

6.6: Le Chatelier's Principle

In [Chapter 1](#), we describe a very general goal: given that we create a system in some arbitrary initial state (by some “change of conditions” or “removal of some constraint”), we want to predict how the system will respond as it changes on its own (“spontaneously”) to some new equilibrium state. Under these circumstances, we need a lot of information about the system before we can make any useful prediction about the spontaneous change. In this case, we have said nothing about the condition of the system before we effect the change of conditions that creates the arbitrary “initial state”.

Our ability to make useful predictions is much greater if the system and the change of conditions have a particular character. If we start with a system that is at equilibrium, and we impose a change in conditions on it, the “initial” state of the system after the imposed change of conditions will generally not be an equilibrium state. Experience shows that the system will undergo some spontaneous change to arrive at a new equilibrium state. In these particular circumstances, Le Chatelier’s principle enables us to predict the spontaneous change that occurs.

Definition: Le Chatelier’s principle

If a change is imposed on the state of a system at **equilibrium**, the system adjusts to reach a new equilibrium state. In doing so, the system undergoes a spontaneous change that opposes the imposed change.

Le Chatelier’s principle is useful, and it is worthwhile to learn to apply it. The principle places no limitations on the nature of the imposed change or on the number of thermodynamic variables that might change as the system responds. However, since our reasoning based on the principle is qualitative, it is frequently useful to suppose that the imposed change is made in just one variable and that the opposing change involves just one other variable. That is, we ask how changing one of the variables that characterizes the equilibrated system changes a second such variable, “all else being equal.” Successful use of the principle often requires careful thinking about the variable on which change is imposed and the one whose value changes in response. Let us consider some applications.

Vapor–liquid equilibrium

Vapor–liquid equilibrium. Suppose that we have a sealed vial that contains only the liquid and vapor phases of a pure compound. We suppose that the vial and its contents are at a single temperature and that the liquid and the vapor are in equilibrium with one another at this temperature. What will happen if we now thermostat the vial at some new and greater temperature?

We see that the imposed change is an increase in temperature or, equivalently, an addition of heat to the system. The system cannot respond by decreasing its temperature, because the temperature change is the imposed change. Similarly, it cannot respond by changing its volume, because the system volume is fixed. Evidently, the observable consequence of increasing temperature—adding heat—must be a change in the pressure of the system. The principle asserts that the system will respond so as to consume heat. Converting liquid to vapor consumes the latent heat of vaporization, so the system can oppose the imposed addition of heat by converting liquid to vapor. This increases the pressure of the vapor. We can conclude from Le Chatelier’s principle that increasing the temperature of a system at liquid-vapor equilibrium increases the equilibrium vapor pressure.

Now suppose that we have the liquid and vapor phases of the same pure compound in a thermally isolated cylinder that is closed by a piston. We ask what will happen if we decrease the volume. That is, the imposed change is a step decrease in volume, accompanied by an increase in pressure. The new volume is fixed, but the pressure is free to adjust to a new value at the new equilibrium position. The principle asserts that the system will respond so as to decrease its pressure. Decreasing the system pressure is accomplished by condensing vapor to liquid, which is accompanied by the release of the latent heat of vaporization. Since we suppose that the system is thermally isolated during this process, the heat released must result in an increase in the temperature of the system. While the pressure can decrease from the initial non-equilibrium value, it cannot decrease to its original-equilibrium value; evidently, the new equilibrium pressure must be greater than the original pressure.

We again conclude that an increase in the equilibrium vapor pressure requires an increase in the temperature of the system. (If the volume decrease were imposed with the system immersed in a constant temperature bath, the heat evolved would be transferred from the system to the bath. The system would return to its original pressure and original temperature, albeit with fewer moles of the substance present in the gas phase.)

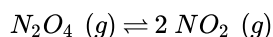
Ice–water equilibrium

Suppose that we have a closed system consisting of ice in equilibrium with liquid water at some temperature and pressure. What will happen if we impose an increase in the temperature this system? We suppose that the system occupies a container of fixed volume. Initially it is at equilibrium with a constant-temperature bath. We impose the change by moving the container to a new bath whose temperature is higher—but not high enough to melt all of the ice. The imposed change is a temperature increase or, equivalently, an addition of heat. The principle asserts that the system will respond by consuming heat, which it can do by converting ice to liquid. Since liquid water occupies less volume than the same mass of ice, the system pressure will decrease. We conclude that the pressure at which ice and water are at equilibrium decreases when the temperature increases. That is, the melting point increases as the pressure decreases.

Again, we can imagine that the equilibrium mixture of ice and water is contained in a thermally isolated cylinder that is closed by a piston and ask how the system must respond if we impose a step decrease in its volume. We impose the volume decrease by applying additional force to the piston. The imposed step change in the volume is accompanied by an increase in the system pressure; the new volume is fixed, but the system pressure can adjust. The principle asserts that the system will respond by decreasing its pressure. The system pressure will decrease if some of the ice melts. Melting ice consumes heat. Since we are now assuming that the system is thermally isolated, this heat cannot come from outside the system, which means that the temperature of the system must decrease. While the pressure can decrease from its initial non-equilibrium value, it cannot decrease to the value that it had in the original equilibrium position. We again conclude that increasing the pressure results in a decrease in temperature; that is, the melting point of ice increases as the pressure decreases.

Chemical reaction between gases

Chemical reaction between gases. Finally, suppose that we have a chemical equilibrium involving gaseous reagents. To be specific, let us again consider the reaction



We suppose that this system is initially at equilibrium at some temperature and that we seek to increase the pressure while maintaining the temperature constant. (We can imagine that the system is contained in a cylinder that is closed by a piston. The cylinder is immersed in a constant-temperature bath. We increase the pressure by applying additional force to the piston. As in the examples above, we view this as a step change in volume that is accompanied by an increase of the pressure to a transitory non-equilibrium value.) The principle asserts that the system will respond by undergoing a change that opposes this pressure increase. The system can reduce its pressure by decreasing the number of moles of gas present, and it can do this by converting NO_2 molecules to N_2O_4 molecules. We conclude that there will be less NO_2 present at equilibrium at the higher pressure.

When we first encounter it, Le Chatelier's principle seems to embody a remarkable insight. As, indeed, it does. However, as we think about it, we come to see it as a logical necessity. Suppose that the response of an equilibrium system to an imposed change were to augment the change rather than oppose it. Then an imposed change would reinforce itself. The slightest perturbation of any equilibrium system would cause the system to “run away” from that original position. Since no real system can be maintained at a perfectly constant set of conditions, any real system could undergo spontaneous change. Equilibrium would be unattainable. If we assume that a system must behave oppositely to the way that is predicted by Le Chatelier's principle, we arrive at a prediction that contradicts our experience.

Le Chatelier's principle is inherently qualitative. We will discuss it further after we develop the thermodynamic criteria for equilibrium. We will find that the thermodynamic criteria for equilibrium tell us quantitatively how two (or more) thermodynamic variables must change in concert if a system is to remain at equilibrium while also undergoing some change of condition.

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