground mass of pearlite.

of these. It is seen from Fig. 139 that the dark pearlite areas are arranged in rows, and that the individual rows frequently run perpendicularly to each other. Moreover, the white cementite of Fig. 139 is broken up by numerous tiny islands. This peculiar structural formation finds its explanation in the way in which pig-iron solidifies (on this point, see p. 173).

If the passage of molten pig-iron into the solid condition at 1130° C. proceeds very slowly, a large proportion of the carbon separates out as—

Graphite

and the material is then described as grey pig-iron. The graphite forms thin plates in the interior of the molten mass; on a section it therefore appears mostly in the form of elongated black threads, as shown in Figs. 141 to 143. If a part only of the carbon separates out as graphite, the material is called mottled iron. The graphitic portions then appear on a fractured surface in the form of small black areas which give a spotted

× 500.

FIG. 141.—Mottled pig-iron.

Boundary between white and grey. White below; bright cementite cut up by small islands of pearlite. Grey above; threads of graphite, surrounded by lamellar pearlite.

(mottled) appearance to the section. The passage from white to grey iron is reproduced in Fig. 141 at 500 magnifications.

× 50.

FIG. 142.—Grey pig-iron.
Black threads of graphite, bright threads of cementite, the remainder pearlite.

× 500.

FIG. 143.—Grey pig-iron.
Same material as in Fig. 142. Shows the lamellar structure of the pearlite.

In many cases, notably when pig-iron is carefully annealed below 700° C., or when the silicon contents are considerable, large white enclosed areas of free ferrite occur. It can be distinguished from cementite that may be present at the same time by applying the scratching test of hardness. This is simply done by lightly scratching the place to be tested with a hardened steel needle. Cementite then remains unattacked, whilst ferrite and pearlite are deeply scratched. Fig. 144 shows a grey iron which has been tested in this manner.

× 500.

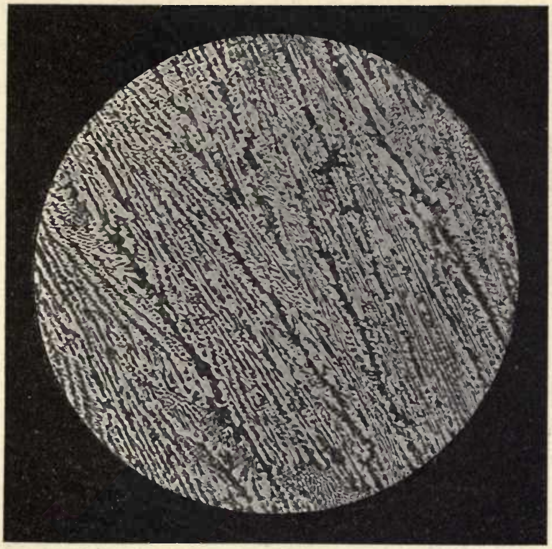
FIG. 144.—Grey pig-iron.

Graphite (black threads), cementite (bright areas), pearlite lamellated ground mass. The surface scratched by a needle, the cementite untouched.

If the freezing of the pig-iron takes place quickly enough to yield white iron, *i.e.* iron free from graphite, the cementite can be decomposed by subsequent annealing in the vicinity of 1000° C., with formation of—

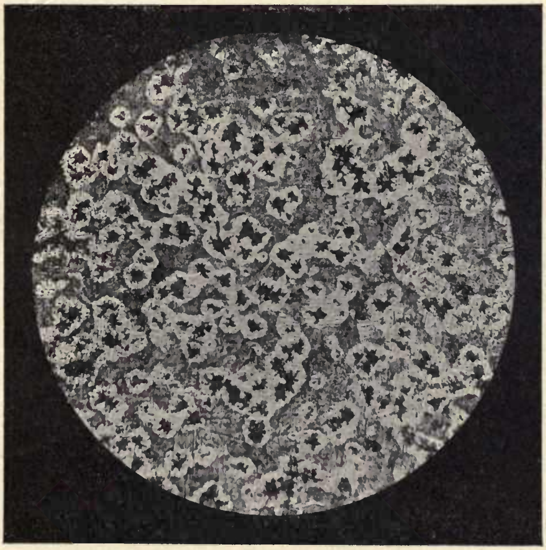
Temper-Carbon.

