(13) 2.00 per cent austenite + graphite = ferrite + cementite, or

(13) 2.00 per cent austenite + graphite = pearlite + cementite.

173. REGION IX, *SP'fh'*, PEARLITE AND CEMENTITE. —GRAPHITE also is habitually present through lag, though theoretically absent. The pearlite and cementite result from reaction (9) which occurs in crossing and leaving region VIII. The graphite is that which formed in freezing, and failed to be converted into cementite by reaction (10) on crossing *EB'R*.

Theoretically no reaction occurs in cooling through this region.

Our theories as to this region still lack proof: they must therefore be accepted very cautiously.

174. SUMMARY. — First there are two very important regions, the austenite region above *GSER*, and the ferrite and cementite or pearlite region below *PSP'*.

Next there are two transition regions, the upper, including the selective freezing regions II and III and the lower including the selective transformation regions V and VIII.

Beyond this the austenite region may be divided into two parts, region VI, the non-graphitiferous, and region VII, the graphitiferous. The graphite of region VII through lag habitually persists in cooling and is present in regions VIII and IX except in their left-hand parts, to the left of the line *eaEd*.

The several reactions which have been given in the preceding sections, 165-173 inclusive, are here summed up in Table 8.

Having thus studied as it were the geography of the iron-carbon compounds in a general way, let us pass on to consider certain features in more detail, particularly with the aim of finding the correspondence between the transformations in the freezing and cooling of the iron-carbon compounds, and the transformations in the freezing of other alloys, as set forth in Chapters II to V inclusive.

175. THE FREEZING-POINT CURVE, *ABC, aBc;* ITS GENERAL FEATURES. — The left-hand part *AB, aB* is evidently of the family of the freezing-point curve of the bismuth-tin alloys, of the limited solubility type, Figs. 33 and 49, pp. 75 and 136, eutectiferous in the middle but not at its ends. The right-hand side of the diagram here given stops short at about 5.70 per cent of carbon; if

TABLE 8. — *Tabular Statement of Reactions in the Freezing and Transformation of the Iron-carbon Compounds.*

| | THE REACTION | THE REACTION IS ONE, OR IS DUE TO LAG | CLASS TO WHICH THE REACTION APPLIES | REGION TO WHICH THE REACTION APPLIES * |
|---|---|---|---|---|
| **Freezing** | (1) molten solution = solid austenite | Theoretical | hypo-eutectic | II |
| | (2) molten solution = solid 2% austenite + molten eutectic | Theoretical | hypo-eutectic | II |
| | (3) molten eutectic = solid eutectic = 2% austenite + graphite | Theoretical | hypo- and hyper-eutectic | (II-VII) * |
| | (4) [= (2) + (3)] molten solution = 2% austenite + graphite | Theoretical | hypo- and hyper-eutectic | (III-VII) |
| | (5) molten solution = supersaturated austenite + graphite, or | Lag | hypo- and hyper-eutectic | II, (II-VII) |
| | (5) molten solution = (2+)% austenite + graphite | Lag | | III, (III-VII) |
| | (6) molten solution = molten eutectic + graphite | Theoretical | hyper-eutectic | " III |
| **Transformation** | (7) austenite = hardenite + ferrite, or | Theoretical Ar₃ | **hypo-eutectoid** | V |
| | (7) austenite = 0.9% austenite + ferrite | Theoretical Ar₃ | hypo-eutectoid | V |
| | (8) hardenite = pearlite = ferrite + cementite, or | Theoretical Ar₁ | hypo- and hyper-eutectoid | (V-VI) |
| | (8) 0.9% austenite = pearlite = ferrite + cementite | | | (VIII-IX) |
| | (8) [= (7) + (8)] austenite = ferrite + cementite | Theoretical Ar₃₋₂₋₁ | hypo-and hyper-eutectoid | V, (V-VI) |
| | (10) Gr + 3Fe = Fe₃C, or | Theoretical Ar₁ | hyper-eutectoid. | VIII, (VIII-IX) |
| | (10) graphite + austenite = cementite | Theoretical Ar₃₋₂₋₁ | hyper-eutectoid. | " |
| | (11) 2% austenite = hardenite + cementite, or | Theoretical | hyper-eutectoid. | V'-II |
| | (11) 2% austenite = 0.9% austenite + cementite | Theoretical | hyper-eutectoid. | VIII, (VIII-IX) |
| | (12) [= (11) + (8)] 2% austenite = ferrite + cementite | Theoretical Ar₃ | 2% carbon or more | (VII-VIII) |
| | (13) [= (10) + (11) + (8)] 2% austenite + graphite = ferrite + cementite, or | Theoretical Ar₁ | 2% carbon or more | (VIII-VIII) |
| | (13) 2% austenite + graphite = pearlite + cementite | Theoretical Ar₃₋₂₋₁ | 2% carbon or more | VIII, (VIII-IX) |
| | (14) molten x% solution = x% austenite | Lag | — | — |

