Thermodynamics
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Lecture 69
Second Law of Thermodynamics: Clausius's Inequality

Let's look at the Clausius's Inequality.

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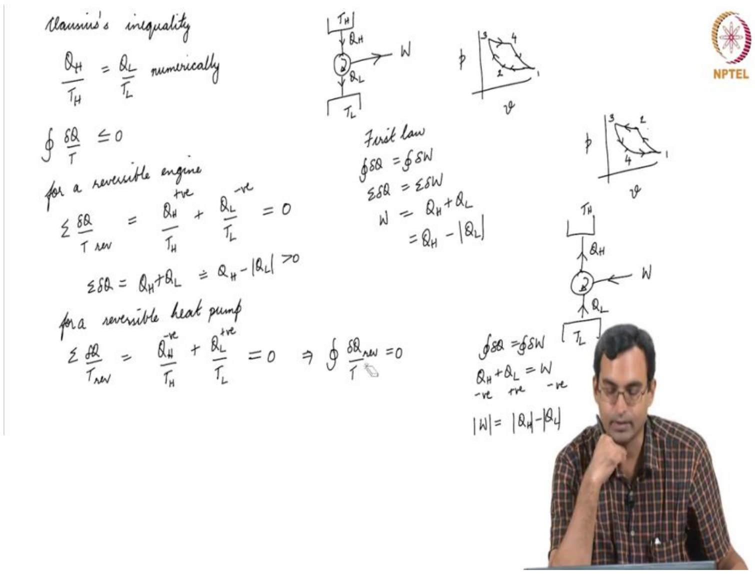

Figure 1.

For a Carnot's engine running between temperature reservoirs at T_H and T_L, the ratio of heat taken in (Q_H) from the reservoir at T_H and the heat rejected (Q_L) to the reservoir at T_L equals the ratio of the temperatures, i.e., $\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$, which can also be written as $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$ (Fig. 1). Here, we are taking absolute values of Q_H and Q_L.

According to Clausius, $\oint \frac{\delta Q}{T} \leq 0$ for a cyclic process. Let's look at the proof of this inequality.

Let's expand $\oint \frac{\delta Q}{T}$ for a Carnot's cycle shown on a p-v diagram in Fig. 1. A Carnot's cycle contains 4 reversible processes, two of which are isothermal and the other two are adiabatic. For adiabatic processes, δQ is 0. Hence, there are heat transfers (Q_H and Q_L) in only two of the processes. The Carnot's heat engine takes in Q_H amount of heat and rejects Q_L amount heat. For the Carnot's cycle, we can write, $\oint \frac{\delta Q}{T} = \sum \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_L}{T_L}$. For a Carnot's engine (reversible engine), according to the first law, work done $W = Q_H - |Q_L|$. Hence, $Q_H - |Q_L| > 0$. Also, for a Carnot's engine (reversible engine), $\frac{Q_H}{T_H}$ and $\frac{Q_L}{T_L}$ are equal in magnitudes but opposite in sign. $\frac{Q_H}{T_H}$ is positive as Q_H is positive and $\frac{Q_L}{T_L}$ is negative as Q_L is negative (T_H and T_L are always positive as they are taken in Kelvin scale). Hence, $\oint \frac{\delta Q}{T} = \sum \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$ for a reversible heat engine. This expression holds true for a reversible heat pump as well as a reversible refrigerator.

For a reversible heat pump or a reversible refrigerator taking in heat Q_L from the temperature reservoir at T_L and rejecting heat Q_H to the temperature reservoir at T_H while taking in some work W, $\frac{Q_H}{T_H}$ is negative (as Q_H is negative) and $\frac{Q_L}{T_L}$ is positive (as Q_L is positive). However, their magnitudes are equal ($\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$). Hence, for a reversible heat pump or a reversible refrigerator also, $\oint \frac{\delta Q}{T} = \sum \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$. Also, $|Q_H| > |Q_L|$ for a reversible heat pump or a refrigerator as, according to the first law, $|W| = |Q_H| - |Q_L|$. The p-v diagram for a reversible heat pump or a reversible refrigerator is also shown in Fig. 1.

In essence, $\oint \frac{\delta Q}{T}$ for a cyclic process involving reversible processes is 0, i.e., $\oint \frac{\delta Q}{T}_{rev} = 0$.

