10,000; the results as interpolated from his curve are given in Table II, along with the appropriate values of $c(=\alpha/22.4$, where α is the absorption coefficient) and of the solubility-product calculated on the basis that nk_1/k_2 is 5600.

K'_C is given by the expression $\log K'_C = \bar{8}.087 - 0.006\ t$; whence one can, using 5600 as the value of nk_1/k_2, calculate the solubility of calcite for any partial pressure of CO_2 at any temperature up to 30°.

Summary.

The graph showing the concentration of calcium in the solution at equilibrium in the system $CaO-H_2O-CO_2$ is made up of three curves, along which the stable solid phase is hydroxide, carbonate, bicarbonate, respectively. The first extends only up to values of P, the partial pressure of CO_2, of about 10^{-14} at 16°; the second, starting from the transition point, decreases to a minimum and then rises again, as the value of P increases continuously, until P is about 15 atm.; beyond the second transition point bicarbonate is the stable solid phase. Along the whole course of the graph, all three ions OH^-, $CO_3^=$, HCO_3^- are present at relative concentrations depending upon P; so in this, as in other analogous cases, the solubility curve ascertained by experiment would have different forms according as one determined one or other of the several molecular species in solution. Thus the maximum concentration of $CO_3^=$ occurs when the solubility—as measured by the concentration of calcium in solution—is a minimum; and it is only within a restricted range of P that the base associated with $CO_3^=$ is more than a fractional proportion of the total base in solution.

The transition pressure at which both hydroxide and carbonate are stable, may be calculated either from the solubilities of hydroxide and carbonate or from their thermal dissociation pressures; these two absolutely independent methods yield results surprisingly concordant, a circumstance which demonstrates the essential correctness of the views discussed in this paper.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

SUGGESTION CONCERNING THE STATEMENT OF THE PHASE RULE.

BY THEODORE W. RICHARDS.

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The most serious difficulty of the Phase Rule for beginners lies in the definition of the word "component," of which many varying definitions have been given by various authorities. Of these most are entirely legitimate, although they may lead to different choices as to the number of components in special cases.[1] The difficulty lies in the fact that the restrictions imposed often cause the number of "components" to be different from the number of individual chemical substances taking part in the reaction.

No attempt will be made here to give all the varying definitions or explain the limitations which must be imposed upon them. The object of this note is to advocate briefly a different method of treatment, perhaps more generally acceptable to chemists and more easily comprehensible by beginners than most of the others. Doubtless it has been used before, but it does not seem to have been clearly stated or commonly recognized. The idea is this: instead of stating the Phase Rule in a very simple equation and placing all the burden of incomprehensibility upon the component, this method abandons the complex older idea of the component and substitutes another, that of the chemical "individual," or "constituent" which is easily understood by the chemist, and places all the necessary restrictions in definite form in a somewhat more complex but easily comprehensible equation defining the Phase Rule.[2]

According to this plan, the definition of the chemical "individual" is as follows: *The* INDIVIDUALS *of any reacting system are the separate chemical substances,* UNDECOMPOSED IN THE REACTIONS CONCERNED, *which are necessary to construct the system. The number of such individuals to be chosen is the smallest number necessary to construct the system.*

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[1] See for example "The Phase Rule" by Alex. Findlay, p. 12 (London, 1904).

[2] Except for the fact that in most minds conversant with the subject the term "component" indissolubly involves restrictions, it would be better to retain this old term, giving it the new and simpler meaning. Professor Lash Miller convinced me that on this account the change of meaning is undesirable. The word "individual," however (suggested in conversation by Professor A. B. Lamb) seems to answer the requirement. The word "constituent" would be almost as good, but not quite so definite and distinctive. This, then, might be used; indeed it has already been used in a sense not very different from the present by Trevor (*J. Phys. Chem.*, 1, 22 (1896)); but his use of the word was somewhat freer than that needed here, as was also Bancroft's ("The Phase Rule," p. 227 (1897)). The qualification given above "undecomposed in the reactions concerned" is a very important one for the present purpose, although it does not appear in the earlier definitions; according to Bancroft's application, n_r would sometimes be a minus quantity (p. 230, "The Phase Rule"—a suggestive book which did much to promote study of the subject). The interesting very recent treatment of Washburn ("Principles of Physical Chemistry, N. Y., 1915") is yet different, involving another idea called the "composition-number," although of course the fundamental idea is the same, as indeed it must be in any sound treatment of the Phase Rule. This present method of statement adopted above makes no attempt to define the kinetic mechanism needful for achieving the result. It records simply the facts, and may be made subject to any interpretation applicable according to any other formulation which likewise expresses the facts. Reference may be made to the interesting papers of Wegscheider (*Z. phys. Chem.*, 43, 89 (1903); 45, 496 (1903); 50, 357 (1904); 52, 171 (1905)).