The phenomenon of the formation of temper-carbon is represented in Figs. 145, 146, and 147. Fig. 145 shows a quickly cooled white iron, which exhibits bright cementite in



× 500.

FIG. 145.—White pig-iron.
Cementite (bright), sorbite (dark).



× 50.

FIG. 146.—Pig-iron containing temper-carbon.
Same material as in Fig. 145, annealed at 900° C. Temper-carbon, black nodules. Ferrite, white areas round the temper-carbon. Pearlite, grey ground mass.

× 500.

FIG. 147.—Same material as in Fig. 146.
Temper-carbon, ferrite, pearlite.

× 500.

FIG. 148.—Malleable cast-iron containing silicon.
Ground mass of ferrite, with residues of temper-carbon.

a relatively fine state of division distributed through a dark ground mass consisting of imperfectly formed pearlite (sorbite). This material, after annealing for fifty hours *in vacuo* at 980° C., showed, after being cooled slowly, the structure of Fig. 146, more highly magnified in Fig. 147. Black irregular patches are surrounded by white areas, and between the latter grey borders of pearlite are found. The previously glass-hard material may now be easily filed, in accordance with its composition (temper-carbon, ferrite, and pearlite). If the temper-carbon produced in this way is removed by some means, *e.g.* by oxidation, an iron remains consisting of ferrite and pearlite only, and is in consequence malleable.

This change of white, brittle, unweldable cast-iron into soft material is called tempering, and the end product malleable cast-iron. The structure of such a piece is reproduced in Fig. 148; this shows only individual grains of ferrite of different shades of colour and a few remnants of the temper-carbon.

Martensite.

Above the line GOSE the carbon of the alloys is in the condition of a solid solution. If it is kept in this condition by quenching in ice-cold water, the transformation corresponding to Ar_1 is suppressed, and a single constituent appears called martensite. On account of the uniform hardness of the mass, the structure of martensite is resolved with difficulty by polishing in relief. The safest method of exposing the structure consists in etching with an alcoholic solution of nitric acid (see p. 135). It is then found to be built up of a system of needles running parallel to the sides of an isosceles triangle, thus pointing to the crystalline structure of the regular system.

Martensite, therefore, does not represent one single constituent of definite composition, but the term includes the whole series of solid solutions of carbon in iron. The other properties of martensite, particularly the hardness, vary correspondingly between that of pure iron and that of the saturated solution which, according to the proposal of Howe,[1] is frequently called "hardenite." Fig. 149 shows the occurrence of martensite.

[1] Howe, "Iron, Steel, and other Alloys."

As martensite, according to the foregoing, is to be regarded as a solid solution of iron carbide in γ-iron, the properties of such solid solutions should be reproduced in martensite. A

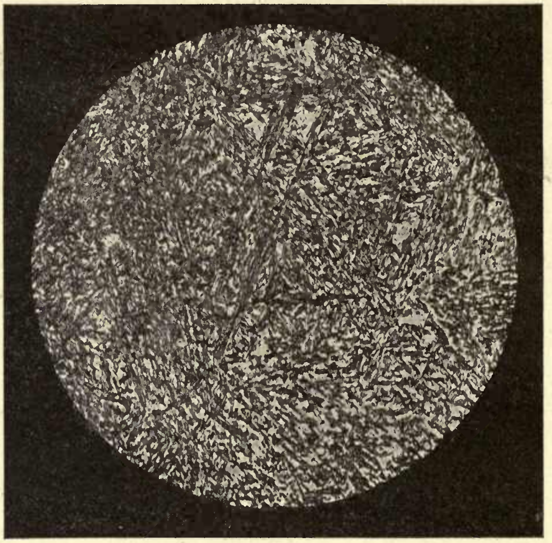


FIG. 149.—Quenched tool steel. Martensite.