* By Region II-VII, III-VII, *etc.*, is meant the boundary between regions II and VII, III and VII, *etc.*

completed the diagram would of course run from carbon 0, iron 100, on the left, to iron 0, carbon 100, on the right. As to the prolongation of this freezing-point curve to the right beyond carbon 5.50 per cent we have little information; our attention thus is confined to what is really but a fragment of the whole freezing-point curve.

The known part of the right side of this diagram is apparently not of the limited solubility but of the complete insolubility type, which was assumed for simplicity for the salt-water and lead-tin cases (§§ 21, 48, pp. 26 and 62). Thus taking the freezing-point curve *ABC, aBc* as a whole, its two sides are of different types, the left being of the limited solubility, bismuth-tin type, while the right is of the complete insolubility, salt-water and lead-tin type.

*B* is evidently the eutectic, corresponding to 4.30 per cent of carbon, and 95.70 per cent of iron. *AB* is the upper freezing-point curve when iron is the excess-metal, *i. e.,* when carbon is below 4.30 per cent and iron above 95.70 per cent, austenite (the solid solution of carbon in iron) beginning to freeze out when the temperature falls to any point on this line. *BC* is the upper freezing-point curve when carbon is the excess-substance, *i. e.,* when carbon is above 4.30 per cent and iron below 95.70 per cent, carbon in the form of graphite beginning to freeze out when the temperature falls to any point on this line.

176. Regions IV and VII, Constitution of Iron at 1050° in the Different Ranges of Composition. Let us assume that the temperature has fallen from the molten state to say 1050°, so that the freezing is complete, the metal is solid throughout, but that the transformations represented by the transformation group of lines *GSER, PSP'* have not yet begun; and let us consider the constitution.

(1) *Region IV, Non-Eutectiferous or Steel Range.* In this region the red-hot or even white-hot metal consists essentially of austenite, the solid solution of carbon in iron, its concentration or in other words its carbon-content increasing progressively as we pass from left to right. When of the eutectoid composition, carbon 0.90 per cent, it is sometimes called *hardenite.*

177. (2) *The Eutectic,* of which cast iron containing 4.30 per cent of carbon consists at this temperature, is intermediate in character between the eutectic of the bismuth-tin or of the

metals *H* and *G,* or limited solubility type of alloys, and that of the lead-tin or complete insolubility type. It of course consists of alternate particles of its two constituents. Its left-hand member, austenite, corresponds to the saturated solid solution, saturated bismuth-bearing tin, of the tin-bismuth eutectic, and should for this reason be a solid solution of iron saturated with carbon, *i. e.,* saturated austenite. Its right-hand member, graphite, corresponds to the assumed lead-less tin at the right-hand of Fig. 24, p. 54. At least the graphite appears to be wholly free from iron; and if not wholly free, is at least nearly free; so that solid iron is certainly very nearly and perhaps quite insoluble in solid carbon. But in either case we may regard this graphite as a saturated solid solution of iron in carbon; since, algebraically speaking, zero per cent of iron would saturate carbon if this insolubility of iron in carbon should prove to be complete.

178. (3) Region VII, Eutectiferous or Cast Iron Range. — Just as points between *a* and *B* and *c* in Figs. 33 and 49 represent a conglomerate of the eutectic plus the excess-metal, bismuth or tin and metal *H* or metal *G,* as the case may be, saturated or not according to whether diffusion has or has not effaced the initial heterogeneousness; so here hypo-eutectic cast iron containing between about 2 and 4.30 per cent of carbon is a conglomerate of (1) the eutectic and (2) the excess-substance, austenite, a solid solution of carbon in iron, saturated or not according to whether diffusion has or has not effaced the initial heterogeneousness of deposition; while hyper-eutectic cast iron containing over 4.30 per cent of carbon is a conglomerate of this same eutectic plus the now excess-substance, carbon, in the form of graphite.

