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Lee O. Case's "Elements of the Phase Rule", Introduction and Explanation

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I. SYNOPSIS

The phase rule is a part of physical chemistry which is normally despised by modern chemists. It is regarded as being "old-fashioned" and irrelevant in the modern contexts of theoretical chemistry based on quantum mechanics and statistical mechanics.

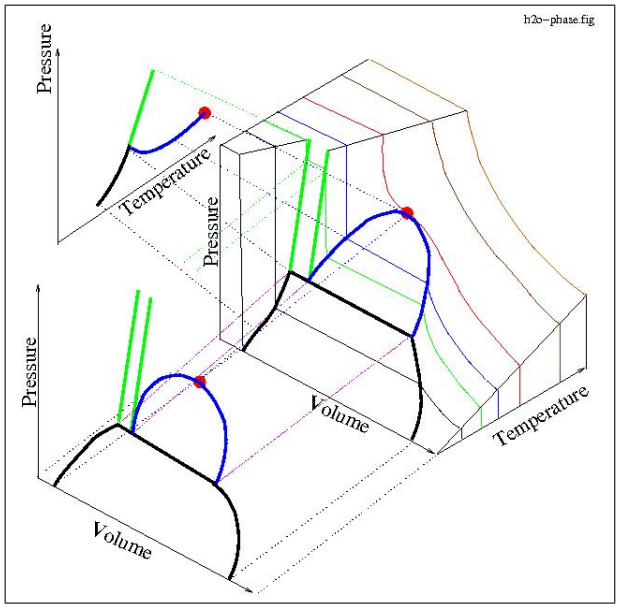

FIG. 1: A Three-Dimensional representation of a simple one-component phase diagram. I used this in teaching freshman chemistry many times, and include it here just for fun (cwd).

As I prepare to retire, I've been cleaning my bookcases of the (almost) tons of books that I've accumulated over the past 46 years of teaching. In doing so, I came across L. O. Case's "Elements of the Phase Rule" and got quite nostalgic. I took Prof. Case's graduate course in Phase Rule in 1960 (I think). It was a preventative innoculant to teaching nursing chemistry, a course whose TA's were inundated with young women seeking help during office hours. In terror of such an assignment, I chose this course, which overlapped with the nursing chemistry course, so that I could not be assigned to it (shame on me).

Anyway, I came across this typewritten copy of Case's book, remembered him for his teaching of physical chemistry lab [1] So, I've scanned his text and annotated it, and that is what you're seeing. The original was copyrighted in 1939 (as can be seen by the length of the sentences employed). My annotations usually will have an accompanying "cwd" indicator.

Since the subject is falling into the crack of obsolescence I thought it might be worthwhile to make sure that it lives as long as this library, this "digital commons" exists. *Sic transit gloria mundi.*

II. INTRODUCTION

The tendency of isolated chemical systems in a uniform environment to approach an eventual state of equilibrium, such that thereafter no further change in the measurable properties of the parts of the system can be observed, is one of the most fundamental observations of chemical experience. The state of equilibrium therefore forms one of the chief concerns in a study of physical chemistry and in the application of physical chemistry to technical problems. Even for systems which are not in a state of equilibrium, the knowledge of the limit imposed by that state is often of great value.

When an attempt is made to classify the various types of equilibria which may occur, the greatest diversity appears. The uniform distribution of a gas in a mixture throughout the volume available, the uniform pressure eventually exerted by the evaporation of a liquid into a closed space, the distribution of a solute between two mutually saturated liquids, the limit of solubility of a salt imposed by the condition of saturation, the production of distillates of fixed composition from continuous run distillations, the stability of hydrated crystals in contact with an atmosphere of controlled relative humidity, as well as the numberless varieties of chemical reaction equilibria, represent well-known but at first sight unrelated phenomena. The apparent lack of connection among these phenomena is no doubt enhanced by the fact that different quantitative generalizations are used in the description of each; among these may be cited: the Clausius-Clapeyron equation, Dalton's Law, Raoult's Law, the Distribution Law, the Law of Mass Action. Evidently the introduction of a more general principle which will serve equally for the description of all the examples of equilibrium met with will be well worth while.

