

# $C = C' - r$ , A Silver Bullet for Evaluation of Components in Simple Equilibrium Reactions: The Relation Revisited

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**Abstract** Phase rule is an integral part of the undergraduate curriculum in many universities across the globe. In an appreciable number of universities, it is dealt with in the freshman year. The students find it extremely confusing to find the number of components even in simple equilibrium reactions. Normally they end up giving wrong answers, or if at all they give correct answers, they are just conjectures. To overcome this overwhelming confusion we have first considered different simple and relatively uncomplicated equilibria from standard physical chemistry books and research journals. In these different equilibria first we evaluated the number of components as illustrated in the books. In each of the book, dissimilar methods were employed to evaluate the number of components which is not a straightforward task for the freshmen students. Then we presented an easy generic method which involved the use of the less involving relation  $C = C' - r$ . Our endeavour in this article is to present a terse and lucid method, by means of which the number of components can be evaluated. Finally, one feels, after going through this article, that this convenient and handy relation  $C = C' - r$  is undeniably a silver bullet for the evaluation of components in simple and relatively less complicated equilibria.

**Keywords** Phase, Components, Restrictions, Constituents, Phase Rule

## 1. Introduction

It has been found that one of the most difficult areas in physical chemistry at freshman level is the phase rule, which requires large amount of imagination on the part of the students when it comes to evaluation of the number of components, one of the vital terms in phase rule. Even though there are easy formulae to overcome this requirement, the students are not made aware of. One such formula is  $C = C' - r$  for the evaluation of number of components  $C$ . Here  $C'$  is the total number of number of chemical constituents in the system, and  $r$  is the number of restrictions imposed on the independent variation of these constituents. In this article, we have shown how the use of the relation  $C = C' - r$  is far more superior to the other methods when it comes to the ease of evaluation of number of components.

## 2. Objective

As described in the title the very purpose of writing this article is to revisit the relation  $C = C' - r$ . This generic and

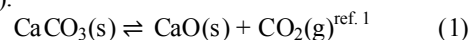
handy relation enables easy evaluation of components in various equilibria, especially for freshmen students. Even in the case where large amount of imagination is required to evaluate the components, the relation  $C = C' - r$  comes to aid.

## 3. Method

Since this article involves the use of the handy relation  $C = C' - r$ , the method is less involving. The evaluation of components of various equilibria from standard physical chemistry text books and research journals are examined. Finally the easy evaluation of the components using the handy relation is presented and verified.

## 4. Discussion

Most of the textbooks give the example of decomposition of calcium carbonate reaction to illustrate the evaluation of number of components in an equilibrium reaction (and so does Glasstone<sup>1</sup>).



It might appear, at the first sight, that there are three components, viz.,  $\text{CaCO}_3$ ,  $\text{CaO}$  and  $\text{CO}_2$ , but it is evident that these substances are not independent, as required by the definition of the component; thus  $\text{CaCO}_3$  is really equivalent to  $\text{CaO} + \text{CO}_2$ . The two components may

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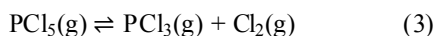
consequently be taken as CaO and CO<sub>2</sub>, so that the composition of calcium carbonate can be represented as  $x\text{CaO} + x\text{CO}_2$ , that of the calcium oxide as  $y\text{CaO} + 0\text{CO}_2$ , while that of carbon dioxide gas phase is  $0\text{CaO} + z\text{CO}_2$ . The two components might equally have been chosen as CaCO<sub>3</sub> and CaO, when the composition of the gas phase would be given by  $z\text{CaCO}_3 - z\text{CaO}$ . The actual nature of the components is not important; it is their number that is significant, and this should always be the same for a given system if the components are chosen properly.

We shall now consider other examples. Let us take the example when ethanol<sup>2</sup> and acetic acid are mixed. At the first sight, we might predict two components because there are two constituents viz. HOAc and EtOH. However these constituents react to give ethyl acetate and water. Therefore ethyl acetate and water are also present at equilibrium together with the reactants. This raises the number of components from 2 to 4.



But because of equilibrium condition and since at equilibrium  $[\text{EtOAc}] = [\text{HOH}]$ , the number of components is reduced back to 2.

If we consider the example of decomposition of pure  $\text{PCl}_5$ <sup>ref2</sup>,



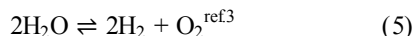
Three chemical species are apparent but the number of components is reduced to one. This is because of equilibrium condition and the relation  $[\text{PCl}_3] = [\text{Cl}_2]$ .