If we define the individuals in this simple and reasonable way, the Phase Rule may be expressed as follows, without any need of reference to the number of "components" as usually defined:

$$F = (n_i + n_E) - (n_\phi + n_r) \qquad (1)$$

in which F = the actual variance, or the number of degrees of freedom in the special case; n_i the number of individuals as defined above; n_E the number of physical manifestations of energy (mechanical, thermal, electrical, etc.) which are brought into play in the reaction; n_ϕ the number of phases; and n_r the number of independent restrictions or fixed conditions which are determined by the circumstances of the case, but not included in the definition of the individuals. Each quantity is, of course, a small whole number. This method of statement separates sharply the characteristics (n_i and n_E) tending to *increase* the variance, from those (n_ϕ and n_r) tending to *diminish* the variance, and seems to me to place the whole subject in a clearer light.

Ordinarily where only mechanical and thermal energy come into play, $n_E = 2$. Then the equation for the Phase Rule becomes

$$F = (n_i + 2) - (n_\phi + n_r). \qquad (2)$$

This is, of course, the ordinary statement of the Phase Rule, with the addition of n_r, the number of restrictions, as a last term. Equation 2 thus given is used in the subsequent exemplification.

Because all the subtlety of the Phase Rule is concentrated in the last new term, n_r, one must be especially careful in studying each case to be sure that the value of this term is properly estimated—in other words, to be sure that one has counted correctly all the independent restrictions. Moreover, each restriction (especially those concerning concentration. which apply to a variable phase) must be carefully examined in order to show that it is really not involved in another previously determined upon or in the definition of the individuals. This procedure, of course, involves thought, but I know of no method by which the Phase Rule can be applied properly to any but the simplest cases without thought, according to any definition. One must remember, of course, that no restriction can be applied to the quantity of any *phase;* a drop of a solution in true equilibrium is as effective as a bucketful for the purposes of the Phase Rule. Thus in the case of calcium carbonate discussed below, a limitation of the quantity of the carbon dioxide to that of the lime is not a real restriction. Adding more lime has no effect on the equilibrium.

In most cases no great difficulty arises in the interpretation of the new term n_r. So far as I can discover it may include only two different classes of restrictions; on the one hand, the intensity-factor of some form of energy may be restricted, or kept constant; on the other hand, one individual may (either from chemical necessity or arbitrary choice) be kept in definite weight-ratio to some other individual, or at definite concentration in a variable phase.[1] This duality of type might be indicated if desired by substituting for n_r its equivalent $n_{r'} + n_{r''}$, in which the two modified subscripts represent the two different types. A new restriction belonging to either of these types adds one to their sum n_r. For example, if temperature and pressure are both fixed, but no other fixed requirements exist, $n_{r'} = 2$ and $n_{r''} = 0$, therefore, $n_r = 2$. If neither temperature nor pressure is fixed, but one individual must always bear a definite quantitative relation to another, $n_{r'} = 0$ and $n_{r''} = 1$, therefore, $n_r = 1$.

It will be noted that the usual definition of the number of "components" makes this number equal to $(n_i - n_{r''})$.

Let us interpret individual cases in the light of the Phase Rule equation given in terms of chemical individuals. For example, let us take the familiar case of the decomposition by heat of calcium carbonate. There we have the individuals $CaO + CO_2$, that is $n_i = 2$. When the two solids and gas are present in equilibrium $n_\phi = 3$, of course. If no restriction is placed on the concentration of the variable gas phase (or on the pressure or temperature of the gas) $n_r = 0$. Therefore, $F = 1$, that is, the system is univariant.[2] If either temperature or pressure is fixed, $n_r = 1$ and $F = 0$.

