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THE GENERAL PRINCIPLES OF EQUILIBRIA IN DIVIDED SYSTEMS.

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The general conditions for heterogeneous equilibria, summarized in the ordinary phase rule, are only applicable to systems where the different phases present are not subdivided. An extension of the principles is necessary for the treatment of systems in which one of the phases is divided into separate portions. The purpose of this article is to consider the conditions necessary for equilibrium in such "*divided systems.*"

In deriving the phase rule in its familiar form, the only variables considered are the pressure and temperature of the system (and the concentrations in the different phases). In the following treatment, however, we shall consider the possibility that any number of variables besides pressure and temperature may affect the equilibrium. Moreover, we shall make no restrictions as to the equality throughout the system of the pressure or other variables, with the exception of temperature. We shall thus obtain a very general equilibrium rule.

Definition of Region.—A system in equilibrium may be divided for purposes of discussion into a number of separate *regions*, throughout each of which the properties of the matter are either uniform or are a continuous function of the (macroscopic) position.

Definition of Phase.—In the case of the systems considered in the derivation of the ordinary phase rule, the number of regions, r, is the same as the number of phases, p. In the case of divided systems, however, some of the regions will contain matter belonging to the same phase. Two regions will obviously contain matter of the same phase, when the two regions are identical in thermodynamic properties. Two regions which are not identical, however, will also be said to contain the same phase when a continuous isothermal change in the independent variables determining one of the systems will cause continuous change in its properties until they become identical with those of the other systems. In general, this will be true when the two regions can be made identical by an isothermal change without the appearance of any surface of discontinuity within the regions.[1]

Derivation of the Equilibrium Rule.—Let us consider a system in equilibrium made from c components.[2] We shall be interested in the number of separate regions, r, which can exist at equilibrium. The necessary condition for isothermal equilibrium is that any component shall have the same free energy[3] in all the different regions of the system. In all we shall have cr free energies. Now the free energy of each component of a region can be stated as a function of the $(c - 1)$ concentrations which determin the composition of the region and of certain further variables which will be sufficient to complete the thermodynamic description of the region. Let v be *just enough* variables besides the concentrations to determin completely the free energy of each component in each region. We have, then, in all cr free energies, $(c - 1)r$ concentrations, and v further algebraic quantities between which certain algebraic relations will exist. Each of the cr free energies will be some function of the other variables which will give us cr equations, and at equilibrium we shall have $c(r - 1)$ further equations, since each component must have the same free energy in any one region as in the other $(r - 1)$ regions.

We have in all, then, $cr + (c - 1)r + v$ algebraic quantities which are connected at equilibrium by $cr + c(r - 1)$ equations. Evidently we can arbitrarily specify but $\{cr + (c - 1)r + v\} - \{cr + c(r - 1)\}$ variables if the system is to be in equilibrium. In other words, the number of degrees of freedom is

$$f = c - r + v. \qquad (1)$$

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[1] Changes in the total mass of the regions or in the concentrations of their components may be necessary to make them identical and such changes are of course permissible. The introduction of new substances into the system, however, is, of course, not permissible.

[2] The term component has the same meaning as in the usual applications of the phase rule. "As components of a system there are to be chosen the *smallest number* of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation." (Findlay, "The Phase Rule," **1904**, p. 12.) For a discussion of the term see Roozeboom, *Z. physik. Chem.*, **15**, 150 (1894); Wegscheider, *Ibid.*, **43**, 89 (1903).

[3] By the free energy of a component we shall mean the partial free energy per unit mass of the component. For a definition of the term partial free energy per unit mass, see for example Lewis, THIS JOURNAL, **35**, 1 (1913). Throughout the discussion, instead of free energy, we might have used the fugacity, activity, thermodynamic potential or any other measure of the isothermal escaping tendency.

For undivided systems where the number of regions, r, is identical with the number of phases, p, and the only variables permitted are two (the pressure on the whole system and the temperature), the above equation reduces to the familiar phase rule

$$f = c - p + 2.$$

Negligible Variables.—Since the thermodynamic properties of matter are to some degree affected by an enormous number of variables, such as intensity of illumination, strength of magnetic field, etc., we might be at a loss in applying our equilibrium rule, equation (1), to know how many variables, v, really have to be considered. In actual practice, however, such a difficulty seldom arises, since it is evident from the nature of our derivation that we only need to consider those variables upon which the thermodynamic properties of our different regions are *appreciably* dependent.