Logically the approach to such a principle is through

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the Science of Thermodynamics. Indeed an exact statement of every equilibrium problem is possible in precise thermodynamic terms. Unfortunately the statement of a problem in precise terms is only the first step in its solution. Chemical substances are still marketed and used in terms of weights and concentrations rather than entropy units and activities, and in the translation of thermodynamic into practical units such extensive simplifications are still necessary that the most valued quantitative generalizations possess a range of validity which is relatively limited in comparison with the entire field of experimentally accessible knowledge. Consequently the application of thermodynamics, valuable as it is, can be expected not to replace, but at the most only to redirect, experimental effort.

Thus the investigator of chemical equilibrium must continue to collect data concerning vapor pressures, solubilities, melting and boiling points, and other physical properties. However, although thermodynamics is still not in a position to predict numerical values for these important quantities, it remains the most valuable mass of experimental data relating to equilibrium, once it has been collected The thermodynamic generalization which makes this most directly possible is known as the Phase Rule, first enunciated by J. Willard Gibbs in 1876, and since extended and applied by so many investigators that its literature has grown to be one of the most voluminous known to physical science.

The merits and demerits of the phase rule both derive from its generality. On the one hand, the results obtainable from it are, as far as they go, perfectly precise for systems of the most diverse types in a true state of equilibrium under accurately stated conditions. Consequently it serves to reveal similarities in the behavior of different systems which might be otherwise unsuspected, it conserves experimental labor by indicating the directions in which effort may be profitably expended and it facilitates the critical evaluation of the experimental data obtained. On the other hand, since the results obtainable from it are purely qualitative in nature, it not only can predict no numerical values for the conditions of equilibrium but it cannot even indicate what particular equilibria will be found in a given system.

In form the phase rule represents one of the simplest possible of relations among three variables, viz., $V = C+2-p$. If there are any difficulties connected with its use, they must clearly depend not upon the equation itself, but upon the interpretation of the quantities involved in it and of the results derivable from it. It is this interpretation which constitutes the study of the phase rule.

III. THE PHASE RULE A RULE OF ALGEBRA

As a matter of fact the phase rule represents simply the application to certain chemical and physical problems of the familiar rule of algebra that the number of independent equations in a set of simultaneous equations must be equal to the number of variables involved in order that the values of the variables shall be fixed [2]. The ultimate understanding of the phase rule greatly assisted by pursuing a little further the algebraic analogy before proceeding with the development and application of the phase rule itself. If a number of variables U are connected by a set of J independent equations, then the rule just referred to may be stated by saying that the number of missing equations, or of additional equations required for a complete solution, is $V = U - J$. If $U > J$, the additional equation necessary might be supplied by arbitrarily assigning numerical values in general to any V of the variables; corresponding to each such arbitrary selection of course different numerical values would result for the other variables. If $U = J$, then no choice whatever is left, all the variables being fixed by the relations already existing. If, finally, $U < J$, (remember that J is the number of *independent* equations), then too many restrictions have been imposed upon the variables might be called the "variance" or the "number of degrees of freedom" of the system of simultaneous equations.

A more general aspect of the phase rule can be illustrated with reference its algebraic counterpart. Even if $U > J$ the problem need not be completely barren of useful results, since by elimination of as many as possible of the variables among the set of equations, a simplified relation may be obtained among the remaining variables. Evidently, since a single equation must remain, the limit of this process is the elimination of $(J-1)$ variables, the variables remaining in the resulting equation being therefore $U - (J-1) = (V+1)$ in number. Of these, V are said to be independent, one dependent. (The choice as to which variable is to be considered the dependent one is of course arbitrary.) Consideration of the nature of the single equation thus obtainable not only verifies the earlier statement that the assignment of definite values to V of the variables will fix the remaining one, but also introduce the idea of continuous variation, i.e., that the dependent variable varies in general as (sic) continuous function of the V independent ones. It is this property which accounts for the name "variance" assigned to the symbol "V" in the phase rule expression. The "variance" in other words represents the number of *independent* variables which remain after as many as possible have eliminated among the relations connecting them.

Another point that may be noted in this connection is that since different combinations of variables may be selected for elimination, as many different functions may be thus derived as there are possible combinations of $(V+1)$ variables in a set of U variables . From the theory of permutations and combinations , this number of possible functions is

$$\frac{U!}{(U-V-1)!(V+1)!};$$

convenience in a given case will dictate which of these are selected for further study.

