

## 13.1: The Gibbs Phase Rule for Multicomponent Systems

In Sec. 8.1.7, the Gibbs phase rule for a pure substance was written  $F = 3 - P$ . We now consider a system of more than one substance and more than one phase in an equilibrium state. The phase rule assumes the system is at thermal and mechanical equilibrium. We shall assume furthermore that in addition to the temperature and pressure, the only other state functions needed to describe the state are the amounts of the species in each phase; this means for instance that surface effects are ignored.

The derivations to follow will show that the phase rule may be written either in the form

$$F = 2 + C - P \quad (13.1.1)$$

or

$$F = 2 + s - r - P \quad (13.1.2)$$

where the symbols have the following meanings:

$F$  = the number of degrees of freedom (or variance)

= the maximum number of intensive variables that can be varied independently while the system remains in an equilibrium state;

$C$  = the number of components

= the minimum number of substances (or fixed-composition mixtures of substances) that could be used to prepare each phase individually;

$P$  = the number of different phases;

$s$  = the number of different species;

$r$  = the number of independent relations among intensive variables of individual phases other than relations needed for thermal, mechanical, and transfer equilibrium.

If we subdivide a phase, that does not change the number of phases  $P$ . That is, we treat noncontiguous regions of the system that have identical intensive properties as parts of the same phase.

### 13.1.1 Degrees of freedom

Consider a system in an equilibrium state. In this state, the system has one or more phases; each phase contains one or more species; and intensive properties such as  $T$ ,  $p$ , and the mole fraction of a species in a phase have definite values. Starting with the system in this state, we can make changes that place the system in a new equilibrium state having the same kinds of phases and the same species, but different values of some of the intensive properties. The number of different independent intensive variables that we may change in this way is the **number of degrees of freedom** or **variance**,  $F$ , of the system.

Clearly, the system remains in equilibrium if we change the *amount* of a phase without changing its temperature, pressure, or composition. This, however, is the change of an extensive variable and is not counted as a degree of freedom.

The phase rule, in the form to be derived, applies to a system that continues to have complete thermal, mechanical, and transfer equilibrium as intensive variables change. This means different phases are not separated by adiabatic or rigid partitions, or by semipermeable or impermeable membranes. Furthermore, every conceivable reaction among the species is either at reaction equilibrium or else is frozen at a fixed advancement during the time period we observe the system.

The number of degrees of freedom is the maximum number of intensive properties of the equilibrium system we may independently vary, or fix at arbitrary values, without causing a change in the number and kinds of phases and species. We cannot, of course, change one of these properties to just any value whatever. We are able to vary the value only within a certain finite (sometimes quite narrow) range before a phase disappears or a new one appears.

The number of degrees of freedom is also the number of independent intensive variables needed to specify the equilibrium state in all necessary completeness, aside from the amount of each phase. In other words, when we specify values of  $F$  different independent intensive variables, then the values of all other intensive variables of the equilibrium state have definite values determined by the physical nature of the system.

Just as for a one-component system, we can use the terms *bivariant*, *univariant*, and *invariant* depending on the value of  $F$  (Sec. 8.1.7).

### 13.1.2 Species approach to the phase rule

This section derives an expression for the number of degrees of freedom,  $F$ , based on *species*. Section 13.1.3 derives an expression based on *components*. Both approaches yield equivalent versions of the phase rule.

Recall that a *species* is an entity, uncharged or charged, distinguished from other species by its chemical formula (Sec. 9.1.1). Thus,  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  are different species, but  $\text{CO}_2(\text{aq})$  and  $\text{CO}_2(\text{g})$  is the same species in different phases.

Consider an equilibrium system of  $P$  phases, each of which contains the same set of species. Let the number of different species be  $s$ . If we could make changes while the system remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we could independently vary the temperature and pressure of the system as a whole and the amount of each species in each phase; there would then be  $2 + Ps$  independent variables.

The equilibrium system is, however, in transfer equilibrium, which requires each species to have the same chemical potential in each phase:  $\mu_i^\beta = \mu_i^\alpha$ ,  $\mu_i^\gamma = \mu_i^\alpha$ , and so on. There are  $P - 1$  independent relations like this for each species, and a total of  $s(P - 1)$  independent relations for all species. Each such independent relation introduces a constraint and reduces the number of independent variables by one. Accordingly, taking transfer equilibrium into account, the number of independent variables is  $2 + Ps - s(P - 1) = 2 + s$ .

