

form; and we remove part of this graphite by means of iron oxide in a bed of which these castings are heated. The reaction is of the following type:



As the carbon at the very skin of the casting is thus removed, that within diffuses outwards to take its place. We may suppose that the actual diffusion is of the carbon in the solid-solution or austenite state; that this diffusion and the change of its carbon from the dissolved to the free or graphitic state occur side by side; and that it is this free graphite which is directly attacked by the iron oxide.

We may regard these castings as in effect a variety of gray cast iron, but with the special advantage over the common gray iron that the particles in which the graphite forms when the metal is thus reheated into region VII are extremely fine, and therefore much less injurious, less weakening and less embrittling, than the coarse flakes of graphite which form in regions II and III, in the freezing of the molten metal. The graphite generated in the solid metal in region VII has no opportunity of coalescing into flakes, as that does which is generated in the passage from the molten to the solid state; it remains as an impalpable powder.

Besides being less injurious, this finely divided graphite is also susceptible of being removed in considerable part, especially from the very outside of the casting, by surface oxidation, which is not the case with the coarse graphite flakes of common gray cast iron.

We may call this finely divided graphite "temper graphite," a modification of Ledebur's name "temper carbon."

These castings are relatively cheap like cast iron, not so much because the cost of conversion into steel is avoided, — indeed for this conversion has to be substituted the long annealing process by which the cementite is changed into temper graphite; — but because the lower melting-point of the metal as a whole greatly lessens the foundry expenses. At the same time these castings avoid the weakness and brittleness of white cast iron due to its great proportion of cementite, and they avoid the weakness and brittleness which the large size of the graphite flakes in common gray cast iron causes.

CHAPTER X.—THE PHASE RULE

228. IN GENERAL. — What is the Phase Rule? What is it about, and why is it of importance to metallurgists? The answer to these questions will be made easier by refreshing our memory on certain elementary matters.

We have seen that, just as crystalline rocks are composed of perfectly definite and distinct mineralogical entities called minerals, such as the mica, quartz and feldspar of a granite, so our alloys when solid are in general composed of similar definite entities, which correspond to the minerals of our crystalline rock. These entities, these minerals in one case and quasi-minerals in the other, are called "Phases," a term which will be more closely defined later. The phase rule has to do with these phases.

We have further seen that these microscopic constituents actually present in an alloy may or may not be those which should normally be present at the existing temperature. For instance we have seen that the constituents normal to slowly cooled steel are ferrite and cementite, partly free, partly mechanically mixed as the quasi-eutectic conglomerate called pearlite. We have further seen that, if the steel is cooled suddenly from above the critical range, instead of consisting when cold of these normal constituents, it actually consists chiefly of austenite. The austenite is not normal at this temperature; it exists normally only at temperatures in and above the critical range; but it may be preserved by sudden cooling; when so preserved it is abnormal, and in this sense the suddenly cooled steel is not in molecular equilibrium.

The phase rule is one which by superior analysis, and almost by inspection, helps us to answer such questions as (1) whether in any given alloy the constituents actually present are those which ought normally to be present, *i. e.*, whether the alloy is in molecular equilibrium in this sense; and (2) for any given transformation or change of state, what are the normal constituents which ought to result, *i. e.*, which correspond to equilibrium in this sense; and (3) many other related questions.

This it does essentially through telling us the "degree of liberty" of the alloy regarded as a system, *i. e.*, whether the ex-

isting constitution of the alloy has such a degree of stability that it can survive a change of temperature or of concentration, or cannot. Roughly speaking we may say that we find out what the "degree of liberty" is by comparing (1) the number of different "components" or "constituents," such as free metals (and metalloids if any), present in any given alloy and also certain other entities, with (2) the number of "phases," *i. e.*, the number of distinct, and as it were mineralogical entities or distinct "minerals," or quasi-minerals, present in it.

For instance, pure carbon steel contains two components, iron and carbon. If hardened by sudden cooling it may be taken provisionally to consist of three distinct "minerals" or phases, the austenite which has been in large part preserved by the sudden cooling, unstable in the cold, tending to change back to ferrite and cementite; (2) a little ferrite and (3) a little cementite, both formed by the transformation of a little of the austenite in spite of the suddenness of the cooling. As a whole the molecular equilibrium is unstable; there is a residual tendency, and a powerful one though held in check, for the rest of the austenite to change back to ferrite and cementite. Here are two components, but those components are present in three distinct phases or conditions.

The ferrite and cementite of slowly cooled steel, on the other hand, are normal for the existing temperature and represent stable equilibrium. On slightly reheating slowly cooled steel, *i. e.*, annealed steel, its "system" undergoes no change, *i. e.*, it remains composed of ferrite and cementite. Here as before are two elements, iron and carbon, but these components exist in only two phases or conditions, ferrite and cementite.

