

those which have occurred in such a cooling, they should consist in simply reversing this initial instalment. But instead of this, what first occurs on reheating is the remainder, *i. e.*, suppressed complement of the H-to-L transformation, because heating relaxes the molecular rigidity which had suppressed or restrained that complement; and when the heating eventually reaches the transformation temperature, it is not an instalment but the whole of the H-to-L transformation which is now reversed, the initial 10 per cent instalment plus the suppressed complement.

Could the heating leap absolutely instantaneously back to the transformation temperature without consuming any time, at that temperature it would be only the initial instalment of H-to-L transformation which would be reversed, so that in this case the transformation in reheating would be the exact equivalent of that which occurred in the sudden cooling, or in other words there would be complete reversibility, although the suddenly cooled steel was certainly not in equilibrium. But such an instantaneous rise can never occur; it is indeed hardly thinkable; this rise from the cold to the transformation temperature must occupy a finite time, no matter how brief. Our heating must traverse the range between the room temperature and that transformation temperature, and what takes place in that range is the suppressed complement of the H-to-L transformation, and not simply a fraction of the reverse or L-to-H transformation.

Thus one criterion of whether the transformations normal to cooling have been completed, *i. e.*, of whether the cold alloy is in a state of molecular equilibrium, is that the series of transformations which it has undergone in cooling are exactly reversed in heating, or in short are *reversible*.

Thus, to say that the condition or molecular constitution of an alloy or other system reached through cooling is in molecular stability, and to say that the transformations through which it has passed are reversible, are synonymous. To say that the transformation temperatures during heating (*i. e.*, during rise of temperature), are higher than those during cooling is to say that there is lag and a period of molecular instability; to say that the transformation temperatures in heating and cooling are identical is to say that there is no such lag, and that the transformations in both heating and cooling occur promptly on reaching their normal temperature.

Terminology of the Phase Rule

237. COMPONENT AND PHASE. — The meaning of these two words must be clearly grasped. Let me attempt to define them, and to explain them by means of examples.

In the terminology of the phase rule, the "components" of an alloy or other system are the free elements and those compounds which in the nature of the case are undecomposable under the conditions contemplated, and so play the part of elements; those which enter directly into the equilibrium of the system. The components are the uncombined elements and compounds equivalent to elements in this sense. Lead and tin (elements), are the components of a lead-tin alloy, iron and carbon (elements), are those of steel, chloride of sodium and water (chemical compounds), are those of a salt-water solution.

The components may pass from one physical state (solid, liquid or gaseous) to another (water boils or freezes), and they may combine with each other and dissolve in each other in various ways, two components merging in each other in the form of a solution or compound (iron and carbon uniting to form cementite or austenite), or emerging thence into the free state (cementite, splitting up into graphite and iron); and when they so merge, each of the compounds or solutions thereby formed tends to become homogeneous: it must become homogeneous before equilibrium can exist. Every such homogeneous compound or solution and every free element is a phase; and each of them is a distinct and different phase for every different physical state. Phases then are "the homogeneous states, whether of freedom, solution, or combination, and whether solid, liquid or gaseous, into which the components present pass or group themselves." The components are the entities in play, the entities of which we are studying the reciprocal behavior; the phases are the states, physical and chemical, in which these components exist, and into which they pass.

The usual definitions are, for phase "a mass chemically and physically homogeneous or a mass of uniform concentration, the number of phases in a system being the number of different homogeneous masses, or the number of masses of different concentrations:"* and for components "the substances of independently

*W. D. Bancroft, "The Phase Rule," p. 1, 1897.

variable concentration in the phase or system under consideration."* These definitions seem very exact; they may not, however, convey a very clear idea to an unwilling mind; good as tests, but not as explanations.

