Thermodynamics
Professor Anand T N C
Department of Mechanical Engineering
Indian Institute of Technology, Madras
Lecture 79
Entropy Part 6

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What is Entropy?

First law
$$dE = \delta Q - \delta W$$

Second law
$$dS_{rev} = \delta Q/T$$

Change = Ratio of heat transferred to the temperature at which it occurs

Term be used in everyday life: e.g. rubbing hands, cooling coffee, making ice-cream all increase entropy!

General objective: for higher efficiency, achieve goal with a smaller total increase in entropy.

Statistical thermodynamics: entropy is defined in terms of probability.

The net increase in entropy that occurs during an irreversible process can be associated with a change of state from a less probable state to a more probable state.

Let's recap some of the concepts.

For a process, the first law is written as $dE = \delta Q - \delta W$. For a cyclic process, the first law is written as $\oint \delta Q = \oint \delta W$. Using the second law, we were able to obtain $\oint \frac{\delta Q}{T} = 0$ for a reversible cycle. A change in entropy for a reversible process is the ratio of heat transfer to the temperature at which heat transfer takes place. For a process, $dS \geq \frac{\delta Q}{T}$. In reality, most of the processes are irreversible, and entropy is generated in the process. Hence, almost all the processes in practice increase the entropy of the universe.

We use a lot of engineering devices. Our goal is to increase the efficiency of these devices. We know that the reversible process produces the maximum possible work output (power) and consumes the least work (power) for the given conditions. The irreversible processes, because of entropy generation, are less efficient than the reversible processes. However, as mentioned before, almost all the practical processes taking place in devices are irreversible. Hence, the goal is to achieve a process with as little entropy generation as possible in the system as well as surroundings so that the efficiency of the device increases.
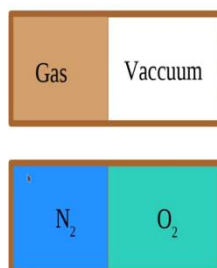
Figure 1.

In statistical thermodynamics, we define entropy in terms of probability. The net increase in entropy that occurs during an irreversible process can be associated with a change of state from a less probable state to a more probable state.

In statistical thermodynamics, entropy is defined as $S = k \ln(w)$, where k is the Boltzmann constant, w is the thermodynamic probability (number of possible configurations). Let's take an example.

Figure 1 shows a box with a partition separating gas and vacuum. The box is well insulated and rigid. There is no heat and work interaction. It means the internal energy of the gas remains constant. There are also no changes in kinetic and potential energy of the system (gas). As the partition is removed, the gas molecules move into the vacuum side. Initially, when the partition was there, suppose that the probability of finding a gas molecule anywhere in the rigid box is p_1. When the partition is removed, the gas molecules occupy the entire space available in the box. Now, the probability of finding a gas molecule anywhere in the rigid box is more than p_1. Hence, removing the partition increases the entropy of the system. The number of possible configurations has increased. This process is unrestrained expansion of the gas, which, we know, is irreversible.

Mixing of two gases is also an irreversible process. Figure 1 shows an insulated and rigid box with a partition separating nitrogen and oxygen. The partition divides the volume equally. As the partition is removed, the gases mix (given sufficient time). Now, the probability of

finding nitrogen as well as oxygen molecule anywhere in the rigid box has increased as compared to the case when those molecules were separated by the partition, i.e., it is more likely that we will find a nitrogen or oxygen molecule anywhere in the rigid box than to find it in their respective halves when the partition was present. The number of possible configurations for the molecules of both the gases has increased. Hence, the mixing of nitrogen and oxygen after removing the partition increases the entropy of the system (nitrogen and oxygen). Bringing back the nitrogen and oxygen molecules from their mixture to their initial respective halves when the partition was present needs a lot of work to be done on the system. Hence, the mixing of gases is irreversible.

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Configuration with only one type of energy (e.g.: P.E.)