The solution of acetic acid<sup>3</sup> in water is also a case in point



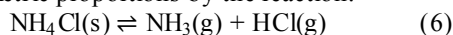
There are many chemical species; clearly, however, the presence of two species can imply the presence of other species determined by the equilibrium relations that exist.

Avoiding the strict attention to the possible equilibria among the species of the system, the consideration of the example, (gaseous system of water vapor, hydrogen and oxygen) will yield meaningful inference. In the presence of electric arc or suitable catalyst, the equilibrium can be described as



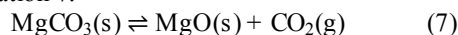
This system has two components. It can be seen that if the concentration of any two species is arbitrarily set, the concentration of third is fixed and can be calculated from equilibrium constant.

In the thermal decomposition of ammonium chloride, there are three chemical species. NH<sub>3</sub> and HCl are formed in fixed stoichiometric proportions by the reaction.



And therefore, the composition of both phases can be expressed in terms of a single species NH<sub>4</sub>Cl suggesting that there is only one component in the system.

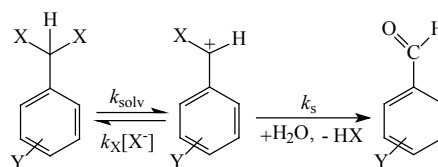
The decomposition of magnesium carbonate can be described by equation 7.



There are three constituents but the number of components is two. The explanation for this is same as that for

decomposition of calcium carbonate (as already explained).

The solvolysis of benzyl-*gem*-dichloride<sup>4,5</sup> is depicted in scheme 1 (for X = Cl).



Scheme 1. Depicting the solvolysis of benzyl-*gem*-dichloride

In our earlier study<sup>5,6,7,8</sup> wherein we had sought insight into the mechanism of this reaction by testing the conformity of the data to the Hammett's equation, the first equilibrium step and the subsequent step, were considered separately. It would be instructive to treat the equilibrium step separately. In this simple solvolysis reaction, the solvolysis step involves a simple equilibrium. The equilibrium constant can be written as  $K_{\text{eq}} = [\alpha\text{-chloro-carbocation}] / [\text{benzyl-}gem\text{-dichloride}]$ . From the knowledge of  $K_{\text{eq}}$  and the concentration of any one of the species  $\alpha$ -chloro-carbocation or benzyl-*gem*-dichloride the concentration of other can be obtained. Thus the number of components is one. In a similar manner, in the equilibrium of solvolysis of benzyl-*gem*-dibromide<sup>6</sup> and benzyl-*gem*-diazide<sup>7</sup>, the number of components obtained would be one.

In the above simple ten equilibria, the manner in which the components are evaluated is not the same for all the systems. This places a heavy toll on the grey cells of the freshman teenagers.

## 5. Conclusions and Results

The system is discussed and concluded as correct when the result obtained from  $C = C' - r$  is the same as we imagined.

In the forgoing examples for the illustration of evaluation of components, uniformity in the explanation is not maintained. Therefore a general expression for evaluation of components would be of much benefit, both to the teacher and taught. The number of components in a system can be determined in the following general manner<sup>1</sup>.

Let  $C'$  be the number of chemical constituents in the system, and let  $r$  be the number of **restrictions imposed on the independent variation of these constituents**. The number of components  $C$  is given by the equation:

$$C = C' - r \quad (8)$$

For instance, let us apply the relation 8 to reaction 1. Here  $C' = 3$  and  $r = 1$  i.e. the equilibrium condition restricts the independent variation of the constituents. Hence  $C = 2$ .

In reaction 2,  $C' = 4$  and  $r = 2$  i.e. equilibrium and the relation  $[\text{EtOAc}] = [\text{HOH}]$  restrict the independent variation of the constituents. Hence  $C$  i.e. number of components is 2.

In reaction 3,  $C' = 3$  and  $r = 2$  i.e. the equilibrium condition and the relation  $[\text{PCl}_3] = [\text{Cl}_2]$  restrict the independent variation of the constituents. Therefore  $C = 1$ .

In reaction 4,  $C' = 4$  and  $r = 2$  i.e. the equilibrium

condition and the relation  $[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+]$  restrict the independent variation of the constituents. Hence  $C = 2$ .

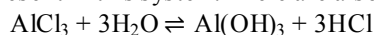
In reaction 5,  $C' = 3$  and  $r = 1$  i.e. the equilibrium condition restricts the independent variation of the constituents. Hence  $C = 2$ .

