

**Thermodynamics**  
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**Lecture 62**

**Second Law of Thermodynamics: Reversible Process**

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- Definition of reversible process 
- This is a process that once having taken place can be reversed and in doing so leave no change in either system or surroundings
- Has the *maximum efficiency*.  
- Rapidly occurring process cannot be reversible – a reversible process should be a quasistatic (slow) process. But not all quasi-static processes are reversible.
- Factors like friction, unrestrained expansion, heat transfer through a finite temperature change, mixing of two different substances and chemical reaction (combustion), make the process irreversible. Slowly occurring processes, heat transfer through a negligible temperature difference and fully resisted processes may be reversible 



We looked at direct heat engines. If the processes are reversed, it can run as a reverse heat engine (a heat pump or a refrigerator).

A reversible process is a process that once having taken place can be reversed and in doing so leave no change in either system or surroundings.

A reversible process has the maximum efficiency of all the other processes.

Rapidly occurring processes (non-quasi-static processes) cannot be reversible. A reversible process should be a quasi-static process. However, not all the quasi-static processes are reversible. We saw that in a non-quasi-static process, a system may be partially resisted. Hence, we may not get the maximum amount of work possible.

Factors like friction, unrestrained expansion, heat transfer through a finite temperature change, mixing of two different substances and chemical reaction (combustion) make the process irreversible.

If friction is involved in a process, it will be present during the process reversal also. Friction generates heat. It is independent of the direction of the process. Hence, the process cannot be reversed without affecting the system and surroundings.

Unrestrained expansion is a non-quasi-static process. It cannot be reversed without leaving a trace on the system or the surroundings. For example, if a piston in a frictionless vertical piston-cylinder assembly moves up suddenly, we need to work on the assembly to bring back the piston to its original location. We cannot do this without affecting the system or the surroundings.

A process of heat transfer from a hot substance to a cold substance happens naturally. However, transfer of heat from the cold substance to the hot substance can happen only when the work interaction with the surroundings is involved according to the Clausius statement of the second law of thermodynamics. So, the reverse process leaves a trace on the surroundings. Hence, it is irreversible. However, isothermal heat transfer (as in phase change) is reversible. Heat transfer through negligible temperature difference is reversible.

A chemical reaction converts reactants into products. To get back reactants from products, we need to do something which may leave a trace on the system as well as surroundings. Hence, it is irreversible.

Also, for the process to be reversible, it should be fully resisted (?).

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- Internal and external irreversibilities
- A process is said to be internally reversible if no irreversibilities occur within the boundaries of the system during the process. During an internally reversible process, a system proceeds through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state.
- A process is called externally reversible if no irreversibilities occur outside the system boundaries of the system during the process. Heat transfer between a reservoir and a system is an externally reversible process if the outer surface of the system is at the temperature of the reservoir.



We further classify these irreversibilities as internal and external.

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If a system follows a particular path during a process from state 1 to 2 on, for example, a p-v diagram and it follows exactly the same path during the reverse process, the process is internally reversible.

A process is called externally reversible if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the outer surface of the system is at the temperature of the reservoir. There should not be any finite temperature gradient between those two.

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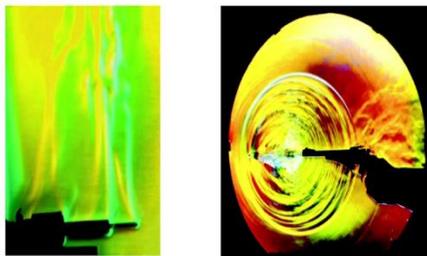


Figure 1.

Figure 1 shows some systems undergoing a process. The images of a hot soldering iron and the bullet being fired from a gun are taken using the technique called shlieren imaging.

The temperature of soldering iron is significantly higher than the surroundings. Hence, the process of heat transfer is highly irreversible. Also, the soldering iron does not become hot just by keeping it in hot gas.

Figure 1 shows the shockwaves being generated because of the gun firing the bullet. This process is highly irreversible as (1) there is a presence of friction because of air viscosity, (2) combustion is involved which is highly irreversible, (3) there is generation of sound and light. Also, there is no way that the bullet can be put back into the gun, i.e., we cannot reverse the ‘firing a bullet’ process.

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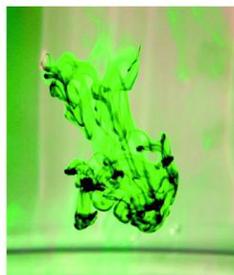


Figure 2.

Figure 2 shows a dye mixing in a liquid. If we stir it, there is no way to reverse the process, i.e., unmix the dye and the liquid. The process is highly irreversible.