Another familiar case is the case of steam, oxygen and hydrogen in equilibrium at a high temperature, the hydrogen and oxygen being in equivalent proportions resulting from the decomposition of water. The usual definition of component would give only one component to this system, but many chemists may be better satisfied by taking, according to the definition given above, hydrogen and oxygen as the "individuals" concerned making $n_i = 2$. As there is only one phase, $n_\phi = 1$; and here $n_r = 1$, because a restriction is placed on the ratio of concentrations of the oxygen and hydrogen in the single phase, which is a variable one. Therefore, $F = 2$, and the system is bivariant.

It may be noted that the essential question of this kind of restriction is concerned with the variable phase, and involves the relative concentration of the individuals in this phase. The variable phase always holds the key to the situation.

Taking a more complicated case, we see that the definition applies equally

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[1] The requirement that a given volume of gas shall contain a given weight is a valid restriction in this sense.

[2] Let me urge once more the use of the purely Latin terms univariant, bivariant, etc., as indicating the degrees of freedom instead of the hybrid Greek-Latin terms monovariant, etc. This consistent terminology was suggested in 1898, *Am. J. Sci.*, [4] **6**, 201 (1898)). It has been supported also by Trevor, but has not always been adopted.

well, for example, to a mixture of a dilute solution of sodium bromide and potassium chloride in equilibrium with its vapor. If the solution remains dilute and no new phase appears, this may be looked upon from two equally legitimate points of view. In the first place, we may take as the individuals of the system: sodium bromide, potassium chloride and water, that is, $n_i = 3$, $n_\phi = 2$, $n_r = 0$, therefore $F = 3$. On the other hand, we may look upon the individuals as the four ions Na', Br', K', Cl' (or the four corresponding elements) and water—five in number—bearing in mind later the two independent restrictions: concentration Na = concentration Br; and concentration K = concentration Cl. According to this better interpretation, we should have $n_i = 5$, $n_\phi = 2$, $n_r = 2$, therefore, $F = 3$ as before.

As regards the former of these interpretations, trouble begins, in a case of this kind, when the solution is so far evaporated that a metathetical product separates out; or when a new salt containing the same elements (*e. g.*, sodium chloride) is added. In that case, although the elements and ions present remain the same, a new individual, in the sense used in this interpretation, has really been added, and the old, usually accepted explanation is somewhat puzzling, although it is legitimate.[1]

On the other hand, the latter interpretation involving five individuals, which is now demanded by the strict phraseology of the definition of the term, offers no difficulty whatever. Thus if with this system sodium chloride separates (both the other salts being decomposed in the process, but the five individuals remaining unchanged), the two restrictions named above have merged into one.[2] Conc. (K + Na) = conc. (Cl + Br); and the new freedom is exactly offset by the new phase: *i. e.*, $n_i = 5$, $n_\phi = 3$, $n_r = 1$, therefore, $F = 3$. Similar reasoning is involved if a little sodium chloride is dissolved in the dilute solution of KCl and NaBr without causing the appearance of a new phase; but here, of course, the result is $F = 4$.

These considerations and others lead me to the conclusion that the use of the conception of chemical "individuals" as defined above gives greater flexibility and clearness than the usual way of first calculating components and then considering those in the Phase Rule equation.

The mathematical verification of Equations 1 and 2 follows directly, it seems to me, from that of the old familiar Phase Rule equation; they are really only different methods of stating the same idea.

Perhaps it may be worth while to give here a brief statement of an inductive method of presenting the Phase Rule, which I have found very efficacious for beginners. Doubtless others have used this method, but

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[1] See for example Bancroft, "The Phase Rule," p. 230 (1897).

[2] It is true that this restriction existed in the system before the NaCl was added; but it was not independent of the other two previously present.