FIG. 150.—Upper part—grey pig-iron. Lower part—pure ingot-iron with a little pearlite.

prominent property of solutions consists in the fact that the dissolved material behaves like a gas, and endeavours to assume the greatest possible volume. The phenomenon of diffusion is a consequence of this, according to which an equalization of composition takes place throughout the whole solution, because the dissolved substance moves from the concentrated to the more dilute parts. That the solid solution of iron carbide in iron also possesses this tendency to diffusion is shown by the following instructive experiment, illustrated by Figs. 150 and 151. If a sample of grey iron is brought into intimate contact with pure carbonless iron, say by wedging, and the whole heated to a temperature exceeding 710° C., the carbon gradually moves from the grey iron into the pure iron. On cooling down again, the pure iron is therefore found to be richer in pearlite, as a comparison of Figs. 150 and 151 shows at once.

FIG. 151.—Same material as in Fig. 150 after annealing. The carbon has passed from the grey into the pure iron, so that the latter has become richer in pearlite.

If a sample of steel is quenched during the critical point Ar_1, or if at the moment of quenching there yet remains undissolved cementite in the sample, a new constituent appears, which Osmond calls—

Troostite,

in honour of the meritorious French investigator, Troost. In his first publications, Osmond expressed himself with the greatest reserve concerning this constituent. It appears, however, from later experiments by Le Chatelier,[1] that the formation

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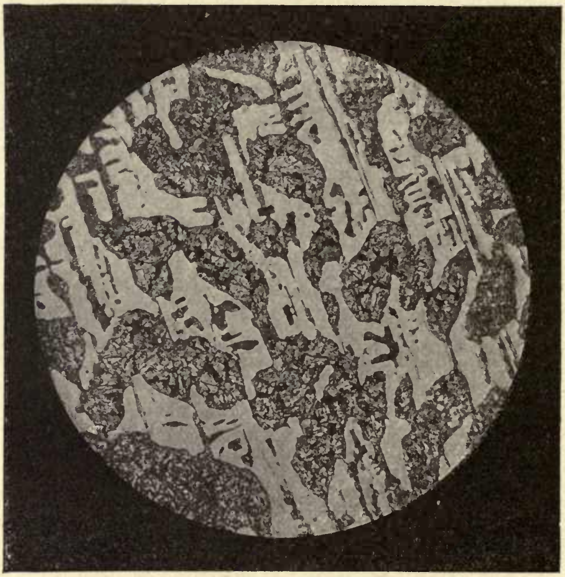
[1] Le Chatelier, "Observations sur le mémoire le M. B. Roozeboom." *Contributions à l'étude des alliages*, p. 379.

of troostite takes place as follows: At the end of the Ac_1 point, cementite dissolves, ultimately yielding martensite, but this phenomenon occurs in two phases, which can be easily followed by observing the expansion during the heating. As soon as the point Ac_1 is reached the alloy suddenly contracts, whereupon an equal expansion, amounting to about 0·1 per cent., immediately follows. Now, if the sample is quenched at the beginning of the contraction, the whole mass still consists of pearlite. (Le Chatelier employed for this experiment a eutectic steel containing 0·9 per cent. of carbon.) If quenched at the instant of greatest contraction, the sample consists only of troostite, with a little pearlite and martensite. Pure martensite appeared as soon as the sample had assumed its original volume.



× 50.

FIG. 152.—White pig-iron, quenched.
Large white areas—cementite. Black patches—troostite. Ground mass—austenite-martensite.

Under the microscope troostite appears in the form of hard nodules, which are coloured brown to bluish-grey by picric acid, iodine, etc. Figs. 152, 153, and 154 show that it occurs very frequently in the immediate vicinity of the cementite.

