

6.10: Duhem's Theorem - Specifying Reversible Change in A Closed System

We view a chemical system as a collection of substances that occupies some volume. Let us consider a closed system whose volume is variable, and in which no work other than pressure–volume work is possible. If this system is undergoing a reversible change, it is at equilibrium, and it is in contact with its surroundings. Because the system is at equilibrium, all points inside the system have the same pressure and the same temperature. Since the change is reversible, the interior pressure is arbitrarily close to the pressure applied to the system by the surroundings. If the reversibly changing system can exchange heat with its surroundings, the temperature of the surroundings is arbitrarily close to the temperature of the system. (If a process takes place in a system that cannot exchange heat with its surroundings, we say that the process is *adiabatic*.)

We can measure the pressure, temperature, and volume of such a system without knowing anything about its composition. For a system composed of a known amount of a single phase of a pure substance, we know from experience that any cyclic change in pressure or temperature restores the initial volume. That is, for a pure phase, there is an equation of state that we can rearrange as $V = V(P, T)$, meaning that specifying P and T is sufficient to specify V uniquely.

For other reversible systems, the function $V = V(P, T)$ may not exist. For example, consider a system that consists of a known amount of water at liquid–vapor equilibrium and whose pressure and temperature are known. For this system, the volume can have any value between that of the pure liquid and that of the pure gas. Specifying the pressure and temperature of this system is not sufficient to specify its state. However, if we specify the temperature of this system, the pressure is fixed by the equilibrium condition; and if we specify the volume of the system, we can find how much water is in each phase from the known molar volumes of the pure substances at the system pressure and temperature. For the water–water-vapor equilibrium system, we can write $P = P(V, T)$.

In each of these cases, we can view one of the variables as a function of the other two and represent it as a surface in a three dimensional space. The two independent variables define a plane. Projecting the system's location in this independent-variable plane onto the surface establishes the value of the dependent variable. The two independent-variable values determine the point on the surface that specifies the state of the system. In the liquid–vapor equilibrium system, the pressure is a surface above the volume–temperature plane.

A complete description of the state of the system must also include the number of moles of liquid and the number of mole of vapor present. Each of these quantities can also be described as a surface in a three dimensional space in which the other two dimensions are volume and temperature. **Duhem's theorem** asserts that these observations are special cases of a more general truth:

Duhem's theorem

For a closed, reversible system in which only pressure–volume work is possible, specifying how some pair of state functions changes is sufficient to specify how the state of the system changes.

Duhem's theorem asserts that two variables are sufficient to specify the state of the system in the following sense: Given the values of the system's thermodynamic variables in some initial state, say $\{X_1, Y_1, Z_1, W_1, \dots\}$, specifying the change in some pair of variables, say ΔX and ΔY , is sufficient to determine the change in the remaining variables, $\Delta Z, \Delta W, \dots$ so that the system's thermodynamic variables in the final state are $\{X_2, Y_2, Z_2, W_2, \dots\}$, where $W_2 = W_1 + \Delta W$, etc. The theorem does not specify which pair of variables is sufficient. In fact, from the discussion above of the variables that can be used to specify the state of a system containing only water, it is evident that a particular pair may not remain sufficient if there is a change in the number of phases present.

In Chapter 10, we see that Duhem's theorem follows from the first and second laws of thermodynamics, and we consider the particular pairs of variables that can be used. For now, let us consider a proof of Duhem's theorem for a system in which the pressure, temperature, volume, and composition can vary. We consider systems in which only pressure–volume work is possible. Let the number of chemical species present be C' and the number of phases be P . (C , the number of component in the phase rule, and C' differ by the number of stoichiometric constraints that apply to the system: C is C' less the number of stoichiometric constraints.) We want to know how many variables can be changed independently while the system remains at equilibrium.

This is similar to the question we answered when we developed Gibbs' phase rule. However, there are important differences. The phase rule is independent of the size of the system; it specifies the number of intensive variables required to prescribe an equilibrium state in which specified phases are present. The size of the system is not fixed; we can add or remove matter to change

the size of any phase without changing the number of degrees of freedom. In the present problem, the system cannot exchange matter with its surroundings. Moreover, the number of phases present can change. We require only that any change be reversible, and a reversible process can change the number of phases. (For example, reversible vaporization can convert a two-phase system to a gaseous, one-phase system.)

We want to impose a change on an initial state of a closed system. This initial state is an equilibrium state, and we want to impose a change that produces a new Gibbsian equilibrium state of the same system. This means that the change we impose can neither eliminate an existing chemical species nor introduce a new one. A given phase can appear or disappear, but a given chemical species cannot.