238. EXAMPLES OF COMPONENT AND PHASE, A. *The Components are Elements.* — Applying this to our metals and alloys, molten tin consists of a single component, tin, and a single phase, molten tin. If it cools to the freezing-point and begins freezing, different parts of the metal are simultaneously in two different phases, (1) molten tin and (2) solid tin; these are the two phases of the single component, tin. There is, strictly speaking, a third phase, the vapor of tin and usually the atmospheric oxygen and nitrogen; but we may simplify our whole discussion by ignoring the vapor in all cases, and suiting our formulas to this intentional omission.

In any lead-tin alloy (§ 48, p. 62), there are two components, lead and tin; if such an alloy of eutectic ratio is molten, and if the tin and lead are assumed to be wholly soluble in each other, so that the solution is homogeneous, there is one phase, this solution; when it begins to solidify and break up into the eutectic of plates of tin interstratified with those of lead, three phases are present, (1) the molten alloy, a molten solution and therefore a single as it were mineralogical entity, (2) the plates of solid lead, and (3) the plates of solid tin.

In a lead-zinc alloy (§ 98, p. 117), there are two components, these two metals. If a molten lead-zinc alloy is in such proportions that the two are not completely soluble in each other, but exist side by side as an emulsion, a mechanical mixture of two saturated solutions, (1) lead saturated with zinc, and (2) zinc saturated with lead, there are two phases, *viz.*, these two saturated solutions.

Again, in a pure steel consisting solely of iron and carbon, these two unchanging permanent elements are the two components, while the transient decomposable compound, cementite, and the equally transient solution, austenite, are phases, and so are the gaseous, molten and solid states. As the temperature rises past the critical or transformation range, past the melting-point, past the boiling-point, past the dissociation-point, and then descends

* W. D. Bancroft, "The Phase Rule," p. 1, 1897.

again, these two unchanging components, iron and carbon, enter into reciprocal play. They start as two phases free iron, ferrite, and iron carbide, cementite; on passing the critical range they pass from these phases into the solid-solution phase of austenite; when raised to the melting-point the austenite phase shifts into the phase of molten carburized iron (molten austenite, may we call it?). On reaching the boiling-point this phase shifts (let us assume for sake of example), to that of gaseous carburized iron; at the still higher dissociation-point this phase (let us again assume) shifts into that of free gaseous iron and free carbon. On recombining, recondensing, refreezing and retransformation, these phases are passed through in the reverse order. Ferrite and cementite, solid austenite, molten austenite (?), gaseous austenite (?), gaseous free iron and free carbon, these, let us assume, are the successive phases (some of them hypothetical), through which the unchanging components, iron and carbon, pass.

Here is a value of this word phase; it keeps us in face with the fact that we are regarding these systems as the resultants of some change from some other system; we regard a solid granite as resulting from state of fusion or at least from metamorphosis; we regard the constitution of a solid alloy habitually as resulting from the solidification of that alloy from its prior molten state. (See § 2, p. 2.)

239 B. EXAMPLES IN WHICH THE COMPONENTS ARE CHEMICAL COMPOUNDS. — We have thus far considered systems of which the components are elements; let us go a step farther and consider some in which the components are chemical compounds, playing the part of elements in that they are undecomposable under the conditions assumed.

A salt-water solution is frozen, and this ice is again melted; here the two components chloride of sodium and water start in the phase or condition of liquid solution; they then in freezing pass into the phases of solid chloride of sodium and solid water or ice; on remelting they pass back into the phase of liquid solution. Here the phases are three (1) the liquid salt-water solution, (2) solid salt, and (3) ice. But what are the components? Manifestly the water and the salt; it is they that, each remaining undecomposed, play back and forth between these different phases, quite as the uncombined elements tin and lead, lead and zinc, and iron and carbon, did in the cases which we have been studying. In the pres-

ent case it is clearly not the chlorine, the sodium, the hydrogen and the oxygen which are to be regarded as components. They do not directly enter into play; each is initially combined with another element, the chlorine with the sodium, and it is no longer free to act as chlorine; you can neither smell nor taste it. It is not directly between these elements, but between the water and salt that equilibrium exists; we are studying not the reciprocal behavior of these elements but of these compounds. Therefore these compounds, salt and water, are the components.