2 units of energy: 2 equally likely configurations: some S

Add 2 units of heat: total energy = 4 units

Floor	0	1	2	3	4
No. of obj.	3	0	0	0	1
	2	1	0	1	0
	2	0	2	0	0
	1	2	1	0	0
	0	4	0	0	0

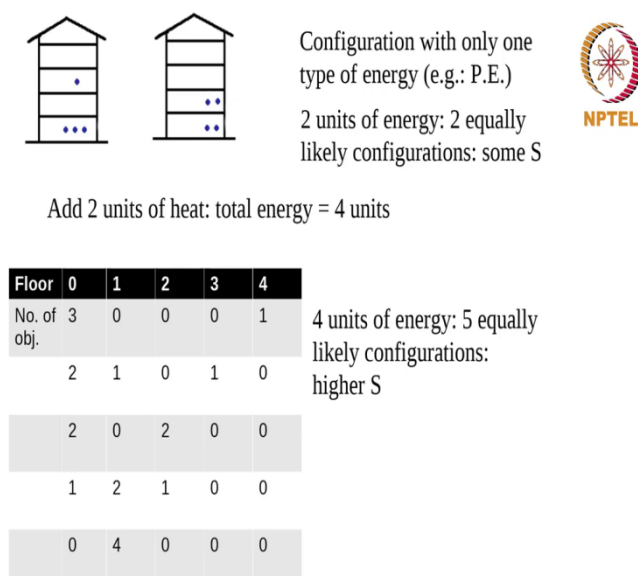4 units of energy: 5 equally likely configurations: higher S

Figure 2.

Figure 2 shows houses (a house-like structure) with 5 floors (0 to 4) and 4 objects in it. This configuration has only one type of energy, e.g., potential energy. The objects have only potential energy. The units of potential energy the object has depends on which floor the object is. For example, the object on the 0th floor has 0 units of potential energy, whereas the object on the 4th floor has 4 units of potential energy.

In the first configuration, 3 objects are on the 0th floor and 1 object is on the 2nd floor. Hence, the total energy is 2 units. In the second configuration, 2 objects are on the 0th floor and the other 2 are on the first floor. Hence the total energy is 2 units. These are the only two possible and equally likely configurations with four objects having 2 units of energy in total. The entropy corresponding to these configurations is S. Let's add 2 units of energy (heat). Now,

we have 4 units of energy in total. What are the possible configurations of the objects having 4 units of energy in total? The table in Fig. 2 shows 5 equally likely configurations of the objects. For example, one of the configurations has all the 4 objects on the 1st floor (each object has one unit of energy). Each of the configurations has 4 units of energy in total. Initially, we had 2 possible configurations with 2 units of energy in total. After adding 2 units of energy (heat), the number of possible configurations increased to 5. Hence, the entropy of the system has increased. The more the number of the possible configurations, the larger is the entropy.
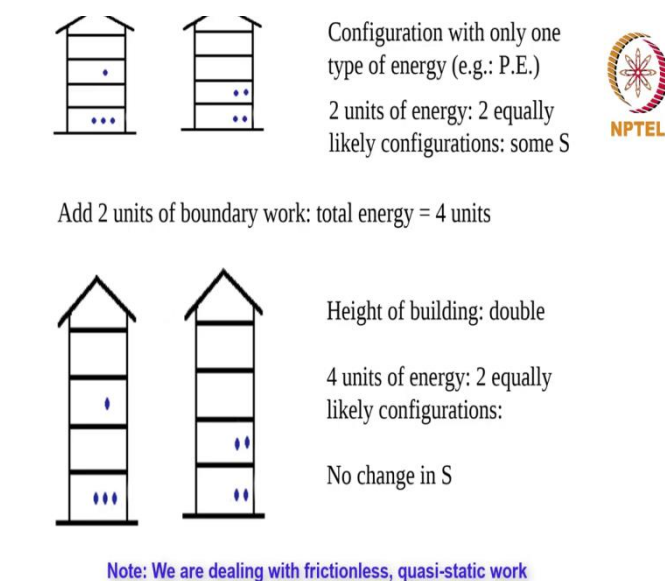
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Figure 2.

What if instead of adding 2 units of heat we add 2 units of work (frictionless, quasi-static)?