We can find the number of independent variables for this system by an argument similar to the one we used to find the phase rule. To completely specify this system, we must specify the pressure, temperature, and volume of each phase. We must also specify the number of moles of each of C' chemical species in each phase. This means that $P(C' + 3)$ variables must be specified. Every relationship that exists among these variables decreases by one the number that are independent. The following relationships exist:

1. The pressure is the same in each phase. There are $P - 1$ pressure constraints.
2. The temperature is the same in each phase. There are $P - 1$ temperature constraints.
3. The volume of each phase is determined by the pressure, the temperature, and the number of moles of each species present in that phase. (In Chapter 14, we find that the volume of a phase, V , is given rigorously by the equation $V = \sum_k n_k \bar{V}_k$, where n_k and \bar{V}_k are the number of moles and the partial molar volume of the k^{th} species in that phase. The \bar{V}_k depend only on pressure, temperature, and composition.) For P phases, there are P constraints, one for the volume of each phase.
4. To completely specify the system, the concentration of each species must be specified in each phase. This condition creates $C'P$ constraints. (We can also reach this conclusion by a slightly different argument. To specify the concentrations of C' species in some one phase requires C' constraints. A distribution equilibrium relates the concentrations of each species in every pair of phases. There are $P - 1$ independent pairs of phases. For C' chemical species, there are $C'(P - 1)$ such constraints. This is equivalent to the requirement in our phase rule analysis that there are $C(P - 1)$ equilibrium relationships among C components in P phases. In the present problem, the total number of concentration constraints is $C' + C'(P - 1) = C'P$.

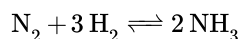
Subtracting the number of constraints from the number of variables, we find that there are

$$P(C' + 3) - (P - 1) - (P - 1) - P - C'P = 2$$

independent variables for a reversible process in a closed system, if all work is pressure-volume work. The number of independent variables is constant; it is independent of the species that are present and the number of phases.

It is important to appreciate that there is no conflict between Duhem's theorem and the phase-rule conclusion that F degrees of freedom are required to specify an equilibrium state of a system containing specified phases. When we say that specifying some pair of variables is sufficient to specify the state of a particular closed system undergoing reversible change, we are describing a system that is continuously at equilibrium as it goes from a first equilibrium state to a second one. Because it is closed and continuously in an equilibrium state, the range of variation available to the system is circumscribed in such a way that specifying two variables is sufficient to specify its state. On the other hand, when we say that F degrees of freedom are required to specify an equilibrium state of a system containing specified phases, we mean that we must know the values of F intensive variables in order to establish that the state of the system is an equilibrium state.

To illustrate the compatibility of these ideas and the distinction between them, let us consider a closed system that contains nitrogen, hydrogen, and ammonia gases. In the presence of a catalyst, the reaction



occurs. For simplicity, let us assume that these gases behave ideally. (If the gases do not behave ideally, the argument remains the same, but more complex equations are required to express the equilibrium constant and the system pressure as functions of the molar composition.) This system has two components and three degrees of freedom. When we say that the system is closed, we mean that the total number of moles of the elements nitrogen and hydrogen are known and constant. Let these be n_N and n_H , respectively. Letting the moles of ammonia present be $n_{\text{NH}_3} = x$, the number of moles of dihydrogen and dinitrogen are $n_{\text{H}_2} = (n_H - 3x)/2$ and $n_{\text{N}_2} = (n_N - x)/2$, respectively.

If we know that this system is at equilibrium, we know that the equilibrium constant relationship is satisfied. We have

$$K_P = \frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}} = \frac{n_{NH_3}^2}{n_{H_2}^3 n_{N_2}} \left(\frac{RT}{V} \right)^{-2} = \frac{16x^2}{(n_H - 3x)^3 (n_N - x)} \left(\frac{RT}{V} \right)^{-2}$$

where V is the volume of the system. The ideal-gas equilibrium constant is a function only of temperature. We assume that we know this function; therefore, if we know the temperature, we know the value of the equilibrium constant. The pressure of the system can also be expressed as a function of x and V . We have

$$P = P_{H_2} + P_{N_2} + P_{NH_3} = \left[\frac{(n_H + n_N)}{2} - x \right] \left(\frac{RT}{V} \right)$$

If we know the system pressure and we know that the system is at equilibrium, we can solve the equations for K and P simultaneously to find the unknowns x and V . From these, we can calculate the molar composition of the system and the partial pressure of each of the gases. (We discuss ideal-gas equilibrium calculations in detail in [Chapter 13](#).) Thus, if we know that the system is at equilibrium, knowledge of the pressure and temperature is sufficient to determine its composition and all of its other properties.

If we do not know that this system is at equilibrium, but instead want to collect sufficient experimental data to prove that it is, the phase rule asserts that we must find the values of some set of three intensive variables. Two are not sufficient. From the perspective provided by the equations developed above, we can no longer use the equilibrium constant relationship to find x and V . Instead, our problem is to find the composition of the system by other means, so that we can test for equilibrium by comparing the value of the quantity

$$\frac{P_{NH_3}^2}{P_{H_2}^3 P_{N_2}} = \frac{16x^2}{(n_H - 3x)^3 (n_N - x)} \left(\frac{RT}{V} \right)^{-2}$$

to the value of the equilibrium constant. We could accomplish this goal by measuring the values of several different combinations of three intensive variables. A convenient combination is pressure, temperature, and ammonia concentration, x/V . When we rearrange the equation for the system pressure to

$$P = \left[\frac{(n_H + n_N)}{2V} - \left(\frac{x}{V} \right) \right] RT$$

it is easy to see that knowing P , T , and x/V enables us to find the volume of the system. Given the volume, we can find the molar composition of the system and the partial pressure of each of the gases. With these quantities in hand, we can determine whether the equilibrium condition is satisfied.

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