In order to appreciate the nature of the functions obtained by the process outlined above, one might naturally employ graphical methods, corresponding values of the variables being plotted in a suitable coördinate system. If the variables happened to relate to a chemical system in a state of equilibrium, the result would be a "phase rule diagram". While clearly to be recommended in the

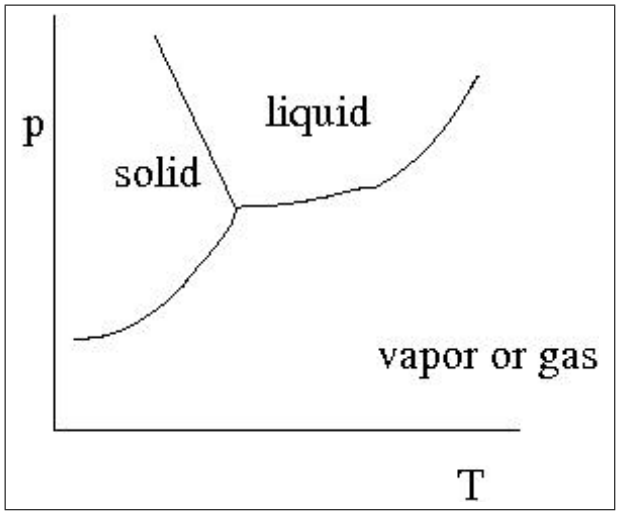

FIG. 2: A simple one-component phase diagram

algebraic case, the graphical treatment is indispensable for the corresponding chemical problem, since usually the functions with which one has to deal in the latter connection are given, not in the form of equations, but as collections of experimental data,, It is probably this situation which leads to the greatest difficulty in gaining a proper appreciation of the phase rule. The lack of definite algebraic equations with which to work leaves a great gap between the simple statement of the rule and the construction and use of phase rule diagrams. Consequently, unless conscious effort is directed toward maintaining this important connection, a so-called "study" of the phase rule is apt to degenerate into the memorization of certain specific diagrams for particular systems, for which purpose the phase rule itself would be quite unnecessary. It is for this reason that in the present treatment continued attention will be given to this intervening ground between the rule itself and the diagrams which it is intended to clarify and correlate

IV. DERIVATION OF THE PHASE RULE

As has been indicated above, the object of the derivation is to obtain a result for the number of independent variables which are necessary for the description of a state of equilibrium. This number, designated by V, is obtained from the expression $TV = U - J$, where U is the total number of variables and J is the number of independent relations connecting them. The application of this principle to the problem of chemical equilibrium requires

- a decision as to what constitute the variables and relations for a state of chemical equilibrium,
- proper enumeration of these quantities, and
- reduction of the expression resulting from a substitution of the values for U and J in the equation above.

Before this can be done, however, it will be necessary to obtain a more precise idea of the meaning of some of the terms used in the discussion of the phase rule. The first of these is the term "phase" . A "phase" may be defined as any homogeneous portion of matter bounded by a physical, surface, not necessarily continuous. Examples are: a gas, a pure liquid, a solution, a homogeneous solid. Note that solutions occur in all three physical states– gaseous, liquid and solid – these being completely indistinguishable from the standpoint of the phase rule. By a "solution" is meant simply a homogeneous portion of matter, the composition of which is continuously variable at least within a certain range. A "continuous series of solutions" is spoken of if the limits of the composition range are the pure individuals in the same physical state; otherwise limits may be imposed by one or more so-called "saturated solutions". Perhaps this is the place to point out that while all degrees of solubility are met with in the liquid and solid states, all gases are completely soluble in one another in all proportions; it is therefore impossible to have more than one gas phase. The word "homogeneous" as here used means "homogeneous with respect to ordinary means of chemical and physical analysis." The boundary cases presented by colloidal solutions are not included in ordinary phase rule discussions .

A system is said to be "homogeneous" if it consists of a single phase, "heterogeneous" if of more than one phase.

In defining the term "phase" the statement was made that the physical boundary need not be continuous . Thus a liquid forms a single phase even if broken up into drops. Similarly a collection of crystals of $CuSO_4{:}5H_2O$, constitutes a single solid phase. On the other hand, a mixture of crystals of $NaC\ell$ and sugar, no matter how intimately mixed, consists of two phases since within every crystal of the same substance the properties are uniform, and different from those of the other substance. As a matter fact, in the case of difficultly resolvable mixtures, the phase rule itself sometimes can be used to determine the correct number of phases.

A more difficult concept is presented by the term "component". Further examination of this, however, will be deferred until later, since its definition will appear in the course of the derivation. Instead, at the outset, one of the terms, "constituent" or "chemical individual" will be employed, by which is meant any substance which can be represented by a definite chemical formula. Examples are: H_2O, $(H_2O)_2$, $CuSO_4{:}5H_2O$, $SO_4{}^{=}$.