The upper half of Fig. 2 shows the initial configurations having 2 units of energy each. The corresponding entropy is S. When we do boundary work on the system (the house), it gets stretched in the vertical direction (the boundary gets stretched in the vertical direction) as we are considering only the potential energy. The boundary cannot stretch in the horizontal direction as it would not increase the potential energy of the system. The stretched houses are now double the height of the original houses. In this new building, an object on the 0th floor still has 0 unit of energy. However, the object on the 1st, 2nd, 3rd and 4th floor has 2, 4, 6 and 8 units of potential energy as the houses' height is doubled now. We see that the number of possible configurations are still the same after doing boundary work of 2 units. In the first configuration, the three objects on the 0th floor have 0 unit of energy each, whereas the object

on the 2nd floor has 4 units of energy. In the second configuration, the two objects on the 0th floor have 0 unit of energy each, whereas the two objects on the 1st floor have 2 units of energy each adding to 4 units in total. As the number of possible and equally likely configurations has not changed after doing a boundary work of 2 units, the entropy of the system does not increase. So, adding 2 units of energy through heat transfer increased the entropy of the system, whereas adding 2 units of energy through work transfer (frictionless, quasi-static) did not.

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This brings us to grades of energy. According to the first law, energy can neither be created nor destroyed, but it can be transformed from one form to another.

It is easy to convert 100 J of work to 100 J of heat. For example, 100 J of work from a battery can be converted to 100 J of heat using a resistance, assuming steady state operation. So, the complete conversion of work to heat is possible. It is also possible in a cyclic process (Joule's experiment).

Can we convert 100 J of heat to 100 J of work in a cyclic process?

It is not possible according to the second law. In a cyclic process, if you want to convert heat to work, some amount of heat needs to be rejected, i.e., out of the heat supplied, some gets converted to work, and the remaining heat needs to be rejected. The complete conversion of heat to work is not possible in a cycle as it violates the second law. The maximum possible conversion of heat to work can happen in a Carnot's engine.

There is a distinction between work and heat. Heat and work are the forms of energy. The first law says that the energy can be transformed from one form to another. However, there are restrictions on the complete conversions from one form to another as we just saw.

So, we can have a cyclic process converting work into heat completely. However, we cannot have a cyclic process converting heat into work completely. Work is useful because we can use it either as work or we can convert it into heat. Heat is not as useful because we can use it as heat, but we cannot convert it back on into work completely. Hence, we have grades of energy.

Mechanical work, potential energy, kinetic energy and electrical energy are high grades of energy. They can be converted into each other among themselves. For example, (a) mechanical work can be converted into electrical energy, potential energy, and kinetic energy, (b) potential energy of the falling object gets converted into kinetic energy. Some losses do happen during conversion.

Chemical energy is low grade energy. In most of the applications, we cannot convert chemical energy directly into work. We usually convert chemical energy into heat and then convert heat into work. For example, chemical energy of fuels is converted into heat by burning them, and the heat released can be converted to work (e.g. thermal power plant). However, the losses here are larger compared to conversions of high grades of energy among themselves.

Heat is the lowest grade of energy. Its complete conversion to other useful forms of energy is not possible.

The first law does not put any restriction on the complete conversion of heat into work and vice versa, but the second law does, as mentioned before.

In India, we get most of the electricity from thermal power plants where chemical energy of coal is converted into heat, which is then converted into mechanical work, which finally is converted into electricity. The electricity is then transmitted though wires to our homes. We run various electrical appliances using the electricity. There are lot conversions from one form of energy to other at the power plant. Assume efficiency of thermal power plant to be around 30 % (quite close to the actual one). It means that for running a bulb of 100 W at our home, we need to burn coal to give around 330 W of heat at the power plant. Hence, when we forget to turn off a 100 W bulb while leaving our home, we are actually wasting around 330

W of power. Hence, it is advised to turn off electrical appliances when they are not in use. In essence, we are converting low grade energy to high grade energy at the power plant. This high grade energy is again converted into low grade energy at our homes (almost all the times) through electrical appliances.