For example, we are often interested in the possibility of adjusting the value of some variable so as to bring a given region into equilibrium with the rest of the system. If the variable in question, however, is one on which thermodynamic properties are not appreciably dependent, for example, the intensity of illumination, it is evident that such adjustment is in general not possible if the values of the other variables concerned throw the free energies of the region appreciably out. Thus by negligible variables we mean those whose possible changes produce but small variation in free energy compared with the other variables determining the system.

Divided Systems with Identical Regions.—As a special case of divided systems, we find those containing regions which have identical properties. For these systems it is possible to derive a simplified form of the equilibrium rule.

If we have a system in equilibrium, it would seem as though a new region identical in properties with one of those already present could be introduced without disturbing the equilibrium or changing the number of degrees of freedom of the system, unless the free energies should be appreciably dependent on the total number of such identical regions present or what we call the "concentration of regions." Hence we might expect that r in our equilibrium rule (1) could be taken as the number of unduplicated regions, if at the same time we discard any of the v variables whose specifications are merely necessary for determining the free energies in the duplicatory regions, and also keep in mind that the "concentration of regions" of any species may also be a variable that has to be considered. As a matter of fact a simplified form of the equilibrium rule applicable to this particular case can be derived as follows:

Consider a system containing in all $(r + r_i)$ regions, where each of the r_i regions is thermodynamically identical with some one of the other

r regions. The necessary condition for isothermal equilibrium is that the free energy of each component in any region shall be the same as in all other regions. In all we shall have $c(r + r_i)$ free energies where c is the number of components. The free energy of each component of a region can be stated as a function of the $(c - 1)$ concentrations which determin the composition of the region and of certain further variables which complete the thermodynamic description of the region. Let v be *just enough variables* besides the concentrations to determin completely the free energies of the r non-identical regions, and v_i be any variables used for the thermodynamic description of the r_i duplicatory regions. We have in all, then, $c(r + r_i)$ free energies, $(c - 1)$ $(r + r_i)$ concentrations, and $(v + v_i)$ further quantities between which certain algebraic relations will exist. Each of the $(c - 1)r_i$ concentrations in the r_i duplicatory regions will be equal to a concentration in some one of the r non-identical regions, each of the v_i variables which are used for determining the free energies in the r_i duplicatory regions will be equal to one of the v variables which determin the free energies in the r non-identical regions, each of the $c(r + r_i)$ free energies will be some function of the other variables, and at equilibrium we shall have $c(r + r_i - 1)$ further equations, since each component must have the same free energy in any one region as in the other $(r + r_i - 1)$ regions. Of these latter equations, however, cr_i are not independent, since the equality of the free energies in the r_i duplicatory regions could evidently be predicted beforehand from the above mentioned $(c - 1)r_i + v_i + c(r + r_i)$ relations. In all we shall have $c(r + r_i) + (c - 1)(r + r_i) + (v + v_i)$ algebraic quantities which are connected at equilibrium by $(c - 1)r_i + v_i + c(r + r_i) + c(r - 1)$ *independent* equations. Hence the number of degrees of freedom will be

$$\begin{aligned} f &= c(r + r_i) + (c - 1)(r + r_i) + (v + v_i) \\ &\quad - \{(c - 1)r_i + v_i + c\,(r + r_i) + c\,(r - 1)\} \\ f &= c - r + v. \qquad (2) \end{aligned}$$

In this simplified equilibrium rule, which very interestingly has the same form as the general equilibrium rule (1), r is the number of non-identical regions, and v is the least number of variables whose specification, together with the concentrations in the various regions, will permit a complete thermodynamic description of each of the non-identical regions. It is obvious that among these v variables may be the "concentration of identical regions" of any species. In fact, in the case of very highly dispersed systems we find that free energies are sometimes appreciably dependent on the "concentration of dispersoid."

In case the total number of regions present is too small for the free energy of any region to depend on the "concentration of regions," we may state the simple principle that the equilibrium and number of degrees of freedom in a divided system is the same as though the duplicate regions were all removed. An evident illustration of this principle is the fact that with a number of vessels of water under a bell jar we have the same equilibrium as with one vessel of water.