The constitution or "system" of annealed steel, then, is evidently more stable than that of hardened steel, since it is not changed by this slight reheating, this change of condition; or in other words it can without itself changing survive this change of environing condition. In the language of the phase rule the former system has a greater "degree of liberty" than the latter. All this will be defined more precisely later.

Now we know it as a fact that the former system is more stable than the latter; but if it so happened that we were in ignorance of this, the phase rule would instruct us, without our having to make a direct experiment. And whereas we do happen to know it in the familiar case of steel, in many other like cases we should not

know by direct experiment which of such two states was the more stable, and indeed we might not know anything about the stability, absolute or relative, of the two systems. Here, too, the phase rule would stand us in like stead.

In the comparison between suddenly and slowly cooled steel, the phase rule bases its finding on the comparison between the numbers (1) two components but in three phases in the former, and (2) still two components but in only two phases in the latter. This too will be explained more fully beyond.

229. THE VALUE OF THE PHASE RULE to the metallurgist is chiefly as a guide for interpreting phenomena and planning investigations. When the investigator has before him a set of facts the explanation of which is not clear, he may on one hand proceed in ignorance, frame many conceivable theories by which these particular facts can be reconciled, and then proceed to test these different theories. The phase rule on the other hand may enable him to test them, and reject many or perhaps all of them immediately, by inspection and without making direct experiments; or it may immediately point out to him crucial tests which will enable him to decide quickly between two different theories.

Its present importance for students of alloys lies less in the present than in the prospective results of its application to this subject, in view of the present very active efforts of many investigators to apply it. This activity is so great that it would be hardly proper, even in a fragmentary work like the present, to pass the phase rule by without an attempt to outline its meaning.

Let us now look into certain of these matters a little farther, especially into the conditions of equilibrium and the terminology of the phase rule, before taking up that remarkable rule itself.

230. MEANING OF EQUILIBRIUM. — We have seen that, although most aqueous solutions and most molten alloys are simply homogeneous solutions, *e. g.*, of one metal in another, of carbon in iron, *etc.*, when they freeze they often split up into different distinct entities, such as (1) solid-solutions (silver in gold), or (2) pure metals (assumed to be true for lead and tin), or (3) pure metalloids (graphite in cast iron), or (4) definite chemical compounds (chloride of sodium, antimonide of copper, aluminide of gold). We have further seen that these molecular rearrangements take place not only in selective freezing, but also, as in case

of the iron-carbon compounds, through transformations in the solid but red-hot plastic mass. The molecular rearrangements of both classes, but more especially the sluggish transformations in the solid metal, often remain very far from complete when the metal has completely cooled, (1) because cooling at any common rate may not give the time which their completion requires, and (2) because, thanks to the slowness of diffusion, two constituents which would react on each other were they in actual contact, may be isolated from each other by a third constituent. Were there sufficient time for diffusion, these two constituents thus isolated would reach each other, react, and bring the system to molecular equilibrium. Once the metal is cold, what we may call molecular rigidity or molecular viscosity prevents these transformations; the cold like a brake, as it were, locks the atoms in their existing condition, abnormal for this range of temperature and in that sense unstable, striving to change to the molecular grouping normal at the existing temperature, but restrained by this molecular rigidity.

Thus even in relatively slowly cooled alloys equilibrium may be very imperfect, solid solutions remaining far supersaturated (§ 96, p. 113), and transformations being restrained. Of course rapid cooling, as in the hardening of steel (§ 198, p. 221), should leave the system still farther from equilibrium, so that there are strong residual unsatisfied tendencies to molecular regrouping, rearrangement, transformation.

If there are such unsatisfied tendencies pressing to assert themselves, such strained and eager springs, then on even slight reheating and consequent relaxation of the brake of molecular rigidity, the tendencies which have been resisted by the sudden cooling now reassert themselves, the restrained transformations go on, the atoms whose sluggishness held them in the wrong path now repent and return, and a certain degree of regrouping takes place.

231. AN EXAMPLE OF UNSTABLE EQUILIBRIUM. — Let the tempering of hardened steel illustrate this. This has already been discussed at length in § 204, p. 230, to which the reader is referred. To recapitulate the matter, above the critical range A_1 to A_3 , the metal spontaneously assumes the condition of austenite normal to that upper range; if it is cooled slowly below that critical range it changes spontaneously to the condition of ferrite and cementite

normal to this lower range of temperature.* If the steel is cooled rapidly from above the critical range to the room temperature, the change from austenite to ferrite and cementite is in large part arrested, so that most of the metal remains in the condition of austenite even in the cold, although this condition is not normal to this lower range of temperature. This is the *hardening* of steel.