We obtain the same result if a species present in one phase is totally excluded from another. For example, solvent molecules of a solution are not found in a pure perfectly-ordered crystal of the solute, undissociated molecules of a volatile strong acid such as HCl can exist in a gas phase but not in aqueous solution, and ions of an electrolyte solute are usually not found in a gas phase. For each such species absent from a phase, there is one fewer amount variable and also one fewer relation for transfer equilibrium; on balance, the number of independent variables is still  $2 + s$ .

Next, we consider the possibility that further independent relations exist among intensive variables in addition to the relations needed for thermal, mechanical, and transfer equilibrium. (Relations such as  $\sum_i p_i = p$  for a gas phase or  $\sum_i x_i = 1$  for a phase in general have already been accounted for in the derivation by the specification of  $p$  and the amount of each species.) If there are  $r$  of these additional relations, the total number of independent variables is reduced to  $2 + s - r$ . These relations may come from

1. In the case of a reaction equilibrium, the relation is  $\Delta_r G = \sum_i \nu_i \mu_i = 0$ , or the equivalent relation  $K = \prod_i (a_i)^{\nu_i}$  for the thermodynamic equilibrium constant. Thus,  $r$  is the sum of the number of independent reaction equilibria, the number of phases containing ions, and the number of independent initial conditions. Several examples will be given in Sec. 13.1.4.

There is an infinite variety of possible choices of the independent variables (both extensive and intensive) for the equilibrium system, but the total *number* of independent variables is fixed at  $2 + s - r$ . Keeping intensive properties fixed, we can always vary how much of each phase is present (e.g., its volume, mass, or amount) without destroying the equilibrium. Thus, at least  $P$  of the independent variables, one for each phase, must be extensive. It follows that the maximum number of independent *intensive* variables is the difference  $(2 + s - r) - P$ .

Since the maximum number of independent intensive variables is the number of degrees of freedom, our expression for  $F$  based on species is

$$F = 2 + s - r - P \quad (13.1.3)$$

### 13.1.3 Components approach to the phase rule

The derivation of the phase rule in this section uses the concept of **components**. The number of components,  $C$ , is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed-composition mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system.

It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of  $\text{CaCO}_3$  and  $\text{CaO}$  and a gas phase of  $\text{CO}_2$ . Assume the reaction  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$  is at equilibrium. We could prepare the  $\text{CaCO}_3$  phase from  $\text{CaO}$  and  $\text{CO}_2$  by the reverse of this reaction, but we can only prepare the  $\text{CaO}$  and  $\text{CO}_2$  phases from the individual substances. We could not use  $\text{CaCO}_3$  to prepare either the  $\text{CaO}$  phase or the  $\text{CO}_2$  phase,

because  $\text{CO}_2$  or  $\text{CaO}$  would be left over. Thus this system has three substances but only two components, namely  $\text{CaO}$  and  $\text{CO}_2$ .

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of  $P$  phases in which each substance present is a component (i.e., there are no reactions) and each of the  $C$  components is present in each phase. If we make changes to the system while it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation  $\sum_i x_i = 1$ ). This is a total of  $2 + P(C - 1)$  independent intensive variables.

When there also exist transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish  $P - 1$  independent relations for each component ( $\mu_i^\beta = \mu_i^\alpha$ ,  $\mu_i^\gamma = \mu_i^\alpha$ , etc.) and a total of  $C(P - 1)$  relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

$$F = [2 + P(C - 1)] - C(P - 1) = 2 + C - P \quad (13.1.4)$$

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of  $F$ , which is still equal to  $2 + C - P$ . If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation  $\sum_i \nu_i \mu_i = 0$  for the reaction; again the changes cancel.

We may need to *remove* a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electroneutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured.

We conclude that, regardless of the kind of system, the expression for  $F$  based on components is given by  $F = 2 + C - P$ . By comparing this expression and  $F = 2 + s - r - P$ , we see that the number of components is related to the number of species by

$$C = s - r \quad (13.1.5)$$

### 13.1.4 Examples

The five examples below illustrate various aspects of using the phase rule.

