

12.5: Another Perspective on the Principle of Le Chatelier

When we apply Le Chatelier's principle, we imagine an equilibrium system on which we impose some step-wise change. Immediately following the imposition of this change, we isolate the system from all further interactions with its surroundings. This isolated system is a hypothetical construct, which can be only approximated in any real experiment. It has peculiar features: While the changed and isolated system has the properties of the original system, it is also free to undergo a further change that the original system could not. The hypothetical isolated system is no longer at equilibrium; it can undergo a spontaneous process of further change until it reaches a new position of equilibrium. The principle asserts that this further change opposes the imposed change.

The principle is inherently qualitative. This contributes to its utility in that we do not have to have quantitative data in order to use it. However, a qualitative prediction is less useful than a quantitative one. Let us now attempt to apply our second-law based quantitative models to the sequence of changes envisioned by Le Chatelier's principle. We begin by restating the principle in more mathematical language. We then illustrate these ideas for the specific case of vapor-liquid equilibrium with temperature and pressure as the independent variables.

Let us suppose that W , X , Y , and Z are a set of thermodynamic variables that is adequate to specify the state of the system. In any equilibrium state, the entropy of the system is then a function of these variables; we have $S = S(W, X, Y, Z)$. For present purposes, we assume that we know the function $S(W, X, Y, Z)$. Given small changes, dW , dX , dY , and dZ , in the independent variables, we can find the change in dS for a reversible transition from (W, X, Y, Z) to $(W + dW, X + dX, Y + dY, Z + dZ)$:

$$dS = \left(\frac{\partial S}{\partial W} \right)_{XYZ} dW + \left(\frac{\partial S}{\partial X} \right)_{WYZ} dX + \left(\frac{\partial S}{\partial Y} \right)_{WXZ} dY + \left(\frac{\partial S}{\partial Z} \right)_{WXY} dZ$$

When we impose the change creating the hypothetical isolated system, we imagine that some characteristic of the system changes instantaneously, and that it does so without changing the other properties of the system. Since we suppose that nothing about the system changes in the perturbation and isolation step, the entropy of the perturbed, isolated, hypothetical system remains the same as that of the original equilibrium system.

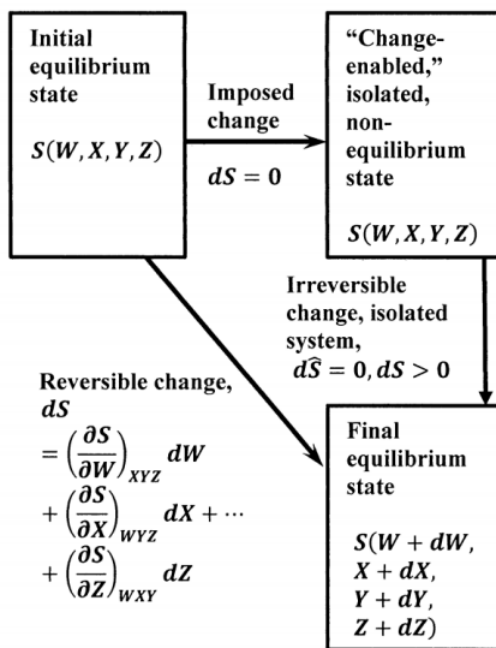


Figure 2. Spontaneous and reversible processes connecting the same equilibrium states.

Figure 2 shows the entropies for three states in the cycle that comprises the Le Chatelier model for change. The entropy of the original equilibrium system is $S(W, X, Y, Z)$ and that of the final equilibrium system is $S(W + dW, X + dX, Y + dY, Z + dZ)$. The same final equilibrium state is reached by both the irreversible transition from the change-enabled hypothetical state and by a reversible transition from the initial equilibrium state. Since entropy is a state function, its change around this cycle must be zero. Hence, the incremental changes dW , dX , dY , and dZ that occur in the thermodynamic variables must satisfy the inequality

$$\left(\frac{\partial S}{\partial W}\right)_{XYZ} dW + \left(\frac{\partial S}{\partial X}\right)_{WYZ} dX + \left(\frac{\partial S}{\partial Y}\right)_{WXZ} dY + \left(\frac{\partial S}{\partial Z}\right)_{WXY} dZ > 0$$

We can view the application of this inequality to the hypothetical, change-enabled, isolated system as a mathematical expression of Le Chatelier's principle. To see this more clearly, let us suppose that we are able to keep W and Z constant. We suppose that the imposed change requires that the final value of X be $X + dX$. For the system to remain at equilibrium, the remaining variable, Y , must change by an amount, dY , that satisfies this inequality. That is, to reach the new equilibrium state, the change in Y must satisfy

$$\left(\frac{\partial S}{\partial X}\right)_{WYZ} dX + \left(\frac{\partial S}{\partial Y}\right)_{WXZ} dY > 0$$