In the case of divided systems in which the *only* division of phases is into identical regions, it is to be specially noted that the number of non-identical regions, r, is the same as the number of phases, p, and the equilibrium rule takes the form,

$$f = c - p + v.$$

We shall refer to this fact in a subsequent article in which dispersed systems are discussed.

Divided Systems Containing Non-Identical Regions.—We may now consider as another case of divided systems those which have non-identical regions containing the same phase. For these certain special relations can also be derived.

Consider, for example, a *one-component* system, into which we introduce a region containing the same phase as some region already present, but not identical with that region. If the regions should differ in the value of only one variable, it is evident from our definition of phase that by a continuous change in this variable the properties of the two regions could be made identical. Hence if the two regions do differ in the value of only one independent variable, for example, the pressure, it is obvious that the free energy of the two regions cannot be the same and they cannot both exist at equilibrium.[1] Equilibrium in a one-component system can only exist when non-identical regions containing the same phase differ in the value of at least two independent variables.[2]

For example, consider two vessels of water under a bell jar in contact with water vapor. Let the water in one vessel, however, be under a higher pressure than in the other, making use, for example, of a piston permeable to vapor. Equilibrium cannot exist. The water under the higher pressure has the greater free energy and will distil over into the other vessel. Equilibrium can be attained, however, if we introduce a difference in the value of another variable which describes the two regions. For example, their difference in height. By lowering the vessel which is under pressure the free energy of the water can be decreased to the same value as that in the open vessel, and equilibrium attained.

For a *two-component* system the free energy of each component in any region must be the same as in any other region. Take now a region which differs from some other region, filled with material belonging to the same phase, in the value of one variable; to give to the free energy of *both*

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[1] The tacit assumption is made that the free energy is an unambiguous function of the variable.

[2] Regions not containing the same phase can differ in the value of only one variable and be in equilibrium.

components the same value as in the second region we shall have to vary at least *two more* variables. Hence, in a two-component divided system any region to be in equilibrium must either be identical with all other regions containing the same phase, or differ in the values of at least three variables.

In general, with a system made from c components, a region can exist in equilibrium only when it is identical with some other region or differs in the value of at least $(c + 1)$ variables. Of these $(c + 1)$ variables, $(c - 1)$ may be the concentrations whose specification determins the composition of the region. Hence we may state as our general rule that a region can exist at equilibrium only if it differs from all other regions filled with material belonging to the same phase in the value of at least two variables besides the concentrations. We shall find applications of this principle in a treatment of colloids.

We may apply our equilibrium rule $f = c - r + v$ to the analysis of systems containing non-identical regions of the same phase. Consider a system of c components composed of r_d regions, containing different phases, and described by v_d variables. The number of degrees of freedom will be

$$f = c - r_d + v_d.$$

Let us now introduce, without destroying the equilibrium, r_s new, non-identical regions which contain the *same* phases as some of the r_d regions already present. Let v_s be the number of added variables necessary for the description of these new regions. If the number of added regions is small enough so that the free energies are independent of the concentration of regions the number of degrees of freedom will be

$$f = c - (r_d + r_s) + (v_d + v_s).$$

It is evident from our previous discussion that v_s must be at least as great as $2\,r_s$ if we are to have equilibrium. In the simple case that $v_s = 2\,r_s$ the equilibrium rule becomes

$$f = c - r_d + v_d + r_s.$$

Thus for each added non-identical region, containing one of the same phases already present, the number of degrees of freedom is increased by at least one, if equilibrium is maintained. This increase in the number of degrees of freedom is due of course to the fact that for each new region introduced, at least two new variables have to be introduced. As to the nature of these added degrees of freedom, however, an important distinction must be made. Since the r_s added regions in no way increase the stability of the r_d regions already present, it is evident that the *added degrees* of freedom will only permit the arbitrary specification of some of the $r_s(c - 1)$ concentrations or v_s new variables which determin the free energies in the *newly added* r_s regions.