Or, to look at it in the language of the usual definition, the salt and water are "of independently variable concentration in the phase or system under consideration" in that we can vary the concentration of either of these independently of the other. We can add or remove water (by evaporation), and so shift the degree of concentration; but we cannot remove chlorine without removing the sodium with which it is combined, nor can we remove hydrogen without removing the oxygen with which it is combined. No one of these four elements can be removed from the system or added to it independently of the element with which it is combined, without changing the system into a wholly new and different one. To remove some of the sodium would change the system into a three component one, consisting of water, salt, and the free chlorine left by the removal of that sodium.

Again, in a typical granite composed of muscovite (potash) mica, quartz, orthoclase (potash) feldspar, we have (1) the three phases, each of these minerals being a phase, and (2) three components, silica, alumina and potash. It is true that there are four elements, silicon, aluminium, potassium and oxygen present, assuming that each of our minerals is quite pure. But for purposes of equilibrium we need not consider the number of elements; it is quite sufficient that, ignoring them, we concentrate our attention on the number of phases and of components, because in the nature of the case, in melting and refreezing our granite, in passing back and forth through different ranges of temperature, though these three components, these three oxides, may group themselves together in different ways, no one of them would be decomposed; as far as equilibrium is concerned they might as well be elements.

Again, when hydrated cupric sulphate is dissolved in water, then again crystallized out, then dehydrated, then again rehy-

drated and redissolved, the two unchanging entities are anhydrous cupric sulphate and water; it is these two that are the components; it is they that play back and forth through the phases of anhydrous salt, solid hydrated salt, and solution of different degrees of concentration. It is true that there are three chemical elements, copper, sulphur and oxygen; but this is beside the mark, for neither the cupric sulphate nor the water is liable to be decomposed through the changes of temperature contemplated. No one of these three elements enters directly and by itself into any reaction or change of state or of concentration, or into the equilibrium of the system; nor can either be varied independently of the others. That is to say, we cannot remove from the system part of its oxygen without simultaneously removing either the hydrogen or the copper and sulphur with which that oxygen is combined.

240. ALLOTROPIC MODIFICATIONS ARE DISTINCT PHASES. — Again, every distinct allotropic form of an element is a distinct phase. If graphite, diamond and amorphous carbon coexisted, they would constitute three distinct phases, because a mixture of different allotropic forms, and indeed of crystals of different forms, cannot be called "chemically and physically homogeneous."

241. COMPOSITE EUTECTICS ARE NOT PHASES. — Although cold steel of 0.90 per cent of carbon, when slowly cooled, consists solely of pearlite, nevertheless it consists of two phases, *viz.*, the ferrite and cementite of which that pearlite is composed. As pearlite is not a mineralogical but a lithological entity, not homogeneous but heterogeneous, not a single substance but a mechanical mixture of two, it is not a phase at all, for mechanical mixing up does not constitute a phase. So although hypo-eutectoid steel when slowly cooled consists of pearlite plus ferrite, it contains only two phases, ferrite and cementite; for the fact that part of this ferrite is mechanically intermixed with the whole of the cementite in the form of pearlite does not affect the number of phases present.

242. HOMOGENEOUSNESS OF PHASES. — It has been said that every phase must be homogeneous; let us look at this matter further. Oil floating on water, or mixed up with the water as an emulsion typifies a di-phase system. A homogeneous solution of salt in water is a mono-phase system. But how about a heter-

ogeneous solution, either liquid, molten or solid? Is it a phase, or if not, what is it?

We may answer this in two ways. First the phase rule bears upon the question of equilibrium; but it is perfectly evident that no system can be in equilibrium which contains a heterogeneous solution, because there must exist in that solution an unfulfilled tendency to diffuse so as to efface that heterogeneity. Thus it is not necessary to resort to the phase rule to decide as to the equilibrium of such a system.