The last preliminary to be disposed of before proceeding with the derivation is the delimitation of the conditions imposable from outside the system with respect

to which the equilibrium state is to be established. For the customary form of the phase rule expression, these "external" conditions are (only) pressure and temperature. This means that effects of such forces as those due to gravitation, electrical and magnetic fields, and surface and light energy are excluded. It should be understood not that these factors must be left out of consideration, but only that with their omission a sufficiently broad and useful field of investigation is left to include most of the problems of practical interest.

With these preliminary ideas in mind, it is now necessary to decide what constitutes the variables required for the description of a state of chemical equilibrium. Perhaps the easiest way to answer this question is to suppose that one has a system already at equilibrium and wishes to duplicate it; what information will be required? Suppose that the parts or"phases" of which the system consists be separated from one another without any other changes in their condition (for example, by a set of impermeable walls). Then each phase is separately in equilibrium with its environment. It is evident that any particular phase can be reconstructed (except as to shape) if the mass of each constituent and the temperature and pressure are known. If, however, it is desired to reproduce only the specific properties of the phase (density, refractive index, specific internal energy, etc.) the information necessary is further limited. For, if the phase as a whole is in equilibrium, any portion of it is also in equilibrium with the remainder, for example, that portion which has a volume of one liter, or which contains one thousand grams of one constituent, or which comprises a total of one or one hundred mols of all the substances present. But these specifications are precisely of the type which serve to define the so-called concentration scales, all of which have the well-known characteristic that the number of independent concentrations in a set is always one less than the total. (This characteristic is perhaps most immediately evident for the mol fraction or weight per cent scales, but is similarly recognizable for all.) Now it will be evident that any specific property must be the same in the entire phase as in that portion of the phase which contains the basis of the concentration scale and hence such properties depend, in addition to pressure and temperature, only upon the independent phase concentrations, in number one less than the number of constituents in the phase. The concentrations may, of course, be in any convenient units, e.g., weight-ratios, volume-ratios, mol-ratios, weight fractions, mol fractions, mol percents, molal concentrations etc.

Hence, in order to produce an entire system identical In all its specific properties with the one considered, the following quantities must be known (an "x" represents a concentration, subscripts refer to constituents, superscripts to phases):

For phase 1:	$x'_1, x'_2, x'_3, \cdots, x'_{n-1}, p, T$
For phase 2:	$x''_1, x''_2 x''_3, \cdots, x''_{n-1}, p, T$
For phase 3:	$x'''_1, x'''_2 x'''_3, \cdots, x'''_{n-1}, p, T$
$\vdots$	$\vdots$
For phase P:	$x^p_1, x^p_2 x^p_3, \cdots, x^p_{n-1}, p, T$

(Since in this list the pressures and temperatures have not been distinguished by accents, it is clear that the assumption has been made that presure and temperature are uniform throughout the system at equilibrium. Like the other restrictions previously introduced, this is not absolute requirement, but obviously a practical one, which will lead to results applicable to the great majority of systems of interest.)

The sum of all the quantities in the above list represents the total number of variables, U, for the system in equilibrium under the specified conditions. Hence, if P represents the number of phases, and N the number constituents or chemical individuals,

$$U = P(N-1) + 2 \tag{4.1}$$

It is important to note that, in addition to temperature and pressure, the variables include only *phase* concentrations, not *total* concentrations.

Now it is found that, due to the existence of the state of equilibrium, not all these variables are independent, so that it is necessary to know the values of not all but only some of them in order to define, i.e., reproduce, the system. Algebraically, this means only that certain relations exist among the variables when equilibrium is established. The next step, is to enumerate these relations.

In carrying out this step, it is found that the relations in question can be conveniently grouped into two types. The first of these, which may be described as "distribution relations" may be introduced by means of an example. Suppose that, at a given temperature, gaseous CO_2 is brought to equilibrium with ether and water; the CO_2 will distribute itself in a definite way among the two liquid phases and the gas phase, such that to each value of the partial pressure of CO_2 in the gas phase there correponds a definite value of its concentration in each liquid phase. It is true that even in this relatively simple case the distribution probably will not follow the simple Distribution Law,

$$x'_1 = k_1 x''_1 = k_2 x'''_1$$

(in which k_1 and k_2 are distribution *constants*), over any considerable range of the variables. Whether or not the simple Distribution Law holds, however, the state of equilibrium may be regarded as one in which the tendency of CO_2 to escape from any one of the phases is just balanced by its tendency to leave some other phase and enter the one in question. Various quantities have been defined which accurately measures this escaping tendency from a given phase and which for a given individual most be the same in all phases at equilibrium, e.g., the fugacity,

the partial molal free energy or the chemical potential, etc.