I do not know of its having been published, and it was independently evolved here.[1] After the student has become familiar in the laboratory with such well-known phenomena as the dependence of boiling point and freezing point on pressure and their definiteness under constant pressure, with one individual; and after he has further made himself practically acquainted with the boiling points and freezing points of definite solutions, and with cryohydric and transition points and kindred phenomena, his knowledge may be summed up in the following table:

With one individual, a fixed point (where $F = 0$) is determined by:

	Total fixed conditions.
The coexistence of 3 phases	3
The coexistence of 2 phases and definite pressure	3
The coexistence of 2 phases and definite temperature	3
The coexistence of 1 phase and definite pressure and temperature	3
With two individuals (*e. g.*, H_2O and Na_2SO_4), a fixed point is determined by:	
The coexistence of 4 phases	4
The coexistence of 3 phases and definite pressure	4
The coexistence of 3 phases and definite temperature	4
The coexistence of 2 phases and definite pressure and temperature	4
The coexistence of 2 phases and definite temperature and defined concentration	4

The same method may be extended to more complicated systems and enforced with diagrams, which make clear the fixity of these several points. The student thus sees that three fixed conditions are necessary for invariance with one individual, four fixed conditions with two individuals, five fixed conditions with three individuals, and so on. He sees further that the restricting of any of the variable conditions produces exactly the same effect as the addition of another phase. Thus he perceives that it is legitimate to add n_r to n_ϕ in the expression for the Phase Rule. Of course, the number of degrees of freedom are simply the number of additional restrictions which it is necessary to add to any given system in order to attain invariance.

After the student has become thoroughly familiar with examples in which pressure and temperature are the only energetic intensity-factors to be considered, other manifestations of physical energy may be brought in, and the student is shown the effect of changing surface tension produced by variation in the size particles with its consequent effect upon solubility, the question of electromotive force, etc., using Equation 1 above.[2]

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[1] Essentially the same method has been suggested, but not amplified, in the clear explanation of the Phase Rule in "General Principles of Chemistry," by A. A. Noyes and Sherill, p. 95 (1914).

[2] As Trevor has pointed out (*J. Phys. Chem.*, 1, 349 (1897)), the ordinary two-fluid "reversible" cell is not in true equilibrium because of the osmotic pressure and diffusion at the junction of the two liquids. The beginner is, therefore, advised not to

This outline is, of course, merely a sketch of the method. It needs amplification with the help of many examples, which can easily be provided by anyone even moderately familiar with the principles evolved.

Summary.

To sum up briefly the contents of this note: the idea of the component is replaced by that of the "individual," which is defined in the simplest possible way as an undecomposed chemical substance necessary for constructing the system under consideration, and the number of individuals needed to satisfy the Phase Rule is taken as the least number of such "individuals" needed to construct the system. Into the equation representing the Phase Rule and expressing the number of degrees of freedom of the system is then introduced a term giving the maximum number of independent restrictions involved in the fixation either (*a*) of one or more of the intensity-factors of the forms of physical energy concerned, or (*b*) of some concentration-relation of the individuals in the variable phase. A somewhat obvious method of evolving the Phase Rule inductively for beginners is sketched.

This note is intended rather as the suggestion of an idea than as a final or complete statement of the case. The nomenclature is subject to change if better designations can be found. The object of the note is to remove, if possible, the most serious stumbling-block from the path of the beginner.

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[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY.]

THE COMPRESSIBILITY OF CERTAIN TYPICAL HYDROCARBONS, ALCOHOLS AND KETONES.

BY T. W. RICHARDS AND J. W SHIPLEY.

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This research was a continuation of work already published in several instalments during the last twelve years. The object was to ascertain a large number of compressibilities of pure organic substances under similar conditions. From a physicochemical point of view this is a desirable object, because compressibility has close relations to other properties and is directly concerned with the nature of the several substances.[1]

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attempt the application of the Phase Rule to such cases, which are full of pitfalls. A much simpler case is a dilute amalgam cell with two concentrations of amalgam as the two electrodes. Here the concentration of the electrolyte is without influence and does not form another restriction (Richards and Lewis, *Z. physik. Chem.*, **28**, 7 (1899)).

[1] Richards and Stull, *Pub. Carnegie Inst.*, 7 (1903); *Z. physik. Chem.*, **49**, 1 (1904); Richards, THIS JOURNAL, **26**, 399 (1904); Richards, Stull, Brink and Bonnet, *Pub. Carnegie Inst.*, 76 (1907); *Z. physik. Chem.*, **61**, 77 (1907); *Ibid.*, **61**, 183 (1907); THIS