Second, in a heterogeneous solution there are in a sense an infinite number of phases, because every different degree of concentration represents a different phase. But, as we shall see, if we insist upon applying the phase rule to such a system, that rule shows it to be unstable.

243. PHYSICAL ACTIONS. — In a broad discussion of this subject it would be necessary to consider variations in both temperature and pressure. For our present purpose the whole discussion may be simplified by considering the pressure as constant, and the temperature alone as changing, and this will be done in the remainder of this chapter.

244. INDEPENDENTLY VARYING CONDITIONS. — In considering the equilibrium of a system, and the influence of changes of conditions on that equilibrium, there are two of these varying conditions which we must have in mind: varying temperature and varying degree of concentration of any solutions which are present, whether those solutions are solid on one hand, or liquid or molten on the other hand.

245. ARBITRARY AND CONFORMABLE VARIATIONS IN CONDITION. — Let us recognize that, when temperature and concentration vary, they may vary conformably with each other, or arbitrarily, *i. e.*, without regard to each other.

For example, in a beaker stands a solution of salt in water, at 20°, and just saturated for that temperature. We cool the mass to 10°, and the solution thereby becomes supersaturated, because the water has less solvent power for salt at 10° than at 20°; accordingly the excess of salt crystallizes out, and a new equilibrium is thereby reached. But this has destroyed the mono-phase system, salt solution, and substituted for it a di-phase system, salt solution plus solid salt. This variation in temperature was arbitrary; there was nothing done to compensate for it.

Suppose, however, that when we cooled the mass to 10° we had simultaneously poured in enough pure water, also at 10°, to dilute the liquor to the saturation-point for 10°; no salt would have crystallized out in this case, because we varied the second variable, concentration, conformably with the first, temperature. The system has survived the simultaneous changes in the two variables. In the first case the variation of temperature was arbitrary; but in the second instead of an arbitrary variation we had conformable variations of the two variables.

But if on cooling to 10° we had poured in half the quantity of water which we have just supposed, salt would still have crystallized out, because this smaller quantity of water would not suffice to prevent the supersaturation which the cooling tends to cause; in this case the variations in the two variables would be arbitrary instead of conformable.

246. DEGREE OF LIBERTY. THE PHASE RULE. — By the degree of liberty of a system we indicate whether that system can, without breaking up and becoming converted into some other system, survive an arbitrary variation in one of these two variables at a time, temperature and concentration; or in both of them simultaneously; or in neither of them. We are purposely ignoring variations in pressure, and also ignoring the vapor present, to simplify our discussion.

The degree of liberty is measured by the terms invariant or nonvariant, monovariant and divariant.

An invariant or nonvariant system is one which cannot survive a change either of temperature or concentration (*i. e.*, of either of our variable conditions), but breaks up and passes into some other system if either is changed; and this breaking up, due to a change of either of these conditions, cannot be prevented by any conformable change in the other condition.

A monovariant system is one which can survive a change of either temperature or concentration if accompanied by the conformable change in the other, but cannot survive simultaneous arbitrary changes in both temperature and concentration.

A divariant system is one which can survive simultaneous arbitrary changes in both temperature and concentration.

The degree of liberty of a nonvariant system is 0, that of a monovariant system 1, and of a divariant system 2.

We learn the degree of liberty of any given system, or in other words we learn whether it is nonvariant, monovariant or divariant, by the formula*

$$L = n + 1 - r,$$

in which

$$L = \text{the degree of liberty} \begin{cases} 0 & \text{for a nonvariant system} \\ 1 & \text{for a monovariant system} \\ 2 & \text{for a divariant system} \end{cases}$$

n = the number of components present, and

r = the number of phases present.

This formula is the *phase rule*.

A cold alloy if nonvariant is clearly unstable, since heating breaks it up; a cold monovariant alloy, on the other hand, is stable; and our stable alloys are characteristically of this type, though they pass through an nonvariant stage in freezing.