As an example of the above principles let us consider a two-component system consisting of an open beaker containing a mixture of alcohol and water in equilibrium with the mixed vapor. Let us now introduce a new region containing a liquid mixture of alcohol and water of a different composition. The new region can exist in equilibrium with the liquid one already present only when it differs in the value of at least two other variables than the concentration. We can make these, for example, the height of the new region above the open beaker and the pressure on the new mixture, applied, for example, by a porous piston which is permeable to the vapor. Applying our equilibrium rule

$$f = c - r + v,$$

we shall have in all two components, three regions, and the four variables, temperature, pressure of the vapor (which is identical with the pressure on the open beaker), height, and pressure of the new liquid region. The number of degrees of freedom will be

$$f = 2 - 3 + 4 = 3.$$

Applying our principles, however, it is evident that of the three variables which can be arbitrarily specified at equilibrium one must belong to the newly introduced region. For example, if we specify the temperature and concentration in each of the liquid regions, all the other variables, the pressure of the vapor, the height of the newly introduced region, and the pressure on it are all determined if equilibrium is to exist.

Permanent Systems not in Equilibrium.—The mere fact that a system is apparently stable must not be taken as conclusive proof that equilibrium has been attained. A further examination of the system must be made, first, to see if the different parts of the supposed system really come into contact with each other in such a way as to permit those transferences of matter which are necessary for the attainment of equilibrium, and, second, to see if slow changes in the direction of equilibrium may not actually be in progress.

As a concrete illustration of the first of these points, let us again consider two vessels of water under a bell jar in contact with the vapor of the liquid. If the water in the two vessels is under different pressures we should not expect equilibrium, but should expect the distillation of the water under higher pressure into the vessel of lower pressure. If, however, the pistons which produce these pressures are not sensibly permeable to water vapor the system may be in a perfectly stable state. In other words, in the delimitation of our system from its surroundings we must include only such regions as permit a transference of matter.

As an illustration of the necessity of further examination to determin if slow changes towards a state of equilibrium are not actually in progress, we might consider two open vessels of liquid under a bell jar in contact with the vapor of the liquid. If the vessels are at different levels we should not expect equilibrium, but should expect the liquid to distil from the higher vessel into the lower. If, however, the liquid is very involatil the rate of distillation might be so slow as to make the state of the system apparently stable.

Interesting cases also arise when some of the components of a region are involatil (or insoluble in neighboring regions) while others come readily into equilibrium with the rest of the system. Under such circumstances it is evident that a perfectly stable state is possible without having the free energy of these involatil components the same throughout the whole system. As a matter of fact, if we have a system containing c components one of which is of such an involatil or insoluble nature that its total amount can be *arbitrarily* fixed in a regions or sets of regions, and another whose amount can be arbitrarily fixed in b regions or sets of regions, etc., it can be shown[1] that the total number of degrees of freedom in the quasi-equilibrium state will be given by the equation

$$f = c - r + v + (a - 1) + (b - 1), \text{ etc.} \qquad (3)$$

For example, consider two vessels containing salt solutions of different concentration in equilibrium with the vapor.[2] Since the salt is so involatil that it will not readily pass from one vessel to the other, its free energy does not have to be the same throughout the whole system and the amount in the two vessels can be arbitrarily specified. If now we consider as variables the temperature, pressure (of the vapor), and difference in the level of the two vessels, we have[3]

$$\begin{aligned} f &= c - r + v + (a - 1) \\ &= 2 - 3 + 3 + (2 - 1) = 3, \end{aligned}$$

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[1] This can be seen from a consideration of the method by which the general equilibrium rule, equation (1), was derived. As a condition for equilibrium was taken the necessity that the free energy of each component in each of $(r - 1)$ regions should be the same as that in the one remaining region. This gave us $c(r - 1)$ equations which had to be satisfied at equilibrium. In the case of the quasi-equilibrium, however, the total amount of one particular component, and hence its free energy, can be arbitrarily specified in each of a sets of regions into which the system can be divided. Now there will be $(a - 1)$ sets of regions which do not contain the one particular region designated in our original derivation, and in each of these $(a - 1)$ sets there will be one region in which we may arbitrarily specify the free energy of the component in question. Hence the number of equations which have to be satisfied at equilibrium is reduced by $(a - 1)$ and the number of degrees of freedom increased by the same amount. Similar considerations hold for a further component whose total amount can be specified in each of b sets of regions.