Recapitulating, since at this temperature all cast iron, *i. e.,* all iron containing over about 2 per cent of carbon, is the eutectic (austenite $+$ graphite) either alone or plus austenite or plus graphite, so it is all a conglomerate of austenite plus graphite. The truth of this statement is not affected by the fact that part of these two substances is intermixed as the eutectic, which in turn is intermixed with an excess of one or the other.

If he would avoid confusion, the beginner should here clearly recognize that in any hyper-eutectic cast iron, say in one containing 5 per cent of carbon and 95 per cent of iron, the carbon is the excess-substance and the iron the deficit-substance, in that the

carbon is present in excess over the eutectic ratio, and the iron is below that ratio; and this is true in spite of the fact that the percentage of iron is 19 times as great as that of carbon, and that there are about four times as many atomic equivalents of iron as of carbon present.    (See § 34*A*, p. 40.)

As already pointed out, theoretically the austenite should be exactly saturated. If, to fix our ideas, we assume that 2 per cent of carbon just suffices to saturate it, then the percentage of graphite present should simply be whatever excess of carbon is present above this 2 per cent. But in freezing the carbon appears reluctant to pass from its initial state of solution into that of graphite (reaction (4), Table 8) and to tend rather to remain in solution after freezing. In other words, the passage of the carbon from the state of solution into that of graphite appears to lag, so that the austenite often contains much more than 2 per cent of carbon, and thus appears to be far supersaturated.

179. GENESIS OF THIS 1050° CONSTITUTION. — Let us next consider how the constitution which exists in regions IV and VII comes into existence; and let us follow in Fig. 68 the cooling, from 1600° to 1050°, of typical kinds of iron, *i. e.*, of different irons each containing a typical percentage of carbon. Let us select (1) eutectic cast iron, (2) steel of 1 per cent of carbon, (3) hypo- and (4) hyper-eutectic cast iron. For simplicity we will ignore lag, and assume that the transformations complete themselves as they fall due.

For the purpose now in hand it is well to remember that this steel which we are about to consider differs essentially from these several cast irons in that it is non-eutectiferous, while they are eutectiferous, at least theoretically.

180. (1) 4.30 per cent. *Eutectic cast iron* with 4.30 per cent of carbon undergoes but one change, its freezing and simultaneous splitting up into its alternate plates of graphite and of saturated austenite at temperature *B* (1130°). The cooling curve is like that of any other eutectic, Figs. 10 and 28 *E*, and the correspondence is as follows:

| Fig. 28*E* | Fig. 68 | |
|---|---|---|
| *AC* | *Q″B* | Molten eutectic cast iron cools. |
| *CD* | *B* | It freezes at constant temperature. |
| *DE* | *BB′* | The solid eutectic cast iron cools. |

181. (2) 1.00 per cent. *Steel of 1 per cent of carbon,* (*Q*), on cooling to *q* on the line *AB* begins to freeze selectively quite like our alloy of metals *H* and *G*, *q* in Fig. 49. The first freezing layer or nucleus has composition *p*; and, as the temperature further falls the temperature and composition of the mother-metal slide along *AB* from *q* to *s* as it becomes progressively enriched in carbon by the selection; those of the layers in the act of depositing slide from *p* to *s* as they become correspondingly enriched in carbon, following a line somewhere near the *ps* here sketched; and those of the frozen mass (assuming that diffusion effaces the initial heterogeneousness of deposition), slide simultaneously along *Aa* from *p* to *r* as it too becomes progressively richer in carbon; or, if diffusion is incomplete, then by some other path to some point necessarily on the ordinate *QW*, since the final composition of the wholly frozen mass must be that of the initial molten metal, *Q* = 1 per cent.

The cooling curve is like that of Fig. 30, p. 71, the correspondence being as follows:

| Fig. 30 | Fig. 68 | |
|---|---|---|
| *AB* | *Qq* | Molten steel cools. |
| *BC* | *qr* | It freezes selectively forming unsaturated austenite. |
| *CE* | *rr′* | Solid steel cools. |

182. (3) 2.50 per cent. *The cooling of hypo-eutectic cast iron,* containing say 2.50 per cent of carbon, *Q′*, is like that of a eutectiferous alloy of limited reciprocal solubility when solid, *n*, Fig. 49. On cooling to *n* (1280°), as before, selective freezing begins with the freezing out of austenite, and the temperature and composition of the mother-metal slide from *n* to *B* as selection enriches it: those of the layers in the act of freezing slide from *m* to *e*, thence to *a*, and thence skip to *B*, as they pass successively through the stages of (1) unsaturated austenite, (2) saturated austenite, and (3) the eutectic; while those of the frozen mass as a whole slide from *m* to *a*, as a solid solution; they then slide from *a* to *B* as a conglomerate of austenite and eutectic. The cooling curve is like that of Fig. 31, and the correspondence is as follows:

