The possible variations are (1) rise and (2) fall of temperature; (3) enrichment and (4) impoverishment in tin of the still molten mother-metal. Let us test these variations separately; if the system is truly nonvariant, any one of them should break it up.

(1) Rise of temperature. If we apply heat, the now frozen part of the eutectic will begin to melt, and the temperature will remain constant until the whole of it has melted; then only will the temperature begin to rise. But this complete melting of the eutectic will remove the whole of our solid tin. In short a rise of temperature can occur only after the system has broken up through the elimination of this second phase, solid tin; or in other words the system cannot survive a rise of temperature.

(2) Fall of temperature. In like manner, if we abstract heat by external cooling, the still molten part of the eutectic mother-metal will begin freezing, and the temperature will remain constant until the whole of it has frozen, *i. e.*, until the molten phase of the system has been eliminated; only then will the temperature fall below its initial point of 180°. In short, a fall of temperature can occur only after the system has broken up through the elimination of its third phase, molten solution of tin in lead; or in other words the system cannot survive a fall of temperature.

We saw that in the range of selective freezing, at L', Fig. 24 (as distinguished from the present eutectic freezing), either a rise or fall of temperature could be survived provided that the concentration of the molten phase shifted correspondingly. Here, however, the system could not be saved by any such device, for any rise of temperature would remelt the now solid part of the eutectic, thus eliminating our second phase, solid tin, no matter what the composition of the adjacent molten phase. Further, any fall of temperature would eliminate our third phase, the molten solution or mother-metal, no matter what its composition; because no lead-tin alloy can remain molten below our initial temperature of 180°, for it is the freezing-point of the most fusible lead-tin alloy. Thus any fall of temperature must substitute a solid lead-tin alloy for our molten phase; but this would break up our system, changing it from a tri-phase to a di-phase one, consisting of (1) solid lead and (2) solid tin, since every solid lead-tin alloy must be a mixture of plates of lead and

other plates of tin, thanks to the assumed complete insolubility of these two metals in each other when solid.

Here again, no shifting of concentration can enable our system to survive any change of temperature, for any rise of temperature must eliminate the solid tin phase, and any fall of temperature the molten solution phase.

(3) Enrichment and (4) impoverishment of the molten mother-metal in tin. As the temperature is now by assumption at the freezing-point of the eutectic, and as this is the most fusible lead-tin alloy, the temperature is below the freezing-point of every other lead-tin alloy. Consequently it would be impossible to substitute for this molten phase any other molten alloy either richer or poorer in tin, because no such other alloy could be molten at this temperature. Any alloy either richer or poorer thus substituted would at this temperature be solid; and because solid it would be a mechanical mixture of plates of solid lead and other plates of solid tin, these two metals having been assumed for simplicity to be absolutely insoluble in each other when solid. But our system would then be (1) solid lead, including both (A) the excess of lead over the eutectic ratio frozen out between H and J, and (B) the solid lead in the new solid alloy now added; plus (2) the solid tin in this newly added alloy. In short it would be a new and di-phase system, instead of our original tri-phase system, for the third of our original phases, the molten solution of tin in lead, would have been eliminated. In short our system cannot survive either enrichment or impoverishment of the molten phase in tin.

We have thus found that the system cannot survive any of the four possible changes in temperature or concentration; so that it satisfies all our tests of its complete nonvariance.

254. THE IRON-CARBON COMPOUNDS. — To take a simple series of cases, let us select steel containing 0.50 per cent of carbon, Sh^v of Fig. 68 at six different temperatures, 1600° S. 1500°, 1300° S', 720° S'', 690° h^{iv} and 0° h^v, representing (1) the molten condition, (2) the state of selective freezing, (3) the austenite state, (4) the separation of ferrite just above the recalescence, (5) the recalescence, and (6) the common or room-temperature state. This latter case we will subdivide into two, those of (A) hardened (suddenly cooled) and (B) unhardened (slowly cooled) steel respectively.

There will in every case be two constituents, carbon and iron; the system will be nonvariant if there are three phases, monovariant if there are two, divariant if there is only one.

(1) At 1600° S, there is one phase, molten carburized iron; the system is divariant.

(2) At 1500° during selective freezing, there are two phases, molten carburized iron and solid austenite. The system is monovariant.

(3) At 1300° S', there is only one phase, austenite. The system is divariant.

(4) At 720° S'' there are two phases, (1) the free iron which has already separated out within the plastic redhot mass as ferrite, between h''' and S''; and (2) the residual austenite from which it has separated, and within which it is still enclosed. The system is monovariant.

(5) At 690° h^{iv}, the recalescence, there are three phases, ferrite and cementite (partly interstratified in the form of pearlite), which have already resulted from the decomposition of the austenite, and the residual austenite which has not yet split up into ferrite and cementite. The system is nonvariant.

(6A) At the room-temperature, h^v, if the decomposition of the austenite has been complete, so that only pearlite with ferrite as the excess substance remains, there are only two phases, ferrite and cementite; the system is monovariant; it is in equilibrium; it is not affected by reheating, *e. g.*, to 300°.

(6B) At the room-temperature, h^v, if the steel has been hardened by a cooling so sudden that part of the austenite has failed to decompose into ferrite and cementite, then there are three phases, this residual austenite plus such ferrite and cementite as have resulted from such decomposition of austenite as has occurred in spite of the suddenness of the cooling. The system is nonvariant; it is not in equilibrium; when reheated to 200° as in tempering more of the austenite changes into ferrite and cementite.

The reasoning already given in §§ 248 to 253, pp. 302 to 309, suffices to explain these several cases.

