# Solid State Thermodynamics

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## Entropy and Disorder

What is the entropy? It is a measure of the disorder in the system. An increase in entropy of a system means that its randomness has increased. A solid crystal is more ordered than its liquid since the crystal atoms are arranged in a well defined pattern. The atoms of the liquid move about randomly. Likewise, the vaporization of the liquid results in a higher entropy phase because the motion and configuration of the atoms of the liquid were more ordered than the motions and configuration of the atoms in the gas. The entropy of the a drop of dye placed in a glass of water increases as the dye diffuses and the system mixes. As heat flows down a temperature gradient, entropy increases because energy is dispersed in the system more randomly.

Although all this is correct, we haven't said anything quantifiable yet or anything that can help us solve a thermodynamics problem. To do this we'll have to develop more of the connection between entropy, disorder, reversibility and spontaneous processes, and then we can get back to developing the quantitative rules associated with entropy. Let's be more precise by what we mean by disorder.

### Disorder

Disorder is related to the degree to which energy, atomic configuration, and motion in a system are not ordered. For example, if the atoms in a solid all move together in a uniform way, there is no disorder in their motion. On the other hand, if each atom follows a trajectory which appears independent of the other atoms in the system then the motion of the atoms is disordered, and random. One way to see how much disorder is in a system is to analyze how much detail is required to specify the microscopic state of a system. An ordered system requires very little data to describe it. For example, the location of atoms in a perfect crystal can be specified with the lattice type, basis and lattice constants. On the other hand, the exact structure of a disordered alloy would be impossible to specify. We connect the concepts of disorder and spontaneity by noticing that the amount of order tends to naturally decrease as a process proceeds.

Spontaneity is naturally associated with processes which increase the disorder or entropy of the universe. The entropy of the ball and ground is higher on the n$^{th}$ bounce than it was on the (n-1)$^{th}$ bounce because some of the energy of the ball was converted into the disordered motion of the atoms in the ball and the ground. The entropy of the mixture of dye and water increases with time since at any given point in time our knowledge of the location of the dye decreases. The direction of processes is associated with disorder increasing with time. Furthermore, if processes do not lead to overall decreases in the amount of disorder in the universe, then a process cannot be reversed if it increased the disorder of the universe because in order to reverse it we would have to somehow create the original amount of order from the state of increased disorder. Let's state an axiom here which will make a more precise statement about the entropy and reversibility of processes.

### Entropy

**Axiom 2** *There exists a property of systems called* ***entropy S****, which is functionally related to the measurable coordinates which characterize the system and which is an intrinsic property of the system related to the degree of disorder within the system. For a reversible process, changes in the entropy are given by:*

$$dS = \frac{\delta q}{T}.$$

This relationship between the heat of the process, the temperature and the differential change in entropy of the process only holds for reversible processes. Note also that since the entropy is functionally related to the measurables that characterize the system it must be a state function. We'll discuss this in more detail later. Let's now state another axiom having to do with entropy.

# The Second Law

**Axiom 3** *The* ***Second Law of Thermodynamics*** *states that the change in entropy of the universe (that is the system and its surroundings considered together) is positive and approaches zero for any process which approaches reversibility.*

$$\Delta S_{total} \geq 0$$

*with the equality holding when the process is reversible.*

In other words, a process increases the entropy (disorder) of the universe, unless it is reversible in which case it leaves the entropy of the universe unchanged. Remember, that a process is said to be reversible if its direction can be reversed at any given point in time by an infinitesimal change in the external conditions of the system. So if a process is reversible it must have not been creating entropy since once it has created entropy that entropy cannot be destroyed. This is again because if entropy has increased, then disorder has increased. To return to the state of order from a state of higher disorder would require creating order from disorder, which is impossible, as is implicitly stated by the Second Law. Notice then that the Second Law also implies that a process must be proceeding infinitesimally slowly to not be creating entropy. That is, if the driving forces for the process are finite, then an infinitesimal force cannot reverse them. Since the process cannot be reversed by the infinitesimal driving force then it must be creating entropy so a process which proceeds at a finite rate is not reversible.

For example, if I am melting ice by adding heat very slowly, I can reverse the melting, that is I can refreeze the water by removing heat slowly from the system. This process can be reversed because if it is done slowly it is kept very close to its equilibrium condition because the driving forces for the process are kept infinitesimally small. If I heat the ice too rapidly, then some of the heat might lead to causing the liquid water to heat up, which would cause the molecules to move quickly and dissipate their energy in ways other than in melting the ice. Another example is the isothermal expansion of a gas. Lowering the pressure on the gas slightly allows the gas to expand slowly. Increasing the pressure again causes the gas to compress back to its original state. If the pressure is lowered more than an infinitesimal amount then the gas will expand rapidly, creating temperature and pressure gradients and heat flow and dissipation of the energy of the gas.

Another statement of the Second Law, which can either be viewed as a result of our statement of the 2nd Law or as an alternative statement for it is:

*No process is possible in which the sole result is the adsorption of heat from a reservoir and its complete conversion into work.*

Some heat is always discarded during the process to a cold sink which increases the entropy of the cold sink. This is again related to the fact that order cannot be created from disorder. Creating ordered motion (work) from disordered motion (heat) can be done, but the overall process produces entropy.

# Chapter 3 Main Points

1. A **spontaneous process** is one which occurs with no external driving force and produces entropy.

2. A **reversible** process is one which reverses itself with an infinitesimal driving force. This process involves no production of entropy and occurs infinitely slowly.



3. The natural direction of processes is the direction that leads to increases in the entropy of the universe.

4. There exists a property of systems called **entropy**, which is a function related to the state of the system and which is an intrinsic property of the system related to the degree of **disorder** within the system. For a *reversible process*, changes in the entropy are given by:

$$dS = \frac{\delta q}{T}.$$

1. The **Second Law of Thermodynamics** states that the change in *entropy* of the universe is positive and approaches zero for any process which approaches reversibility.

2. The entropy of a system may decrease for a given process if an entropy transfer to the surroundings is greater than the decrease in entropy of the system.

3. The combined First and Second Laws of thermodynamics:

$$dU = TdS - PdV$$