Fig. 31  Fig. 68

| | | |
|---|---|---|
| $AB$ | $Q'n$ | Molten hypo-eutectic cast iron cools. |
| $BB'$ | $nn'$ | Unsaturated austenite freezes. |
| | | Subsaturation division: }  Selective Freezing |
| $B'C$ | $n'n''$ | Saturated austenite freezes.    period. |
| | | Saturation division: |
| $CD$ | $n''$ | The eutectic freezes at constant temperature. |
| $DE$ | $n''n'''$ | The wholly frozen hypo-eutectic cast iron cools. |

183. (4) 5.00 per cent. *The cooling of hyper-eutectic cast iron,* finally, is like that of our salt-water solution and lead-tin alloys, the components of which we assumed for simplicity to be wholly insoluble in each other. Selection then is rigid, the excess-substance, carbon (which when the mass was molten would be regarded by some as the solvent), freezing out wholly free from the deficit-substance, iron.

During the selective period of the freezing, $T'T''$, then, it is pure graphite which freezes out, the mother-metal becoming correspondingly enriched in iron, *i. e.,* impoverished in carbon, its temperature and composition sliding from $T'$ to $B$, and its carbon-content falling to the eutectic ratio of 4.30 per cent and simultaneously reaching the eutectic freezing-point of 1130°. Now begins the unselective or eutectic-freeing period, during which the mother-metal in freezing forms the eutectic.

The mass when wholly frozen, then is a conglomerate of (1) graphite frozen out between $T'$ and $T''$ and (2) the eutectic frozen out at $T''$.

The cooling curve is like that assumed for ice, lead, and tin, Figs. 8, 28 *B* and 28 *F*, and the correspondence is as follows:

Figs. 28 *B* and 28 *F*    Fig. 68

| | | |
|---|---|---|
| $AB$ | $TT'$ | Hyper-eutectic molten cast iron cools. |
| $BC$ | $T'T''$ | Graphite freezes out, selective period. |
| $CD$ | $T''$ | The Eutectic freezes out at constant temperature, $T''$. |

184. CONDITIONS AFFECTING THE QUANTITY OF GRAPHITE FORMED. — It is a familiar fact that the presence of silicon favors the formation of graphite. All carbon in molten cast iron may be regarded as combined with or dissolved in the iron, because otherwise it would rise to the surface. Of this carbon a variable amount turns into graphite during cooling, the proportion increasing (1)

with the slowness of the cooling, and (2) with the silicon-content of the metal, at least until this latter reaches 0.75 per cent,* but diminishing with the sulphur-content, and under certain conditions with the manganese-content. In foundry parlance, iron either nearly free from silicon, or rich in sulphur or manganese, is apt to be " white," *i. e.,* its fracture reveals little or no graphite; but iron containing at least a moderate proportion of silicon, especially if it is relatively free from sulphur and manganese, is usually gray, *i. e.,* its fracture passes along the plates of graphite which have formed within it during solidification.

So, too, other things equal, the more slowly cast iron is cooled, the grayer it is, *i. e.,* the more graphite is seen in its fracture, because the slowness of cooling favors the formation of graphite during freezing and especially favors its crystallizing in large plates, which readily determine the path of rupture, and hence are the more prominent in the fracture.

The fact that slow cooling stimulates the formation of graphite may reasonably be explained by its giving greater opportunity for the lagging reaction (3) [or (6)] to take place. But it is probably the slow cooling through the freezing-range, and also through region VII, which should stimulate the formation of graphite; and slow cooling through region VIII should lessen the percentage of graphite, by increasing the opportunity for reaction (10), also a lagging reaction, to take place.

These effects of silicon, sulphur, and the rate of cooling are in iron foundry practice played against each other, in order to give to the castings of cast iron the percentage of graphite desired, and through this to ensure their having the proper constitution, *i. e.,* the proper ratio between ferrite and cementite in their matrix. Thus if the percentage of sulphur is greater than usual, the percentage of silicon should be increased. Again, if the castings are going to cool rapidly, either (1) because they are to be thin, or (2) because they are to be cast in green (*i. e.,* moist) sand moulds, or even in iron moulds, instead of in baked (*i. e.,* dried) sand moulds, then since this rapid cooling will tend to restrict the formation of graphite by reaction (3) [or (6)], the percentage of silicon in the iron should be increased so as to offset this, by stimulating the formation of graphite.

