

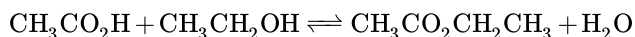
6.8: Gibbs' Phase Rule

Gibbs found an important relationship among the number of chemical constituents, the number of phases present, and the number of intensive variables that must be specified in order to characterize an equilibrium system. This number is called the number of **degrees of freedom** available to the system and is given the symbol F . By specifying F intensive variables, we can specify the state of the system—except for the amount of each phase. The number of chemical constituents is called the **number of components** and is given the symbol C . The number of components is the smallest number of pure chemical compounds that we can use to prepare the equilibrium system so that it contains an arbitrary amount of each phase. The **number of phases** is given the symbol P . The relationship that Gibbs found between C , P , and F is called **Gibbs' phase rule** or just **the phase rule**. The phase rule applies to equilibrium systems in which any component can move freely between any two phases in which that component is present.

We suppose that the state of the system is a continuous function of its state functions. If F , intensive, independent variables, X_1, X_2, \dots, X_F , are sufficient to specify the state of an equilibrium system, then $X_1 + dX_1, X_2 + dX_2, \dots, X_F + dX_F$ specify an incrementally different equilibrium state of the same system. This means that the number of degrees of freedom is also the number of intensive variables that can be varied independently while the system changes reversibly—subject to the condition that there is no change in either the number or kinds of phases present. Moreover, if we keep the system's intensive variables constant, we can change the size of any phase without changing the nature of the system. This means that Gibbs' phase rule applies to any equilibrium system, whether it is open or closed.

A system containing only liquid water contains one component and one phase. By adjusting the temperature and pressure of this system, we can arrive at a state in which both liquid and solid are present. For present purposes, we think of this as a second system. Since the second system can be prepared using only liquid water (or, for that matter, only ice) it too contains only one component. However, since it contains both liquid and solid phases, the second system contains two phases. We see that the number of components required to prepare a system in such a way that it contains an arbitrary amount of each phase is not affected by phase equilibria. However, the number of components is affected by chemical equilibria and by any other stoichiometric constraints that we impose on the system. The number of components is equal to the number of chemical substances present in the system, less the number of stoichiometric relationship among these substances.

Let us consider an aqueous system containing dissolved acetic acid, ethanol, and ethyl acetate. For this system to be at equilibrium, the [esterification reaction](#)



must be at equilibrium. In general we can prepare a system like this by mixing any three substances chosen from the set: acetic acid, ethanol, ethyl acetate, and water. Hence, there are three components. The esterification reaction, or its reverse, then produces an equilibrium concentration of the fourth substance. However, there is a special case with only two components. Suppose that we require that the equilibrium concentrations of ethanol and acetic acid be exactly equal. In this case, we can prepare the system by mixing ethyl acetate and water. Then the stoichiometry of the reaction assures that the concentration condition will be met; indeed, this is the only way that the equal-concentration condition can be met exactly.

In this example, there are four chemical substances. The esterification reaction places one stoichiometric constraint on the amounts of these substances that can be present at equilibrium, which means that we can change only three concentrations independently. The existence of this constraint reduces the number of components from four to three. An additional stipulation that the product concentrations be equal is a second stoichiometric constraint that reduces the number of independent components to two.

If we have a one-phase system at equilibrium, we see that the pressure, the temperature, and the C component-concentrations constitute a set of variables that must be related by an equation of state. If we specify all but one of these variables, the remaining variable is determined, and can be calculated from the equation of state. There are $C + 2$ variables, but the existence of the equation of state means that only $C + 1$ of them can be changed independently. Evidently, the number of degrees of freedom for a one-phase system is $F = C + 1$.

To find the number of degrees of freedom when P such phases are in equilibrium with one another requires a similar but more extensive analysis. We first consider the number of intensive variables that are required to describe completely a system that contains C components and P phases, if the phases are not at equilibrium with one another. (Remember that the description we seek is complete except for a specification of the absolute amount of each phase present. For the characterization of equilibrium

that we seek, these amounts are arbitrary.) In this case, each phase is a subsystem in its own right. Each phase can have a pressure, a temperature, and a

concentration for each component. Each of these properties can have a value that is independent of its value in any other phase. There are $C + 2$ variables for each phase or $P(C + 2)$ variables for all P phases. Table 1 displays these variables.

| | 1 | 2 | ... | P |
|-------------|---------------|---------------|-----|---------------|
| Pressure | P_1 | P_2 | ... | P_P |
| Temperature | T_1 | T_2 | ... | T_P |
| Component 1 | $n_{1,1}/V_1$ | $n_{1,2}/V_2$ | ... | $n_{1,P}/V_P$ |
| Component 2 | $n_{2,1}/V_1$ | $n_{2,2}/V_2$ | ... | $n_{2,P}/V_P$ |
| ... | ... | ... | ... | ... |
| Component C | $n_{C,1}/V_1$ | $n_{C,2}/V_2$ | ... | $n_{C,P}/V_P$ |

If the system is at equilibrium, there are numerous relationships among these $P(C + 2)$ variables. We want to know how many independent relationships there are among them. Each such relationship decreases by one the number of independent intensive variables that are needed to specify the state of the system when all of the phases are at equilibrium. Let us count these relationships.

- The pressure must be the same in each phase. That is, $P_1 = P_2, P_1 = P_3, \dots, P_1 = P_P, P_2 = P_3, \dots, P_2 = P_P$, etc. Since $P_1 = P_2$ and $P_1 = P_3$ implies that $P_2 = P_3$, etc., there are only $P - 1$ independent equations that relate these pressures to one another.
- The temperature must be the same in each phase. As for the pressure, there are $P - 1$ independent relationships among the temperature values.
- The concentration of species A in phase 1 must be in equilibrium with the concentration of species A in phase 2, and so forth. We can write an equation for phase equilibrium involving the concentration of A in any two phases; for example,

$$K = \frac{(n_{A,2}/V_{A,2})}{(n_{A,1}/V_{A,2})}$$

(In [Chapter 14](#), we will find that this requirement can be stated more rigorously using a thermodynamic function that we call the chemical potential. At equilibrium, the chemical potential of species A must be the same in each phase.) For the P phases, there are again $P - 1$ independent relationships among the component- A concentration values. This is true for each of the C components, so the total number of independent relationships among the concentrations is $C(P - 1)$.

While every component need not be present in each phase, there must be a finite amount of each phase present. Each phase must have a non-zero volume. To express this requirement using intensive variables, we can say that the sum of the concentrations in each phase must be greater than zero. For phase 1, we must have

$$(n_{A,1}/V_1) + (n_{B,1}/V_1) + \dots + (n_{Z,1}/V_1) > 0$$

and so on for each of the P phases. There are P such relationships that are independent of one another.

If we subtract, from the total number of relevant relationships, the number of independent relationships that must be satisfied at equilibrium, we find **Gibbs' phase rule**: There are

$$\begin{aligned} F &= P(C + 2) - (P - 1) - (P - 1) - C(P - 1) - P \\ &= 2 + C - P \end{aligned}$$

independent relationships or degrees of freedom needed to describe the equilibrium system containing C components and P phases.

A component may not be present in some particular phase. If this is the case, the total number of relationships is one less than the number that we used above to derive the phase rule. The number of equilibrium constraints is also one less than the number we

used. Consequently, the absence of a component from any particular phase has no effect on the number of degrees of freedom available to the system at equilibrium.

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