For any one constituent in a given phase, each of these measures of tendency will depend upon the concentration of the constituent the pressure and temperature. But still more generally, it will depend upon the independent concentrations of all the other constituents of that phase. (Thus, in the specific example cited above, the fact that at equilibrium some ether will be present in the water phase will be expected to alter the solubility of CO_2 in that phase from the value which it would possess if the ether were absent.) Without particularizing as to just which thermodynamic function is to be employed, the equality of the escaping tendencies for the same constitutent in different phases may be formulated as follows:
For constituent 1:

$$\begin{aligned} f_1(x'_1, x'_2, \cdots, x'_{n-1}, p, T) &= f_1(x''_1, x''_2, \cdots, x''_{n-1}, p, T) \\ &= \cdots \\ &= f_1(x^p_1, x^p_2, \cdots, x^p_{n-1}, p, T) \end{aligned} \tag{4.2}$$

For constituent 2:

$$\begin{aligned} f_2(x'_1, x'_2, \cdots, x'_{n-1}, p, T) &= f_2(x''_1, x''_2, \cdots, x''_{n-1}, p, T) \\ &= \cdots \\ &= f_2(x^p_1, x^p_2, \cdots, x^p_{n-1}, p, T) \end{aligned} \tag{4.3}$$

For constituent n:

$$\begin{aligned} f_n(x'_1, x'_2, \cdots, x'_{n-1}, p, T) &= f_n(x''_1, x''_2, \cdots, x''_{n-1}, p, T) \\ &= \cdots \\ &= f_n(x^p_1, x^p_2, \cdots, x^p_{n-1}, p, T) \end{aligned} \tag{4.4}$$

Thus, for any one constituent, there occur a set of "P" functions which for equilibrium must be equal to one another taken in pairs, these form a set of $(P-1)$ *independent* equations. For the "N" constituents, then, the"U" variables are connected by a number of "distribution" equations:

$$G = N(P-1)$$

If no other relations were involved, the excess of variables over relations connecting them, or the variance, would be, then:

$$\begin{aligned} V = U - G &= P(N-1) + 2 - N(P-1) \\ &= N + 2 - P \end{aligned} \tag{4.5}$$

Up to this point it has been assumed that each constituent is present in every phase. While elementary considerations might seem to indicate as a necessary condition for a state of true equilibrium, nevertheless, from a practical point of view it will usually be preferred to consider individual concentrations as zero if they are too small to affect appreciably the state of the phase taken by itself. From the derivation given above it is obvious, however, that the real or assumed absence of any one actual constituent from a given phase does not destroy the validity of the phase rule, since the consequent disappearance of a concentration variable is accompanied by the loss of a corresponding equation.

The derivation given above and the resulting Equation 4.5 do involve an assumption, however, which is not usually tenable. Since each of the "N" sets of equations included in "G" relates to the distribution of the *same* individual among different phases, the assumption is implied that there are no equilibria among the different individuals, either in the same or different phases. In other words, no chemical equilibria have been considered. But, if such equilibria do exist, they clearly furnish additional restrictions upon the variables – pressure, temperature, and phase concentrations – and should be counted among the relations connecting these variables. Denoting the number of such additional equations involving the variables by "E", the total number of equations is $J = G + E$ and the variance in the general case becomes:

$$V = U - G - E = (N - E) + 2 - P$$

The "number of components", C, is now defined as

$$C = N - E \tag{4.6}$$

giving the final form of the phase rule:

$$V = U - G - E = C + 2 - P \tag{4.7}$$

Some further consideration should be given to the two quantities E and C. First of all, as to the equations "E":

- Since, in the development of the phase rule, it is only the *number* and not the form of the relations which is involved, it is not at all necessary that the simple Mass Action Law should hold in terms of concentrations or partial pressures. The Mass Action Law does hold rigorously, by definition, when, for example, fugacities are employed in place of partial pressures, and since the fugacity of a chemical individual is some function of the concentrations and of the pressure and temperature, there must exist (whether or not of known form) a relation connecting the variables for the individuals involved in a chemical equilibrium.