If this hardened steel is now slightly reheated, even if this reheating carries it only up to 66° C., part of the unstable abnormal austenite changes towards the condition of ferrite and cementite: *i. e.*, the hardening is slightly mitigated, let down, or *tempered*; *i. e.*, the transformation which has been restrained by the rapid cooling now takes place to such degree as the slight reheating and the slight molecular relaxation which the reheating induces, permit.

Note particularly that the relaxation of the brake by such reheating is very slight, so that only a fraction of the restrained transformation occurs on such reheating.

To take up again the simile offered in § 206, p. 231 there is the bent spring of the restrained transformation still striving to complete itself, but restrained by the brake of the low temperature applied by the sudden cooling before the transformation had time to complete itself. Relax the brake slightly by slight reheating, and the spring can now begin to straighten itself; but in this very beginning of its own straightening, the spring loses a fraction of its tension, and this tension quickly falls to a point at which the present diminished grip of the brake suffices to master it, so that the spring moves no farther; equilibrium between spring and brake is reestablished, the restrained transformation goes no farther. Reheat it still farther, *i. e.*, relax the brake still more, the spring further straightens itself correspondingly, its tension falling correspondingly until it again becomes so light that the present friction of the brake again restrains it, and the transformation is again arrested.

Such is the state of affairs in a cold alloy if, regarded as a system, it is unstable.

* M. Osmond recognizes distinct stages of the transformation from austenite into ferrite and cementite and back, and calls metal in these stages *troostite* and *sorbite*. Without questioning the merits of this classification, we may here, for simplicity, treat of the transformation as if it were direct from austenite into pearlite and back. ("Contribution à l'Étude des Alliages," 1901, p. 370.)

232. STABLE EQUILIBRIUM. — If, on the other hand, the several tendencies towards molecular regrouping, towards transformation, have during slow cooling been fully complied with, so that the molecular constitution is normal for the existing temperature, and thus in stable equilibrium; then if the alloy or other system is reheated, no regrouping or transformation takes place, for the simple reason that there is no residual unfulfilled tendency towards regrouping.

233. BEHAVIOR ON REHEATING A CRITERION OF STABILITY. — This, then, is one criterion of stable equilibrium; if such equilibrium exists, reheating does not change the constitution; if not, it does. Conversely, if the constitution is changed by reheating, it was not in equilibrium; if it is not changed by reheating, it was in equilibrium.

This criterion must, of course, be applied with discretion and knowledge. For instance, if hardened steel is reheated to 320° , so that a certain degree of tempering, of change of austenite towards ferrite and cementite occurs, thanks to the increased molecular relaxation at this temperature; if it is then cooled to the room-temperature, and then again heated to 230° , no further change will take place. But yet we know that the metal is still chiefly composed of austenite, *i. e.*, that the equilibrium is still unstable. The fact that reheating to a temperature lower than that to which the quickly cooled metal has previously been reheated, induces no further change of constitution, is no evidence of stable equilibrium.

Conversely if steel is cooled so slowly that the transformation from austenite into pearlite with ferrite or cementite becomes complete, so that the cold metal is in stable molecular equilibrium, nevertheless its constitution will begin changing back to austenite when we reheat it to a critical temperature such as Ac_1 (approximately PSP' in Fig. 68). But this is no evidence that the system is unstable, as the least reflection shows. Water at 80° is stable, a stable system if we may call a single substance a system; the fact that if heated to 100° or cooled to 0° it ceases to be stable and is transformed into steam or ice, is no evidence to the contrary. When we say that it is stable, we refer to stability within the range of temperature in which the existing temperature lies. This range of temperature is bounded by critical points, for instance 0° and 100° in case of water. The range may be narrow or it may be

wide, and the existing temperature may be near or far from one or both boundaries of the range.

Thus if we are asking whether an existing system, as represented by some given alloy, is the system normal to the existing temperature and therefore in equilibrium, and if we seek to answer this question by noting whether on reheating that system undergoes change or not, — if we ask and seek thus, then the reheating which we perform (1) must be to a temperature higher than any which the alloy has reached since it entered its present range; and (2) it must not reach any critical temperature.

234. REVERSIBILITY AND LAG. — This leads us to the subject of reversibility.

The changes of state which occur during cooling are naturally reversed during a subsequent heating; and the same is true of the transformations unaccompanied by change of state which occur in cooling. For instance, if steam at atmospheric pressure is progressively cooled, it first condenses into water at 100° , and then this water freezes into ice at 0° ; if we now raise the temperature, this ice will again melt at 0° , and the resultant water will change into steam at 100° . The changes of state in cooling are exactly reversed in heating, and they are reversed habitually at the very temperatures at which they occurred in cooling; freezing and melting both occur at 0° , boiling and condensation both at 100° .