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* The author, *Trans. Am. Inst. Mining Engineers,* XXX, p. 731, 1900.

185. The Role of Silicon is not yet clearly established, though Tiemann's* results, as well as Royston's,† indicate that it has a direct stimulating effect on the formation of graphite. But the phenomena of the blast-furnace casting house suggest that, beyond this, silicon probably shifts the eutectic composition to the left, and sulphur probably shifts it to the right, as will now be explained.

In hypo-eutectic cast iron, the formation of graphite should occur only when the metal has cooled down to the eutectic freezing-point, *i. e.*, after the austenite which forms during selective freezing, say from $n$ to $n''$, has already frozen; in short after the metal has so far frozen that the graphite as it forms could hardly be expected to separate by gravity, because it would be greatly entangled in the already frozen austenite. But in case of eutectic and hyper-eutectic cast iron, graphite forms in the very first freezing, and therefore at a time when not enough of the metal should have frozen to entangle and mechanically retain the graphite, which is so light that its tendency to remove itself bodily out of the metal by gravity is very great. The great difference in density puts this case into sharp contrast with those of most alloys, in which, as pointed out in § 37, p. 44, the difference in density between the different constituents is too slight to cause perceptible stratification.

Now when cast iron is stored in the great mixers of the blast-furnace casting-house, it is very close to its upper freezing-point, and it is often so cool as to suggest strongly that it is below that point, so that a considerable amount of selective freezing occurs. Indeed a thick crust often forms. Under these conditions a large quantity of graphite rises to the surface of the molten cast iron and is blown thence about the building. This is true even when the iron contains considerably less carbon than the proportion here given as the eutectic ratio, *viz.*, 4.30 per cent. This separation of graphite, and indeed the very presence of this graphite, indicate that the selective freezing which is occurring is the formation of graphite; and this in turn indicates that the metal is hyper-eutectic, in spite of having less than 4.30 per cent of carbon. This, however, implies that the eutectic carbon-content, instead of

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* *Metallographist*, IV, pp. 313, 319 to 321.
† *Journ. Iron and Steel Inst.*, 1897, I, p. 166.

being 4.30 per cent, is a considerably smaller quantity, or in short that the silicon which such cast iron always contains has shifted the position of the eutectic to the left.

The fact that, if cast iron contains much sulphur, no graphite is seen blowing about the casting-house, is quite in accordance with this supposition, for this is just the result which we should expect if sulphur were to shift the eutectic position to the right, quite as we have supposed that silicon shifts it to the left.

The fact that cast iron which contains silicon often has very much less than 2 per cent of its carbon in the combined state as cementite, suggests that the presence of silicon has the further effect of shifting the saturation-point line *Eae* to the left. For if the theoretical reactions were to take place to their full extent there should be in the cold cast iron at least enough carbon as cementite to have saturated the austenite when the cast iron was in region VII. Any lag of the transformations would seem to work in the opposite direction of increasing the percentage of carbon as cementite above this saturation ratio rather than in the direction of reducing it below this saturation ratio.

Thus, (1) the fact that such cast iron, though containing all told perhaps 4.00 or 4.50 per cent of carbon, contains very much less combined carbon, very much less carbon as cementite, than would saturate the austenite if its saturation-point were in the neighborhood of 2.00 per cent, together with (2) the fact that such cast iron ought to contain enough combined carbon to have saturated that austenite at the time when it existed, — these facts jointly suggest strongly that the silicon has lowered the saturation-point of the austenite, or in other words has shifted the line *Eae* to the left.

186. Areas IV to VII Inclusive. Transformation Curves, *GHSE*, *PSP'*. — The underscored V curve *GHSE*, *PSP'* is closely comparable with the freezing-point curves of our complete-insolubility series of alloys, eutectiferous throughout their length, the type to which we assumed for simplicity that salt-water and the lead-tin alloys belong. But instead of representing true freezing-points, *i. e.*, a passage from the molten to the solid state, it represents transformations which take place within the solid but still red-hot and plastic steel. As we have seen composition *S*, about 0.90 per cent of carbon, is that of a definite eutectoid or quasi-eutectic (§ 148, p. 178), pearlite, composed of alternate