[2] My attention was called by Professor Lewis to this interesting system which does not accord with the general equilibrium rule, equation (1), because it is not in true equilibrium.

[3] a is taken as 2 since the gas space is obviously not a region in which the total amount of salt can be arbitrarily fixed.

and, indeed, if we specify the temperature of the system and the concentration of salt in the two vessels, the difference in level between them and the pressure of the vapor of the system are completely determined.

Metastable, Stable, and Indifferent Equilibria.—In the case of divided systems it is often desirable to distinguish between metastable, stable, and indifferent equilibria, and these terms will have their familiar significance. For example, we sometimes find a system which is in equilibrium, but of such a nature that the accidental disappearance of matter from one of the regions is necessarily accompanied by an increase in the free energies of the components in that region, which results, of course, *a fortiori*, in the further disappearance of matter from that region. Such regions where the accidental loss of material results in the loss of the whole region may be called metastable.

As a trivial illustration of metastable equilibria we might consider a balance with vessels containing equal weights of water on the two pans, the whole under a bell jar in equilibrium with water vapor. A slight evaporation of water from one of the vessels will cause the balance to go up on that side, thus increasing the free energy of the water on that side, and equilibrium will not again be attained until *all* the water has distilled out the upper vessel and condensed in the lower.

By stable regions, on the other hand, we shall mean those in which the disappearance of matter is accompanied by a decrease in the free energies of the region. For example, consider a number of vessels of water in equilibrium with water vapor, the same pressure being applied to the water in the different vessels by means of springs which press down on pistons permeable to the vapor. This system will be in stable equilibrium. If water evaporates from one of the vessels the piston sinks, the spring is less compressed, the pressure decreased, and the free energy of that region is lessened so that water will now distil back into that vessel, thus maintaining a permanent state.

Intermediate between stable and metastable regions are those in which the disappearance of matter is unaccompanied by any change in the free energies of the components of the region. Such regions may be called indifferent. For example, if the pressure on the pistons in the preceding illustration were produced by weights, the free energies of the liquid regions would be independent of the amount of the region present, and an accidental decrease in the amount of liquid in one of the regions would be followed neither by the disappearance of the whole region nor by a condensation which would bring the region back to its original size.

Application of the Principles.—The principles of equilibria considered in this article are not only of theoretical interest as a legitimate extension of the phase rule, but may be applied in the consideration of the various divided systems which occur in nature. Moreover, as a particular case of *divided systems*, we may consider the *dispersed systems* including the colloids in which the degree of subdivision of one of the phases, the dispersoid, has become so high that the thermodynamic properties of the system are appreciably dependent on the size or number of the regions. A description of dispersed systems from a thermodynamic point of view and an application of the principles of equilibria found for divided systems is the subject of a following paper.

Summary.—In the foregoing article the general principles of isothermal equilibria in divided systems have been considered, and a generalized equilibrium rule obtained of which the phase rule is a special case.

A *divided system* may be defined as a heterogeneous system in which at least one of the phases is present in more than one *region*, regions being divided from the rest of the system by boundary surfaces where an abrupt change of properties takes place.

The number of degrees of freedom in a divided system is given by the equation

$$f = c - r + v$$

where c is the number of components, r the number of regions, and v the least number of variables whose specification, together with the compositions, is necessary for the thermodynamic description of each of the regions. No restriction was made as to the number or nature of the variables.

For systems containing thermodynamically identical regions, r may be taken as the number of non-duplicated regions, and v the number of variables necessary for the thermodynamic description of these non-duplicated regions. For the case that the only division is into thermodynamically identical regions the equilibrium rule assumes the form

$$f = c - p + v$$

where p is the number of phases.

A special analysis was made of the equilibrium in systems containing *non-identical* regions of the same phase, which showed that such regions must differ from each other in the value of at least two variables besides concentrations, that each new such region, put into an equilibrium system, introduces at least one new degree of freedom, and that the degrees of freedom thus introduced are not identical with those which the system already possessed.

Discussions were given of the conditions under which variables may be neglected, of the conditions in permanent systems which are not in equilibrium, and of metastable, stable, and indifferent equilibria.

The principles developed will find application in a classification of dispersed systems including the colloids.