If we have steel of exactly 0.90 per cent of carbon and cool it from say 900° , on reaching a temperature of about 690° it changes from its initial condition of austenite into ferrite and cementite. If, after this transformation is complete, we reheat the steel, it changes back into austenite. But the temperature, Ar_1 , at which this transformation occurs in cooling is considerably lower than Ac_1 , the temperature at which it is reversed in heating; the transformation is reversed, but at a higher temperature. The fact that there is such a difference of temperature is a clear indication that the transformation in cooling did not occur promptly on reaching the theoretical temperature at which it should begin, and that something of the nature of surfusion took place during cooling. This inaccuracy of the reversing, then, is a first indication that during cooling the transformation lagged, and that during this time of lag the metal was in an abnormal state, one not of equilibrium.

Now if the changes which normally ought to occur in cooling actually do occur, so that the cooled alloy is in molecular equilibrium, then they are reversed on reheating. If, however, the tendencies towards any given change are not fully complied with during cooling, so that the cold alloy is not in molecular equilibrium, then the changes which occur on reheating are not the exact reverse of those which occurred in cooling.

We have steel containing 0.90 per cent of carbon; it has been cooled slowly; it consists of ferrite and cementite. We heat it past A_{c1} and it changes into austenite; we cool it below A_{r1} and it tends to change back to ferrite and cementite. There is thus the tendency on rising past the transformation-point to change from the normal low-temperature state (ferrite and cementite), to the normal high-temperature state (austenite); which change we may for brevity call the Low-to-High-Temperature-State Change, or the L-to-H change. Conversely, on cooling past the transformation-point there is the tendency to change from the normal high-temperature state of austenite to the normal low-temperature state of ferrite and cementite, or for brevity the H-to-L change.

235. HARDENED STEEL ILLUSTRATES IRREVERSIBILITY. — Suppose that this steel is above the transformation-point A_{c1} , and therefore is austenite; suppose we cool it so quickly that, of the H-to-L change which tends to occur as soon as the temperature sinks below A_{r1} , only a first instalment, only 10 per cent actually does occur, before the temperature has sunk too low to permit this change to proceed farther. Only 10 per cent of this change has occurred; the remainder, the complement, 90 per cent, is suppressed, *i. e.*, is arrested, but is still trying to occur. It is the spring of Fig. 71 restrained by the brake of low temperature.

We next relax the brake slightly by reheating to 230° as in tempering (so that a straw-colored film of oxide forms), and a second instalment of this suppressed complement, say a second 10 per cent, now occurs; so that all told 20 per cent of the H-to-L transformation has now occurred, and the complement, 80 per cent of it, still remains restrained by the brake. We then reheat still farther as in tempering at 300° , so that the film of oxide on the steel turns blue, and we thereby relax the brake farther; thereon a third instalment say an additional 15 per cent, of this H-to-L transformation occurs; so that now altogether 35 per cent of it has occurred. There is still a suppressed or restrained comple-

ment of 65 per cent striving to occur, but still prevented by the remaining grip of the brake. We next reheat still farther say to 600° , and we thereby remove the brake apparently completely, so that the 65 per cent complement which at 300° remained restrained, now occurs, and so that the whole of the H-to-L change takes place. The metal is annealed.

If, however, we finally carry the temperature a little higher, up above the transformation-point A_{c1} , the metal now changes from ferrite and cementite into austenite, in short the L-to-H change occurs.

Here, then, our actual transformations are as follows:

(1) in sudden cooling (hardening) from above A_{r1} , only 10 per cent of the H-to-L transformation occurs, and 90 per cent of it is restrained or suppressed. (10 per cent of the austenite changes into ferrite and cementite; the complement, 90 per cent, remains as austenite),

(2) in reheating,

(A) the remaining 90 per cent of the H-to-L change occurs as we reach first 230° (tempering straw), then 300° (tempering blue), and finally 600° (annealing). (The rest of the austenite changes into ferrite and cementite, so that at 600° the austenite has disappeared and the whole mass has changed into ferrite and cementite),

(B) when the temperature rises above A_{c1} the whole of the L-to-H transformation takes place (all the ferrite and all the cementite change back into austenite),

Or in short, in cooling, 10 per cent of the H-to-L transformation; in reheating

(A) 90 per cent of the H-to-L transformation, followed later

(B) by 100 per cent of the L-to-H transformation.

The transformations which here occur in heating clearly are very far from the exact reverse of those which occurred in cooling.

236. WHY IRREVERSIBILITY IMPLIES ABSENCE OF EQUILIBRIUM. — The reasons have really made themselves clear in this example. If cooling is too rapid to permit the H-to-L transformation to perfect itself, then the transformations which actually occur in such cooling are but an initial instalment of the normal ones, the complement of that instalment being suppressed by molecular rigidity. Now in order that the transformations which occur on reheating such rapidly cooled material should be the reverse of