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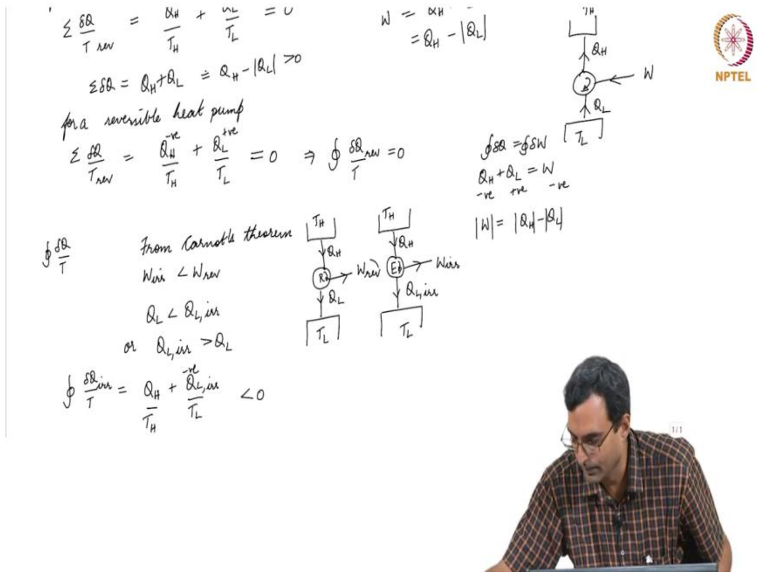

Figure 2.

What if a cyclic process involves irreversible processes?

We know that, according to the Carnot's theorem, of all the engines operating between the given two temperature reservoirs, reversible engines have the highest efficiency.

Consider a reversible heat engine and an irreversible heat engine operating between temperature reservoirs at T_H and T_L (see Fig. 2). Both the engines take in Q_H amount of heat from the reservoir at T_H. As the reversible heat engine is more efficient than the irreversible engine, the work output of the reversible heat engine is more than that of the irreversible heat engine, i.e., $W_{rev} > W_{irrev}$. Hence, according to the first law, the heat rejected by the reversible heat engine to the reservoir at T_L is less than that rejected by the irreversible engine, i.e., $Q_{L,rev} < Q_{L,irrev}$. Now, for the reversible engine, $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_{L,rev}}{T_L} = 0$ ($\frac{Q_H}{T_H}$ is positive and $\frac{Q_{L,rev}}{T_L}$ is negative, and they are equal in magnitude). For the irreversible heat engine, we have $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_{L,irrev}}{T_L}$. We know that $\frac{Q_H}{T_H} = \frac{Q_{L,rev}}{T_L}$ (considering magnitudes). We also know that $\frac{Q_{L,rev}}{T_L} < \frac{Q_{L,irrev}}{T_L}$ (considering magnitudes) as $Q_{L,rev} < Q_{L,irrev}$. Hence, for the irreversible heat engine, taking magnitudes, $\frac{Q_H}{T_H} < \frac{Q_{L,irrev}}{T_L}$, and $\frac{Q_H}{T_H}$ is positive and $\frac{Q_{L,irrev}}{T_L}$ is negative. Hence, for the irreversible heat engine, $\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} + \frac{Q_{L,irrev}}{T_L} < 0$.

We get a similar expression for an irreversible heat pump and irreversible refrigerator.

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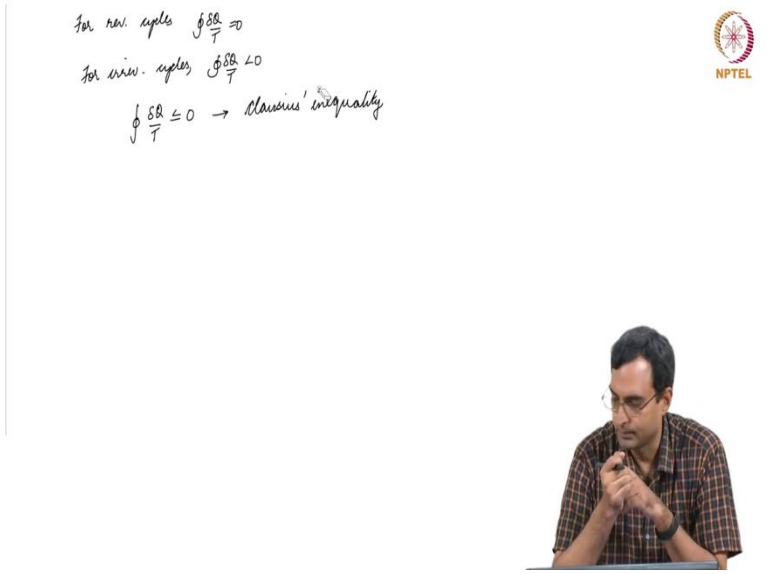

So, $\oint \frac{\delta Q}{T} = 0$ for a cyclic process involving reversible processes and $\oint \frac{\delta Q}{T} < 0$ for a cyclic process involving irreversible processes. Combining these two, we get the Clausius's inequality, $\oint \frac{\delta Q}{T} \leq 0$ for a process.