#### Example 1: liquid water

For a single phase of pure water,  $P$  equals 1. If we treat the water as the single species  $\text{H}_2\text{O}$ ,  $s$  is 1 and  $r$  is 0. The phase rule then predicts two degrees of freedom:

$$\begin{aligned} F &= 2 + s - r - P \\ &= 2 + 1 - 0 - 1 = 2 \end{aligned} \quad (13.1.6)$$

Since  $F$  is the number of intensive variables that can be varied independently, we could for instance vary  $T$  and  $p$  independently, or  $T$  and  $\rho$ , or any other pair of independent intensive variables.

Next let us take into account the proton transfer equilibrium



and consider the system to contain the three species  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{O}^+$ , and  $\text{OH}^-$ . Then for the species approach to the phase rule, we have  $s = 3$ . We can write two independent relations:

1. Thus, we have two relations involving intensive variables only. Now  $s$  is 3,  $r$  is 2,  $P$  is 1, and the number of degrees of freedom is given by

$$F = 2 + s - r - P = 2 \quad (13.1.7)$$

which is the same value of  $F$  as before.

If we consider water to contain additional cation species (e.g.,  $\text{H}_3\text{O}_2^+$ ), each such species would add 1 to  $s$  and 1 to  $r$ , but  $F$  would remain equal to 2. Thus, no matter how complicated are the equilibria that actually exist in liquid water, the number of degrees of freedom remains 2.

### Example 2: carbon, oxygen, and carbon oxides

Consider a system containing solid carbon (graphite) and a gaseous mixture of  $\text{O}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$ . There are four species and two phases. If reaction equilibrium is absent, as might be the case at low temperature in the absence of a catalyst, we have  $r = 0$  and  $C = s - r = 4$ . The four components are the four substances. The phase rule tells us the system has four degrees of freedom. We could, for instance, arbitrarily vary  $T$ ,  $p$ ,  $y_{\text{O}_2}$ , and  $y_{\text{CO}}$ .

Now suppose we raise the temperature or introduce an appropriate catalyst to allow the following reaction equilibria to exist:

1. These equilibria introduce two new independent relations among chemical potentials and among activities. We could also consider the equilibrium  $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{CO}_2(\text{g})$ , but it does not contribute an additional independent relation because it depends on the other two equilibria: the reaction equation is obtained by subtracting the reaction equation for equilibrium 1 from twice the reaction equation for equilibrium 2. By the species approach, we have  $s = 4$ ,  $r = 2$ , and  $P = 2$ ; the number of degrees of freedom from these values is

$$F = 2 + s - r - P = 2 \quad (13.1.8)$$

If we wish to calculate  $F$  by the components approach, we must decide on the minimum number of substances we could use to prepare each phase separately. (This does not refer to how we actually prepare the two-phase system, but to a hypothetical preparation of each phase with any of the compositions that can actually exist in the equilibrium system.) Assume equilibria 1 and 2 are present. We prepare the solid phase with carbon, and we can prepare any possible equilibrium composition of the gas phase from carbon and  $\text{O}_2$  by using the reactions of both equilibria. Thus, there are two components ( $\text{C}$  and  $\text{O}_2$ ) giving the same result of two degrees of freedom.

1. Now to introduce an additional complexity: Suppose we prepare the system by placing a certain amount of  $\text{O}_2$  and twice this amount of carbon in an evacuated container, and wait for the reactions to come to equilibrium. This method of preparation imposes an initial condition on the system, and we must decide whether the number of degrees of freedom is affected. Equating the total amount of carbon atoms to the total amount of oxygen atoms in the equilibrated system gives the relation

$$n_{\text{C}} + n_{\text{CO}} + n_{\text{CO}_2} = 2n_{\text{O}_2} + n_{\text{CO}} + 2n_{\text{CO}_2} \quad \text{or} \quad n_{\text{C}} = 2n_{\text{O}_2} + n_{\text{CO}_2} \quad (13.1.9)$$

Either equation is a relation among extensive variables of the two phases. From them, we are unable to obtain any relation among *intensive* variables of the phases. Therefore, this particular initial condition does not change the value of  $r$ , and  $F$  remains equal to 2.