× 500.

FIG. 153.—Same material as Fig. 152.

Bright white band across the upper part of the figure—cementite. Black areas—troostite. Grey intersecting needles—martensite. Between the latter, bright austenite.

FIG. 154.—Troostite—black. Martensite—grey needles. Austenite—white.

Opinions on the nature of troostite varied very much up to a short time ago. Nevertheless the hypothesis of Benedicks appears to gain more and more in probability as the result of later experiments. Benedicks supposes that troostite consists of a colloidal solution of cementite in iron. Thus if in troostite the cementite has already fallen out of solution, it would exist in such a fine state of division as to be unrecognizable as such under the microscope. Benedicks suggests the following characteristic means of distinguishing troosite from sorbite; if in a specimen there appears under the microscope an unresolvable constituent easily coloured by acids, this must be described as sorbite if the remainder of the mass consists of pearlite, and on the other hand, troosite if martensite or austenite occur in its immediate vicinity.

Austenite.

If an iron-carbon alloy of high carbon contents (more than 1·10 per cent.) is quenched in ice-cold water, a new constituent appears with the martensite, called austenite. This is rather softer than martensite, and is, in general, coloured differently. Dilute hydrochloric acid colours martensite light brown, whilst austenite remains uncoloured. Picric acid colours sometimes one and sometimes the other constituent, so that a certain distinction between them cannot be made by its means. In Figs. 153 and 154, for instance, the martensite is dark, the austenite bright, whereas in Fig. 155, which shows the structure of a tool steel containing 1·5 per cent. of carbon quenched at 1000° C., the reverse is the case. Le Chatelier[1] has pointed out this difficulty; nevertheless martensite can generally be recognized by its form, as it occurs in sharp needles, whereas austenite is an almost structureless mass.

If a specimen containing austenite is dipped in liquid air, the austenite increases in volume so that it appears in relief on a polished surface.

A retrospective glance over the different structural constituents, ferrite, cementite, troostite, sorbite, martensite, and austenite, makes it appear remarkable that only four of them, viz. ferrite, cementite, martensite, and graphite, appear in the

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[2] H. Le Chatelier, "L'austénite." *Revue de métallurgie*, 1904.

freezing-point diagram of the iron-carbon alloys, the remainder finding no place in it. Now, troostite and sorbite are extraordinarily frequently occurring constitutents in practice. The

FIG. 155.—Martensite—bright. Austenite—dark.

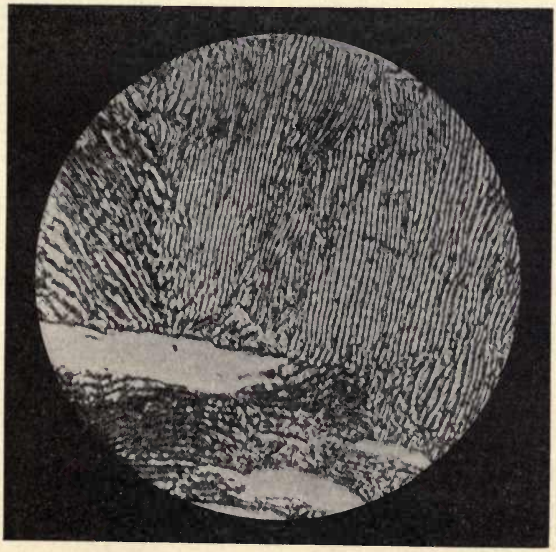

FIG. 156.—Lamellar pearlite and free cementite (bright).