In reaction 6,  $C' = 3$  and  $r = 2$  i.e. the equilibrium condition and the relation  $[\text{NH}_3] = [\text{HCl}]$  restrict the independent variation of the constituents. Hence  $C = 1$ .

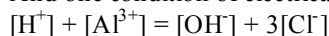
In reaction 7,  $C' = 3$  and  $r = 1$  i.e. the equilibrium condition restricts the independent variation of the constituents. Hence  $C = 2$ .

In the equilibrium of solvolysis of benzyl-*gem*-dichloride,  $C'$  is 2 but the equilibrium restricts their independent variation i.e.  $r = 1$ . Hence  $C = 2 - 1 = 1$ . Analogously in the solvolysis of benzyl-*gem*-dibromide and benzyl-*gem*-diazide the components can be obtained as 1 by applying our simple relation  $C = C' - r$ .

Let us see a system that is a little more complex where in  $\text{AlCl}_3$  is dissolved in water<sup>9</sup>, noting that hydrolysis and precipitation of  $\text{Al}(\text{OH})_3$  occur, giving various ions.  $\text{Al}^{3+}$ ,  $\text{H}^+$ ,  $\text{AlCl}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{O}$  are the seven species present in this system. There are also three equilibria:

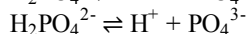
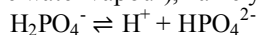


And one condition of electrical neutrality



Hence for this system,  $C' = 7$  and  $r = 4$  i.e. the three equilibria and the condition of electrical neutrality restrict the independent variation of the constituents. Hence  $C = 7 - (3+1) = 3$ .

Let us take a similar but a little more complex example<sup>9</sup> where in one finds the number the components of (a)  $\text{Na}_2\text{HPO}_4$  in water at equilibrium with water vapour but disregarding the fact the salt is ionized. (b) The same but taking into account the ionization of the salt (disregarding the water vapour). In the former case (a) total numbers of constituents ( $C'$ ) are three, namely, salt, water and water vapour, there is an equilibrium condition (restriction) between liquid water and its vapour. Hence the total number of components are  $C = 3 - 1 = 2$ ; In the latter case (b) there are seven ( $C'$ ) species:  $\text{Na}^+$ ,  $\text{H}^+$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_2\text{O}$  and  $\text{OH}^-$ . There also exist three equilibria (disregarding the water vapour), namely



Further there are also two conditions of neutrality, namely

$[\text{Na}^+] = [\text{phosphates}]$  and  $[\text{H}^+] = [\text{OH}^-] + [\text{phosphates}]$  where  $[\text{phosphates}] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$

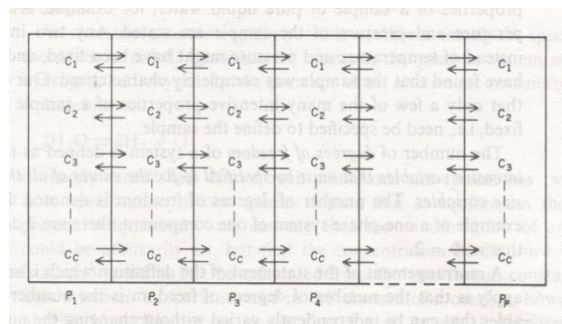
Hence the total numbers of restrictions are the three equilibria, and the two conditions of neutrality i.e., they restrict the independent variation. Thus the total number of components ( $C$ ) are  $C = 7 - (3 + 2) = 2$ .

The comprehension of the important term restriction is better understood if one studies the derivations of phase rule.

The derivation of phase rule<sup>10</sup> was first put forth by J. Willard Gibbs in 1878. Unfortunately it was published in a rather obscure journal *Transactions of the Connecticut Academy of Arts and Sciences*<sup>11</sup> and was overlooked for 20 years. The derivation of phase rule like any other derivations has essential concepts and assumptions embedded in it. It is here the teaching acumen of the instructor is wanting, and it is for the teacher to discern and accentuate the number of intensive variables fixed by free energy equilibrium relations. Let us recapitulate the phase rule obtained by J. Willard Gibbs.

Consider the  $C$  components to be distributed throughout each of the  $P$  phases of a system as schematically indicated in Figure 1.

To get the total number degrees of freedom one has to first add the total number of intensive variables required to describe separately each phase and then subtracting the number of intensive variables, whose values are fixed by free-energy equilibrium relations between different phases. To begin, each component is assumed to be present in every phase.