### Example 3: a solid salt and saturated aqueous solution

Applying the components approach to this system is straightforward. The solid phase is prepared from  $\text{PbCl}_2$  and the aqueous phase could be prepared by dissolving solid  $\text{PbCl}_2$  in  $\text{H}_2\text{O}$ . Thus, there are two components and two phases:

$$F = 2 + C - P = 2 \quad (13.1.10)$$

For the species approach, we note that there are four species ( $\text{PbCl}_2$ ,  $\text{Pb}^{2+}$ ,  $\text{Cl}^-$ , and  $\text{H}_2\text{O}$ ) and two independent relations among intensive variables:

1. We have  $s = 4$ ,  $r = 2$ , and  $P = 2$ , giving the same result as the components approach:

$$F = 2 + s - r - P = 2 \quad (13.1.11)$$

### Example 4: liquid water and water-saturated air

If there is no special relation among the total amounts of  $\text{N}_2$  and  $\text{O}_2$ , there are three components and the phase rule gives

$$F = 2 + C - P = 3 \quad (13.1.12)$$

Since there are three degrees of freedom, we could, for instance, specify arbitrary values of  $T$ ,  $p$ , and  $y_{\text{N}_2}$  (arbitrary, that is, within the limits that would allow the two phases to coexist); then the values of other intensive variables such as the mole fractions  $y_{\text{H}_2\text{O}}$  and  $x_{\text{N}_2}$  would have definite values.

Now suppose we impose an initial condition by preparing the system with water and dry air of a *fixed* composition. The mole ratio of  $\text{N}_2$  and  $\text{O}_2$  in the aqueous solution is not necessarily the same as in the equilibrated gas phase; consequently, the air does not behave like a single substance. The number of components is still three:  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{O}_2$  are all required to prepare each phase individually, just as when there was no initial condition, giving  $F = 3$  as before.

The fact that the compositions of both phases depend on the relative amounts of the phases is illustrated in Prob. 9.5.

We can reach the same conclusion with the species approach. The initial condition can be expressed by an equation such as

$$\frac{(n_{\text{N}_2}^{\text{l}} + n_{\text{N}_2}^{\text{g}})}{(n_{\text{O}_2}^{\text{l}} + n_{\text{O}_2}^{\text{g}})} = a \quad (13.1.13)$$

where  $a$  is a constant equal to the mole ratio of  $\text{N}_2$  and  $\text{O}_2$  in the dry air. This equation cannot be changed to a relation between intensive variables such as  $x_{\text{N}_2}$  and  $x_{\text{O}_2}$ , so that  $r$  is zero and there are still three degrees of freedom.

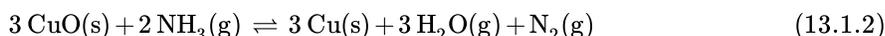
Finally, let us assume that we prepare the system with dry air of fixed composition, as before, but consider the solubilities of  $\text{N}_2$  and  $\text{O}_2$  in water to be negligible. Then  $n_{\text{N}_2}^{\text{l}}$  and  $n_{\text{O}_2}^{\text{l}}$  are zero and Eq. 13.1.13 becomes  $n_{\text{N}_2}^{\text{g}}/n_{\text{O}_2}^{\text{g}} = a$ , or  $y_{\text{N}_2} = ay_{\text{O}_2}$ , which is a relation between intensive variables. In this case,  $r$  is 1 and the phase rule becomes

$$F = 2 + s - r - P = 2 \quad (13.1.14)$$

The reduction in the value of  $F$  from 3 to 2 is a consequence of our inability to detect any dissolved  $\text{N}_2$  or  $\text{O}_2$ . According to the components approach, we may prepare the liquid phase with  $\text{H}_2\text{O}$  and the gas phase with  $\text{H}_2\text{O}$  and air of fixed composition that behaves as a single substance; thus, there are only two components.

#### Example 5: equilibrium between two solid phases and a gas phase

Consider the following reaction equilibrium:



According to the species approach, there are five species, one relation (for reaction equilibrium), and three phases. The phase rule gives

$$F = 2 + s - r - P = 3 \quad (13.1.15)$$

It is more difficult to apply the components approach to this example. As components, we might choose  $\text{CuO}$  and  $\text{Cu}$  (from which we could prepare the solid phases) and also  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Then to obtain the  $\text{N}_2$  needed to prepare the gas phase, we could use  $\text{CuO}$  and  $\text{NH}_3$  as reactants in the reaction  $3 \text{CuO} + 2 \text{NH}_3 \rightarrow 3 \text{Cu} + 3 \text{H}_2\text{O} + \text{N}_2$  and remove the products  $\text{Cu}$  and  $\text{H}_2\text{O}$ . In the components approach, we are allowed to remove substances from the system provided they are counted as components.

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