

## 6.7: The Number of Variables Required to Specify Some Familiar Systems

If we are to model a physical system mathematically, we must abstract measurable properties from it—properties that we can treat as variables in our model. In [Section 6.2](#) we found that the size of the system does not matter when we consider the variables that specify an equilibrium state. A half-size version of an equilibrium system has the same equilibrium properties. We can say that only intensive properties are relevant to the question of whether a system is at equilibrium.

The idea that we can subdivide a system without changing its equilibrium properties is subject to an important qualification. We intend that both subsystems be qualitatively equivalent to the original. For example, if we divide a system at vapor–liquid equilibrium into subsystems, each subsystem must contain some liquid and some vapor. If we subdivide it into one subsystem that is all liquid and another that is all vapor, the subsystems are not qualitatively equivalent to the original.

We can be more precise about the criterion we have in mind: An equilibrium system consists of one or more homogenous phases. Two systems can be in the same equilibrium condition only if all of the phases present in one are also present in the other. If a process changes the number of phases present in a system, we consider that the system changes from one kind of equilibrium system to a second one. We can describe one kind of equilibrium system by specifying a sufficient number of intensive variables. This description will be complete to within a specification of the exact amount of each phase present.

If we apply these ideas to a macroscopic sample of a pure gas, we know that we need four variables to completely describe the state of the gas: the number of moles of the gas, its pressure, its volume, and its temperature. This assumes that we are not interested in the motion of the container that contains the gas. It assumes also that no other extrinsic factors—like gravitational, electric, or magnetic fields— affect the behavior that we propose to model

When we do experiments in which the amount, pressure, volume, and temperature of a pure gas vary, we find that we can develop an equation that relates the values that we measure. We call this an *equation of state*, because it is a mathematical model that describes the state of the system. In [Chapter 2](#), we reviewed the ideal gas equation, van der Waals equation, and the virial equation; however, we can devise many others. Whatever equation of state we develop, we know that it must have a particular property: At constant pressure and temperature, the volume must be directly proportional to the number of moles. This means that any equation of state can be rewritten as a function of concentration. For the case of an ideal gas, we have  $P = (n/V) RT$ , where  $n/V$ , the number of moles per unit volume, is the gas concentration. We see that any equation of state can be expressed as a function of three intensive variables: pressure, temperature, and concentration.

The existence of an equation of state means that only two of the three intensive variables that describe the gas sample are independent of one another. At equilibrium, a sample of pure gas has two degrees of freedom. Viewed as a statement about the mathematical model, this is true because knowledge of the equation of state and any two of the intensive variables enables us to calculate the third variable. Viewed as a statement about our experimental observations, this is true because, so long as the changes are consistent with the system remaining a gas, we can change any two of these variables independently. That only two are independent is shown experimentally by the observation that we can start with a fixed quantity of gas at any pressure, temperature, and concentration and find, after taking the system through any sequence of changes whatsoever, that returning to the original pressure and temperature also restores the original concentration.

In the experiment or in the mathematical model, fixing two of the three intensive variables is sufficient to fix the equilibrium properties of the system. Fixing the equilibrium properties means, of course, that the state of the system is fixed to within an arbitrary factor, which can be specified either as the number of moles present or as the system volume.

Similar results are obtained when we study the pressure–volume–temperature behavior of pure substances in condensed phases. At equilibrium, a pure liquid or a pure solid has two degrees of freedom.

If we consider a homogeneous mixture of two non-reacting gases, we discover that three variables are necessary to fix the equilibrium properties of the system. We must know the pressure and temperature of the system and the concentration of each gas. Because the mixture must obey an equation of state, determination of any three of these variables is sufficient to fix the value of the fourth. Note that we can conclude that three intensive variables are sufficient to determine the equilibrium properties of the system even if we do not have a mathematical model for the equation of state.

If we experiment with a system in which the liquid and vapor of a pure substance are in phase equilibrium with one another, we find that there is only one independent intensive variable. (Figure 4 illustrates this for water.) To maintain phase equilibrium, the system pressure must be the equilibrium vapor pressure of the substance at the system temperature. If we keep the pressure and

temperature constant at equilibrium values, we can increase or decrease the concentration (moles per unit system volume) by removing or adding heat. In this process, we change one variable, concentration, while maintaining phase equilibrium.

If we keep the pressure constant and impose a temperature increase, vaporization continues (the concentration decreases) until the liquid phase is completely consumed. In this process, two variables change, and phase equilibrium cannot be maintained. To reach a new equilibrium state in which both liquid and gas are present at a higher temperature, we must increase the pressure to the new equilibrium vapor pressure; the magnitude of the temperature increase completely determines the required pressure increase. Two intensive variables change, but the changes are not independent.

If we have pure gas, there are two independent intensive variables. If we have pure liquid, there are two independent intensive variables. However, if we have liquid and gas in equilibrium with one another, there is only one independent intensive variable. In the liquid region of the water phase diagram, we can vary pressure and temperature and the system remains liquid water. Along the liquid-gas equilibrium line, we can vary the temperature and remain at equilibrium only if we simultaneously vary the pressure so as to remain on the liquid-gas equilibrium line.

Similar statements apply if we contrast varying pressure and temperature for the pure solid to varying the pressure and temperature along the solid-liquid or the solid-gas equilibrium line. At the triple point, nothing is variable. For a fixed quantity of water, the requirement that the system be at equilibrium at the triple point fixes the system pressure, temperature, and concentration. Evidently, maintaining a phase equilibrium in a system imposes a constraint that reduces the number of intensive variables that we can control independently.

The equilibrium between water and ice is completely unaffected by the state of subdivision of the ice. The ice can be present in a single lump or as a large number of very small pieces; from experience, we know that the equilibrium behavior of the system is the same so long as some ice and some water are both present. A system contains as many phases as there are *kinds* of macroscopic, homogeneous, bounded portions that are either solid, liquid, or gas.

If we add a lump of pure aluminum to our ice-water system, the new system contains three phases: water, ice, and aluminum. The equilibrium properties of the new system are the same if the aluminum is added as a ground-up powder. The powder contains many macroscopic, homogeneous, bounded portions that are aluminum, but each of these portions has the same composition; there is only one kind of aluminum particle. (Molecules on the surface of a substance can behave differently from those in the bulk. When a substance is very finely divided, the fraction of the molecules that is on the surface can become large enough to have a significant effect on the behavior of the system. In this book, we do not consider systems whose behavior is surface-area dependent.)

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