**Figure 1.** Depicting ' $C$ ' components distributed throughout each of the ' $P$ ' phases

In each phase ( $C - 1$ ) quantities will be required to define the composition of the phase quantitatively. Thus, if mole fractions are used to measure the concentrations, one needs to specify the mole fraction of all but one of the components, the remaining one being determined because the sum of the mole fractions must be unity. Since there are  $P$  phases, there will be total of  $P(C - 1)$  such composition variables. In addition, the pressure and the temperature must be specified, giving a total of  $P(C - 1) + 2$  intensive variables if the system is considered phase by phase.

The number of these variables, which are fixed by the equilibrium conditions of the system, must now be determined. Component 1, for example, is distributed between phases  $P_1$  and  $P_2$ . When equilibrium is established for any one component distributed between any two phases, a distribution relation<sup>12</sup> can be written. Thus, if the concentration of a component in phase  $P_1$  is specified, its concentration in phase  $P_2$  is automatically fixed. Similar equilibria are set up for each component between the various pairs of phases. For each component there are  $(P - 1)$  such relations. Thus, for  $C$  components a total of  $C(P - 1)$  intensive variables are fixed by equilibrium conditions.

The number of degrees of freedom, i.e., net adjustable

intensive variables, is therefore

$$\Phi = P(C - 1) + 2 - C(P - 1) = C - P + 2$$

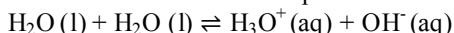
In this derivation of phase rule  $C(P - 1)$  as already described, is the number of intensive variables, whose values are fixed by free energy equilibrium relations. Teachers should try to emphasize this aspect and try to be as lucid as possible. This would enable the students to comprehend the extremely important term 'r' that is the restriction<sup>13</sup> imposed on the independent variation of the constituents. Once the students comprehend this, the evaluation of components would be a blithesome experience.

One million dollar **perplexing query**, the students raise, is that in the decomposition of  $\text{CaCO}_3$ , why isn't  $[\text{CaO}] = [\text{CO}_2]$  although it is analogous to  $[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+]$  for reaction 4 or  $[\text{EtOAc}] = [\text{HOH}]$  for reaction 2 or  $[\text{PCl}_3] = [\text{Cl}_2]$  for reaction 3. The thermodynamic property, intensive variable, answers this query. The "concentration" of a solid, like its density, is an intensive property and therefore does not depend on how much of the substance is present. For example, the "molar concentration" of copper<sup>14</sup> (density:  $8.96\text{g/cm}^3$ ) at  $20^\circ\text{C}$  is the same, whether we have 1 gram or 1 ton of the metal:

$$[\text{Cu}] = 8.96\text{g/cm}^3 \times 1\text{ mol}/63.55\text{g} = 0.141\text{ mol/cm}^3 = 141\text{ mol/L}$$

For this reason, the concentration of solid  $[\text{CaO}]$  is constant, and thus has nothing to do with concentration of  $[\text{CO}_2]$ . And since  $[\text{CaO}]$  is not equal to  $[\text{CO}_2]$ , the number of restrictions is reduced to one in this case. The same reasoning can be extrapolated for decomposition of  $\text{MgCO}_3$ , where  $[\text{MgO}]$  is not equal to  $[\text{CO}_2]$ .

Atkins<sup>15</sup> has a self-test problem, which is, "How many components does autoprotolysis of water has?" and the answer given is one. Let us solve this problem as follows:



Pure liquid water has concentration of  $55.5\text{M}$  (density =  $1\text{g/cc}$  and calculations analogous to concentration of solids, as already explained in the foregoing paragraph), and since negligible concentrations of products are formed, the concentration of water can be taken as constant. The equilibrium expression for this process is  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$ . Therefore if concentration of  $\text{H}_3\text{O}^+$  is known, the concentration of  $\text{OH}^-$  is set. Analogously, if the concentration of  $\text{OH}^-$  is known, the concentration of  $\text{H}_3\text{O}^+$  is set. Hence auto-protolysis is one component system. Thus this example is underpinning the reasoning; put forth in the foregoing paragraph regarding concentration of solids (it is equally applicable for pure liquids).

If we apply our generic formula, then  $C'$  is 4 and  $r$  is 3 i.e. the equilibrium condition, the relation  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  and the relation  $[\text{H}_2\text{O}] = [\text{H}_2\text{O}]$ . Therefore  $C = 4 - 3$  i.e. 1.

Thus this simple relation of  $C = C' - r$  is a silver-bullet for freshman students to evaluate the number of components (for simple equilibrium reactions) when learning the phase rule.

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