In this model, variables X and Y drive the entropy change as the hypothetical system moves toward its new equilibrium position. The imposed change in X changes the entropy of the system by

$$dS_{\text{imposed}} = \left(\frac{\partial S}{\partial X}\right)_{WYZ} dX$$

Since the effect of the imposed change is to drive the system away from its original equilibrium position, we have $dS_{\text{imposed}} < 0$. The system's response changes the entropy of the system by

$$dS_{\text{response}} = \left(\frac{\partial S}{\partial Y}\right)_{WXZ} dY$$

We have $dS_{\text{response}} > -dS_{\text{imposed}} > 0$, so that we can reasonably describe the response, dY , that makes $dS_{\text{response}} > 0$, as a change that opposes the imposed change, dX , that makes $dS_{\text{imposed}} < 0$.

Applying Le Chatelier's principle is something of an art. Central to this art is an ability to devise a hypothetical, change-enabled, isolated, non-equilibrium state that is a good model for the initial state of the spontaneous process. In [Section 6.6](#), we use qualitative arguments to apply Le Chatelier's principle to vapor-liquid equilibrium. To relate these qualitative arguments to the mathematical model we have developed, let us consider the *gedanken* experiment depicted in Figure 3. We suppose that the initial equilibrium system contains the liquid and vapor of a pure substance at pressure, P , and temperature, T . We imagine that we can create the hypothetical isolated system by imposing a step change to the applied pressure without changing the pressure of the system.

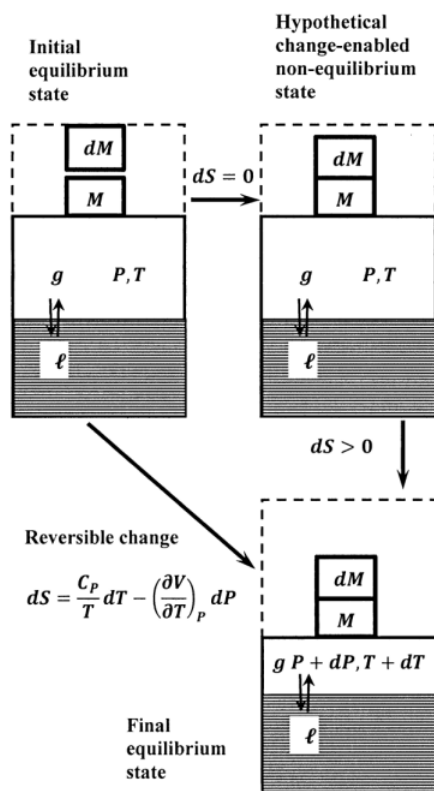


Figure 3. Spontaneous and reversible processes connecting the same liquid-vapor equilibrium states.

To model the pressure perturbation, let us view the liquid–vapor mixture as a subsystem, which is enclosed in a vertical cylinder that is sealed by a frictionless piston. A mass, M , rests on top of the piston. For present purposes, we consider this mass to be a portion of a second subsystem. The gravitational force on this mass creates the pressure applied to the liquid–vapor mixture. Since this is an equilibrium state of the substance, this applied pressure is equal to the pressure, P , of the liquid–vapor subsystem. A small mass, dM , is also a part of the second subsystem. In this original equilibrium state of the system, this smaller mass is supported in some manner, so that it does not contribute to the applied pressure. We assume that the piston is a perfect thermal insulator, so that no heat can be exchanged between the two subsystems.

As sketched in Figure 3, we create the hypothetical change-enabled system by moving the smaller mass so that it too rests on top of the piston. Immediately thereafter, we completely isolate the system from the rest of the universe. We suppose that the applied pressure instantaneously increases to $P + dP$. However, since the liquid–vapor subsystem is unchanged, we suppose that the pressure, entropy, and all other thermodynamic properties of the liquid–vapor subsystem remain unchanged in this hypothetical state. The system is not at equilibrium in this hypothetical state, because the applied pressure is not equal to that of the liquid–vapor subsystem. Spontaneous change to a new equilibrium state can occur. Because the system is isolated, $\Delta\hat{S} = 0$. Therefore, we have $\Delta S > 0$. The final equilibrium temperature is $T + dT$.

With pressure and temperature as the independent variables, this model for Le Chatelier's principle gives rise to the following mathematical requirement:

$$dS = T^{-1}(\partial H/\partial T)_P dT - (\partial V/\partial T)_P dP > 0.$$

We know that T , $(\partial H/\partial T)_P$, and $(\partial V/\partial T)_P$ are positive. Therefore we can rearrange the inequality to find

$$dT > T \left[\left(\frac{\partial V}{\partial T} \right)_P / \left(\frac{\partial H}{\partial T} \right)_P \right] dP$$

If we have $dP > 0$, it follows that $dT > 0$; that is, the liquid–vapor equilibrium temperature increases with pressure.

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