247. EXAMPLES TO TEST THE PHASE RULE. — Some examples which we will now take up will serve both to explain and to test the phase rule. Let us in each case first find what degree of liberty the phase rule assigns to the system under consideration; *i. e.*, whether the phase rule shows it to be nonvariant, monovariant or divariant; and if for instance the phase rule shows it

* This formula for the phase rule is based upon our purposely ignoring not only the gaseous phase always present, but also the variations in pressure. In a more general discussion these ought to be taken into account; and in that case the formula becomes

$$L = n + p - r,$$

in which p = the number of so-called physical actions, temperature and pressure. Here, as before, L is 0 for a nonvariant, 1 for a monovariant, and 2 for a divariant system; or, as is sometimes said:

a nonvariant system has $n + 2$ phases
 a monovariant " " $n + 1$ "
 a divariant " " n "

In any given case the formula given in this footnote, and that given above in the text, lead to the same result. Thus, a mixture of ice and water is nonvariant by either formula; that it is nonvariant by the formula of the text $L = n + 1 - r$ is shown in § 249; that it is also nonvariant by the wider formula of this footnote is easily seen. The number of constituents is 1, water; the number of phases is 3, ice, water, and steam, — *i. e.*, the vapor of water floating above the mixed ice and water; the number of physical actions is 2, temperature and pressure. Hence, $L = 1 + 2 - 3 = 0$.

TABLE 14. — Condensed Statement of the Examples Taken to Test the Phase Rule, §§ 247, to 254, inclusive.

SYSTEM	ELE- MENTS	COMPO- NENTS	PHASES	ENTITIES PRESENT WHICH ARE NOT PHASES	DEGREE OF LIBERTY
Freezing tin	Tin	Tin	Molten tin Solid tin		Nonvariant
Freezing water	H, O	Water	Liquid water Ice		Nonvariant
Salt water above the freezing-point	Na, Cl H, O	NaCl H ₂ O	Salt water (liquid solution)		Divariant
Salt ice	Na, Cl H, O	NaCl H ₂ O	Salt Ice	Eutectic of salt plus ice	Monovariant
Lead-tin alloy, molten	Sn, Pb	Sn, Pb	Mother-metal (molten solution)		Divariant
Lead-tin alloy, solid	Sn, Pb	Sn, Pb	Solid lead Solid tin	Eutectic of lead plus tin	Monovariant
Ditto during select- ive freezing	Sn, Pb	Sn, Pb	Solid lead Mother-metal (molten solution)		Monovariant
Ditto during eu- tectic freezing	Sn, Pb	Sn, Pb	Solid lead Solid tin Mother-metal (molten solution)	Eutectic of lead plus tin	Nonvariant
Molten steel of 0.50 per cent carbon	Fe, C	Fe, C	Molten solution		Divariant
Ditto at 1300°, solid	Fe, C	Fe, C	Solid solution (austenite)		Divariant
Ditto at 720°, S'' (Fig. 68)	Fe, C	Fe, C	(1) austenite (2) ferrite		Monovariant
Ditto at 690° hiv the recalescence	Fe, C	Fe, C	(1) austenite (2) ferrite (3) cementite	Pearlite (eutectoid of ferrite plus cementite)	Nonvariant
Ditto at the room- temperature, after quenching from above A ₁	Fe, C	Fe, C	(1) austenite (2) ferrite (3) cementite	Ditto in small quantity	Nonvariant
Ditto at the room- temperature when slowly cooled = annealed	Fe, C	Fe, C	(1) ferrite (2) cementite	Pearlite	Monovariant
Gray cast iron at the room- temperature	Fe, C	Fe, C	(1) ferrite (2) cementite (3) graphite	Pearlite	Nonvariant
Chilled white cast iron	Fe, C	Fe, C	(1) ferrite (2) cementite (3) graphite (4) austenite	Pearlite	Nonvariant