explanation of these apparent anomalies is to be found in the fact that the freezing-point diagram is constructed from the standpoint of the phase rule, and, consequently, that the reaction Martensite — Cementite — Pearlite, represented in the diagram, is supposed to proceed to completion. This primary stipulation is extremely difficult to fulfil in most cases, and is indeed frequently impossible, so that the definite condition of equilibrium may only be attained first of all at about 1000° C., when the system consists of graphite and ferrite only. The appearance of pearlite presents another case in point. Fig. 156 shows beautifully developed lamellar pearlite, and Fig. 157 structurally free ferrite with cementite; these forms can only be obtained by careful annealing, followed by slow cooling. The various kinds of iron occurring in commerce have for the most part undergone a different treatment. All the forged materials have been cooled rapidly in comparison with the examples selected above, in consequence of which the internal transformations do not proceed quickly enough, and thus intermediate products appear, and sorbite in particular. In the transformation—

FIG. 157.—Structurally free cementite with ferrite.

Martensite → Cementite + Pearlite,

a continuous series of transformation products can be imagined with martensite as the initial member, and granular pearlite as the terminal member of the series. Hence the series would be constituted thus—

Martensite → Troostite → Sorbite → lamellar Pearlite
→ granular Pearlite,

although the individual stages are not sharply marked off from one another, but on the contrary merge into one another like the colours in the spectrum of an incandescent solid body. And just as an orange can be distinguished as a colour between red and yellow, the series of transformation products of martensite can be still further differentiated, as has been done already by Kourbatoff,[1] who identifies troosto-sorbitic constituents.

With respect to austenite, the opinions of different authorities are also conflicting.

Howe[2] calls the solid solution of carbon in iron austenite, and therefore exactly that which Osmond designates martensite. According to Howe's view, martensite is an intermediate product of the reaction—

Solid solution → ferrite + cementite.

The separate stages of this reaction would accordingly be—

Austenite → Martensite → Troostite → Sorbite → lamellar Pearlite → gran. Pearlite.

E. Heyn[3] adopts a different standpoint, and his opinion must be dealt with more closely at this point, because he bases it on several interesting observations, which in part are unique. Osmond's observation that steel of high carbon contents, after heating to a high temperature and plunging in ice-cold water, does not exhibit a homogeneous structure, has also been made in the case of low carbon steels by Heyn, whilst with a content of 0·9 per cent. of carbon the structure is uniform, consisting of extraordinarily fine needles. Heyn explains this phenomenon as follows: Let *MP* in Fig. 158 be the line of separation of ferrite, *PS* that of the separation of massive cementite, and *pp* the eutectic pearlite line. Above *MPS* the whole mass consists of a solid solution of carbon in iron. When, on cooling, the line *PM* or *PS*

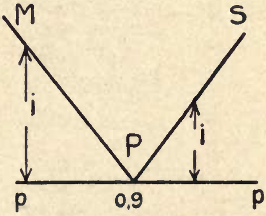

FIG. 158.

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[1] Kourbatoff, *Revue de métallurgie* (1905).

[2] H. M. Howe, "Iron, Steel, and other Alloys," p. 179. Sauveur and Whiting, Boston, Mass., U.S.A., 1903.

[3] E. Heyn, "Labile und metastabile Gleichgewichte in Eisen-Kohlenstofflegierungen." *Zeitschrift für Electrochemie*, 1904, s. 491.

is reached, ferrite or cementite begins to separate, and the separation continues down to the temperature of the line *pp*. Now the more quickly the interval *i* can be traversed, the more completely will the separation of ferrite and cementite be suppressed. At the point *P* this time is manifestly zero, and no separation can take place here, a fact in accord with actual practice. The more the composition of the steel differs from *P*, the greater the interval *i*, and the longer the sample remains at a temperature favourable to a separation. To the right of *P* two products form, one *c*, which approximates to the composition of cementite (austentite), the other *m*, corresponding to martensite with *P* per cent. of carbon. Similarly, separation products *f* and *m* form to the left of *P*, one ferrite-like and the other martensite. As the crystals *f*, in spite of their similar genesis to that of austenite, have received no special name, Heyn proposes to dispense with the name austenite, and to include the mixed crystals under the name martensite.

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THE END

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