

6.14: Thermodynamic Criteria for Change

When the state of an isolated system can change, we say that the system is capable of spontaneous change. When an isolated system is incapable of spontaneous change, we say that it is at equilibrium. Ultimately, this statement defines what we mean by (primitive) equilibrium. From our statement of the second law of thermodynamics, we have criteria for spontaneous change and for equilibrium in any macroscopic system:

- An isolated system can undergo any change that results in an increase in the entropy of the system. The converse is also true; an isolated system whose entropy can increase can undergo change. Any such change is said to be spontaneous. If an isolated system cannot change in such a way that its entropy increases, the system cannot change at all and is said to be at equilibrium.
- A system that is not isolated can undergo any change that results in an increase in the entropy of the universe, and conversely. Such changes are also said to be spontaneous.
- If a system that is not isolated undergoes a change, but the entropy of the universe remains constant, the change is not spontaneous. The entropy changes for the system and the surroundings are equal in magnitude and opposite in sign. The change is said to be reversible.

Although the first statement applies to isolated systems and the second applies to systems that are not isolated, we usually consider that both are statements of the same criterion, because the second statement follows from the first when we view the universe as an isolated system. We can restate these criteria for spontaneous change and equilibrium using the compact notation that we introduce in [Section 6.13](#).

From our definitions, any change that occurs in an isolated system must be spontaneous. From our statement of the second law, the entropy of the universe must increase in any such process. To indicate this, we write $\Delta S_{universe} > 0$. The surroundings must be unaffected by any change in an isolated system; hence, none of the surroundings' state functions can change. Thus, $\Delta \hat{S} = 0$, and since $\Delta S + \Delta \hat{S} = \Delta S_{universe} > 0$, we have $\Delta S > 0$.

For a spontaneous change in a system that is not isolated, ΔS can be greater or less than zero. However, ΔS and $\Delta \hat{S}$ must satisfy

$$\Delta S + \Delta \hat{S} = \Delta S_{universe} > 0.$$

In a system that is not isolated, reversible change may be possible. A system that undergoes a reversible change is at—or is arbitrarily close to—one of its equilibrium states during every part of the process. For a reversible change, it is always true that $\Delta S = -\Delta \hat{S}$, so that

$$\Delta S + \Delta \hat{S} = \Delta S_{universe} = 0.$$

Our criteria for change are admirably terse, but to appreciate them we need to understand precisely what is meant by “entropy”. To use the criteria to make predictions about a particular system, we need to find the entropy changes that occur when the system changes. To use these ideas to understand chemistry, we need to relate these statements about macroscopic systems to the properties of the molecules that comprise the system.

Since an isolated system does not interact with its surroundings in any way, no change in an isolated system can cause a change in its surroundings. If an isolated system is at equilibrium, no change is possible, and hence there is no system change for which the entropy of the universe can increase. Evidently, the entropy of the universe is at a maximum when the system is at equilibrium.

Typically, we are interested in what happens when the interaction between the system and surroundings serves to impose conditions on the final state of a system. A common example of such conditions is that the surroundings maintain the system at a constant pressure, while providing a constant-temperature heat reservoir, with which the system can exchange heat. In such cases, the system is not isolated. It turns out that we can use the entropy criterion to develop supplemental criteria based on other thermodynamic functions. These supplemental criteria provide the most straightforward means to discuss equilibria and spontaneous change in systems that are not isolated. Which thermodynamic function is most convenient depends upon the conditions that we impose on the system.

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