- Obviously, only the *dependent* equilibrium relations should be counted in the total for "E", since an equation which can be derived by combination of

others already given involves no new restrictions on the variables.

As an example, consider the systems C(s), CO(g), CO_2(g), O_2(g). Here $P = 2$ and $N = 4$. What is C? The following equilibrium reactions can be written for the substances concerned:
(1) C(s)+ O_2(g) = CO_2(g)
(2) C(s) $+\frac{1}{2}O_2$(g) = CO(g)
(3) CO(g) $+\frac{1}{2}O_2$(g) = CO_2(g)

Only two of these are independent, however, since the third equation can be obtained by subtraction of the second equation from the first. Hence, $E = 2$ and $C = N - E = 4 - 2 = 2$.

It may be noted in this example that *chemical* equations have been written instead of the corresponding *mass action* equations involving the phase rule variables although the latter are the equations "E" actually desired. This procedure will always be sufficient for phase rule purposes since, as previously stated, it is only the *number* and not the *form* of the equations which is required. In other words, for the sake of simplicity the chemical equations can be taken to symbolize the corresponding mass action expressions.

- In addition to mass action expressions, there may be other restrictions upon the variables either inherent in, or arbitrarily imposed upon the system. If so, they also must be counted in determining the number of relations "E". Thus, in the case of electrolytic solutions, an inherent restriction is the requirement of electroneutrality, i.e., that the sum of the equivalent concentrations of the negative ions must equal the sum of the equivalent concentrations of the positive ions.

An example of an arbitrary restriction may be given with reference to the dissociation of $NH_4C\ell$,

$$NH_4C\ell(s) \rightleftharpoons NH_3(g) + HC\ell(g)$$

which with no restriction as to the relative concentrations of the products, furnishes a system of two components, $(C = 3 - 1)$. If the system is to be formed from pure $NH_4C\ell$, however, the arbitrary restriction is implied that the concentration of NH_3 shall equal that of $HC\ell$. Hence $C = 3 - 2 = 1$.

In this connection it is important to remember that a restricting equation must involve a relation among some of the variables "U" pressure, temperature, and <u>phase</u> (not <u>total</u>) concentrations. Thus, in contrast to the $NH_4C\ell$ system just discussed, the system

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

remains one of two components even if it is formed by the partial dissociation of pure $CaCO_3$ since the resulting formation of CaO and CO_2 in equivalent <u>amounts</u> puts no additional restrictions upon the phase concentrations.

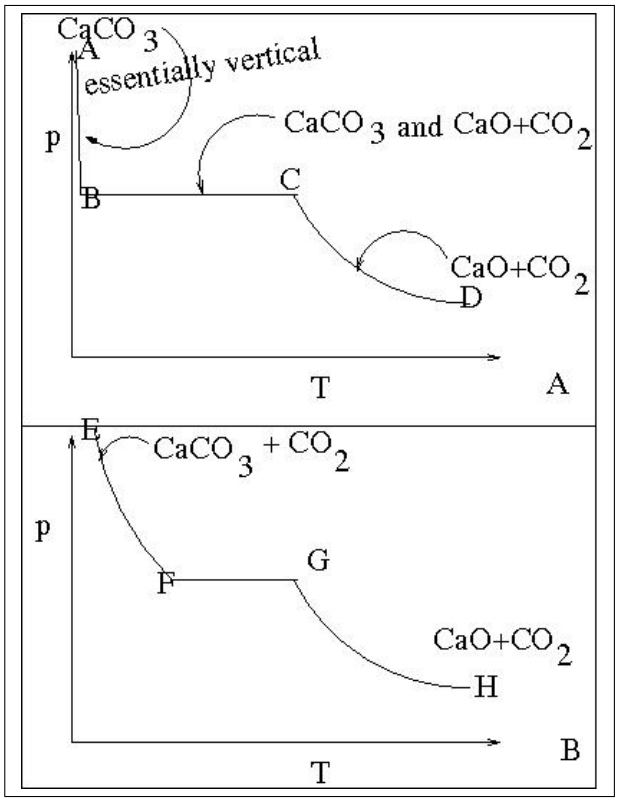

FIG. 3: The calcium carbonate figure under two cases. In Case A, we have pure calcium carbonate decomposing to calcium oxide and carbon dioxide(g). In case B, we have (at high pressure, calcium carbonate and carbon dioxide(g). In both cases, when calcium carbonate(s),calcium oxide(s) and carbon dioxide(g) are all present, the K_p equation holds.