255. THE PHASE RULE APPLIES ONLY TO SYSTEMS PROPERLY SO CALLED. — The unthinking might be puzzled by trying to apply the phase rule to cases to which it is manifestly inapplicable,

to cases which are not systems at all in the sense of the phase rule.

Thus some might reason as follows: "I place a lump of cold sulphur upon a lump of cold iron. Two components, sulphur and iron; two phases, sulphur and iron. Degree of liberty $= n + 1 - r = 2 + 1 - 2 = 1$; hence this is a monovariant system; hence if sulphur and iron are heated they will not react upon each other according to the phase rule. But I happen to know that they will react; hence the phase rule is wrong and misleading."

The answer is that such a mass is not a system at all. The sulphur and iron are not phases into which some prior system has passed. Let the case of the ferrite and cementite illustrate this. While these substances in slowly cooled steel, resulting from the decomposition of the austenite of which the steel consisted when it was above the transformation temperature, form a system, which is di-phase; yet if we were to isolate certain particles of this pure cementite and certain other particles of pure ferrite and shake them up together while cold, this would not constitute a system. The phase rule has nothing to say of such a mass.

Thus if it were true that when molten iron sulphide cooled it resolved itself into separate particles of free sulphur and free iron, then we should justly infer that the system was monovariant, *i. e.* that the sulphur and iron would not recombine on heating.

256. THE PHASE RULE IN ONE ASPECT IS QUALITATIVE, NOT QUANTITATIVE. — While it is true that the phase rule is quantitative as regards the number of components and phases, yet it has nothing to do with the quantity of any of those components or phases, and in this sense is qualitative. Let the case of the lead-tin alloy during selective freezing (§ 252, p. 304) illustrate this. When selective freezing has just begun, when the lead already frozen out amounts to say 1 per cent by weight of the whole alloy, the two phases are:

(1) solid lead, forming 1 per cent of the whole,

(2) molten lead-tin alloy forming 99 per cent of the whole. As the freezing progresses, the solid lead forms a continuously increasing proportion of the whole, and the remaining molten mother-metal a continuously decreasing percentage of the whole; yet the two remain always in equilibrium, and remain one and the same system.

Indeed, the least reflection shows that equilibrium — and it is with equilibrium that the phase rule has to do — is a purely qualitative thing, and has no relation to quantity. Let a simple example verify this idea.

In a large chamber *F, G, H, K* (Fig. 80) is placed a steam boiler *B*, with which are connected a mud-drum *C* and a steam-drum *A*. The boiler is filled with water to about level *L*, and, an escape valve being open from *A* into the open air, the temperature of *F, G, H, K* is raised to 100° C. (212° F.). The water boils until all air is expelled. Then this exit valve is closed, so that the system *A, B, C*, is isolated from without, in short so that no steam can escape and no water can be fed in; but the valves
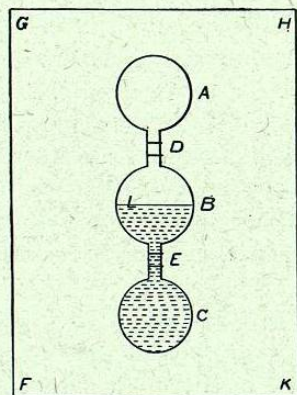

Fig. 80. Equilibrium is not Quantitative but Qualitative.

D and *E* are open, so that the boiler and its drums are in free communication with each other. The temperature is raised to say 121.4° C. (250.5° F.), and the water in *B* evaporates until the pressure of steam (its vapor tension) in the upper part of *B* and in *A* reaches 2 atmospheres (29.5 pounds per square inch). At this pressure and temperature the steam and water are in equilibrium with each other. The further evaporation of water is just balanced by the simultaneous condensation of steam, so that to the eye neither evaporation nor condensation appears to take place.

Now this equilibrium has nothing to do with the quantity of water and steam, or with the proportion between the two, as

is readily seen. Assume that temperature and pressure remaining constant, we close valve *E*; manifestly this will not induce either further evaporation or further condensation; it will have no effect whatsoever. Suppose that now, holding this valve closed, we disconnect this mud-drum *C* and remove it altogether to the outside and destroy it. The quantity of water remaining in the system will be only about one-third as great as originally, while the quantity of steam remains unchanged; the ratio between the quantity of water and of steam has changed greatly, but this change has not in the least affected the equilibrium.

The same would be true if, closing valve *D*, we had removed the steam in the steam-drum *A* from the system; and also if, holding the temperature and pressure constant, we had replaced and reconnected the steam or the mud-drum, or both of them, reopening either or both valves *D* and *E*. Thus we see that no matter what change we bring about in the quantities of water and steam, this change does not affect the equilibrium, provided that temperature and pressure remain constant.

CHAPTER XI. — PROGRESS IN THE MANUFACTURE OF IRON AND STEEL, BETWEEN 1880 AND 1900 *

257. SUMMARY. — In the last twenty years of the nineteenth century the world's production of pig iron more than doubled, and that of steel increased fivefold, while that of wrought iron became of secondary importance. The United States passed from the position of the second to that of by far the greatest producer of both pig iron and steel; their production of the former more than tripled, becoming 54 per cent greater than that of Great Britain, and their production of steel increased to more than eight times that of 1880, becoming more than double that of Great Britain,

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* Most of this chapter appeared in 1902 as the article on Iron and Steel in the supplement to the *Encyclopædia Britannica* published by the London *Times*. To fit it somewhat to the present work, parts have been omitted, others expanded, still others added, and some of the statistical data have been replaced by later ones.

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