A. More on the one/two component nature $CaCO_3$ (cwd)

Assuming one component

C=1	V = 3-P
"	V= 2 if P=1
"	V = 1 if P=2
"	V = 0 if P=3

while assuming 2 components

C=2	V = 4-P
"	V=3 if P=1
"	V= 2 if P=2
"	V = 1 if P=3
"	V = 0 if P=4

As one can see from the two tables (above), the degrees of freedom depend on the number of components one has in the system, as it is automatic to assume that if one started with pure $CaCO_3$ one would have a one component system, while if one started with $CaCO_3$ and, say,

CaO one would have a two component system, exemplified by an arbitrary mixture of CaO and CO_2 which only fortuitously could be stoichiometrically equivalent to $CaCO_3$.

In Figure 3 the path AB in essentially identical (in form, not shape) to path EF. Likewise, path CD is equivalent to path GH. There is no distinguishing them in terms of the phase rule.

The paths BC and FG represent in both cases three phase equilibria, since all three phases are present! If this were a one component system, then V would be zero, which is not true. Therefore, we conclude (with L. O. Case) that this is a two component system, regardless of "common sense"!

V. RETURNING TO THE MAIN DOCUMENT

Once the equations "E" have been properly enumerated in accordance with the principles given above, the determination of that most troublesome concept, the "number of components", reduces to simple substitution in Equation 7. Now since two methods are available for the calculation of V, viz.,

$$V = U - G - E$$

and

$$V = C + 2 - P$$

it might seem that the existence of this partial check will ensure the correctness of the analysis. Unfortunately, this is not the case. It is true that an error in one of the quantities U, G, N, and P will be thus located, but the most likely source of error is in failure to count properly the equations "E", in which event V will be in error by the same amount according to both equations. Nevertheless, although the determination of the number of components remains the most critical step in the analysis, it is believed that the reduction of the concept to the formalism of equation (4.6 should at least mitigate the difficulty in comparison with the application of other methods. At least it may be said that a correct determination of the number of components for a given system will require either formal enumeration of the equations "E" or an instinctive recognition that they exist.

At first sight it might appear that the difficulty in connection with the idea of "number of components" might be satisfactorily avoided by merely retaining for the phase rule expression the equation $V = U - G - E$ without further reduction. That this is not the case is due to the desirability of correlating and comparing the conditions for different types of equilibria in the same chemical system. In other words, from the chemical point of view a much better idea of the relations of interest is gained by comparing the behavior of the same system as it exists in different combinations of phases (fixed C, varying P) than by comparing, for example, different systems involving the same numbers of variables with different numbers of relations connecting them (fixed U, varying J), When the former choice is made the basis of comparison, it is perhaps unfortunate that the concept of"number of components" is so troublesome that the advantages of its use in correlating the behavior of different systems more than compensate for the difficulties occasionally encountered in its correct determination.

At this point it is recommended that, as a means of fixing the basic principles in mind, some practice be gained in the determination of the quantities U, G, N, E, C, P and V for illustrative cases of equilibrium in actual systems. For this purpose a summarization of the rules for the determination of these quantities will be helpful. These are:

- Count one W for each chemical individual, i.e., substance represented by a distinct *chemical* formula.
- Count one G for each independent distribution of the same individual between a pair of phases.
- Count one E for each additional relation among the concentration variables. These include: (a) mass action equilibria, i.e., independent equilibria among different individuals, whether in the same or different phases; (b) inherent restrictions, e.g., electroneutrality; (c) arbitrary restrictions, imposed by the experimenter.
- Variables, U. For each phase, count one less concentration variable than there are individuals in that phase. The sum of all these for all the phases, plus 2 for pressure and temperature, constitutes the number of variables, U.

The remaining quantities are then obtained from the definition equations previously given. The following illustration should suffice:
System consisting of: H_2O(s), $CuSO_4$:5H_2O(s); solution containing H^+, Cu^{++}, $SO_4^{=}$ in $H_2O(\ell)$; H_2O(g).
N = 5. ($CuSO_4$:5H_2O, H_2O, H^+, Cu^{+2}, SO^{2-}.)
P = 4. (two solids, one liquid, one gas)
U = 5. (Any three of the 4 concentrations in the solution, p, T.)
G = 2. (H_2O(s) $\rightleftharpoons$ H_2O(solution) $\rightleftharpoons$ H_2O(g).)
E = 2. ($CuSO_4$:5$H_2O \rightleftharpoons Cu^{2+} + SO_4^{2-} + 5\ H_2O(\ell)$;
$[H^+ + 2[Cu^{2+}] = 2\ [SO_4^{2-}]$
$C = N - E = 5 - 2 = 3$
$V = U - G - E = 5 - 2 - 2 = 1.$
=C+2-P = 3+2-4 = 1.

VI. PHASE RULE VARIABLES.

Although in the reduction of the phase rule to its final form, the quantities U, G and E disappear, it is advisable to retain the term U in the later discussion in order to indicate clearly the nature of the results predicted by the phase rule. Now that the term "number of components" has been defined, however, it will be

best to redefine U in terms of this quantity rather than in terms of the number of individuals. This may be done as follows: Introduction of the definition $C = N - E$ into the derivation of the phase rule gives:

$$\begin{aligned} V &= P(C+E-1)+2-(C+E)(P-1)-E \\ &= [P(C-1)+2]-[C(P-1)] \\ &= U-J \\ &= C+2-P \end{aligned} \tag{6.1}$$

as before. However, in the light of this transformation, there may now be adopted as the definition of the number of variables in the general case:

$$U = P(C-1)+2 \tag{6.2}$$

instead of the earlier expression $U = P(N-1)+2$. Algebraically this operation signifies merely the utilization in a preliminary step of the equations E, together with $E(P-1)$ of the equations G in order to reduce the number of variables remaining by EP. The practical result is that in counting up the number of concentration variables for the system it will be necessary to enumerate concentrations only of components, instead of chemical individuals. Hereafter U as defined by Equation 6.2 will be referred to as the number of "phase rule variables."

A second simplification may be made in a practical sense when it is recalled that the expression for U still implies the presence of every component in every phase. If, however, within the limits of accuracy of the phase rule data, the concentration of a given component in a certain phase is too small to affect appreciably the other phase rule variables it is better to neglect it. Hence the practical rule for determining the number of phase rule variables becomes: For each phase the number of concentration variables is one less than the number of components in that phase. The sum of all such quantities for all the phases, plus 2 (for pressure and temperature) constitutes the number of phase rule variables.

It will be recognized that this is a practical definition only and that later refinements of experimental technique may make significant, contribution that were previously too small to be considered.

VII. PHASE ROLE DIAGRAMS

A. General

Before considering successively particular features of systems containing one, two, three and four components, it is desirable to summarize briefly the point of view and the implications of the phase rule for equilibrium systems in general:

Any system in a state of equilibrium involving one or more phases can be completely described in terms of selected independent variables, chosen from a larger set which includes all its phase concentrations (for most cases of interest) pressure and temperature. It is the function of the phase rule to permit the calculation of the number of these independent variables from the number of phases and the number of components in the system. The latter may be equal to the number of chemical substances contained in the system, but is frequently less than this due to certain special restrictions imposed upon the system either by nature or by the experimenter. Knowledge of the number of independent rariables, designated "V", permits the prediction of the existence of a variety of functions which describe the dependence of one of the variables upon V of the remaining ones. Owing to the fact that the functions in question are commonly not given explicitly but only in the form of numerical data, they are usually studied by graphical means. A graph showing the trend of some of these functions for some of the possible equilibria for a given system is called a "phase rule diagram." The different types of equilibria are represented on such a diagram by means of points, lines and surfaces. In phase rule language, these features may be completely described in terms of the variance: "V", a point (in any number of dimensions) is characterized by a variance of zero, a line by a variance of one, a surface by a variance of two.

At this point, a limitation of the graphical method becomes evident, in that the number of spatial dimensions available for the purpose cannot exceed three in a given diagram. While there is nothing more mysterious about a relation connecting for example five variables than about one involving two only, the former cannot be illustrated directly in physical space. Consequently some ingenuity must be exercised in applying graphical treatment to phase rule data in more complicated cases. The general method of overcoming the difficulty mentioned is to reduce the number of dimensions required by placing appropriate restrictions upon the system; among the most obvious of these restrictions are those of constant pressure, constant temperature, or both. As soon as the remaining variance for the smallest number of coexisting phases which it is desired to illustrate has been reduced to two, three dimensions are obviously sufficient.

Some of the special types of diagrams which have been found most useful for the treatment of particular kinds of systems will be briefly described in the following pages.

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[1] I think he was forced to teach this in his old age, and the phase rule course, because he was regarded as an old fashioned physical chemist, but that just might be my interpretation given my own circumstances.

[2] We would say “possesses a unique solution”.