Thermodynamics
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Lecture 64
Second law of Thermodynamics: Absolute Temperature Scale

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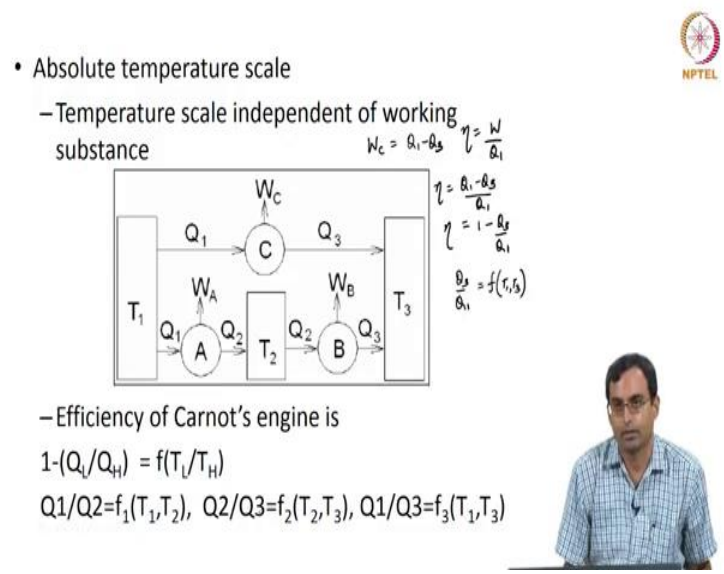
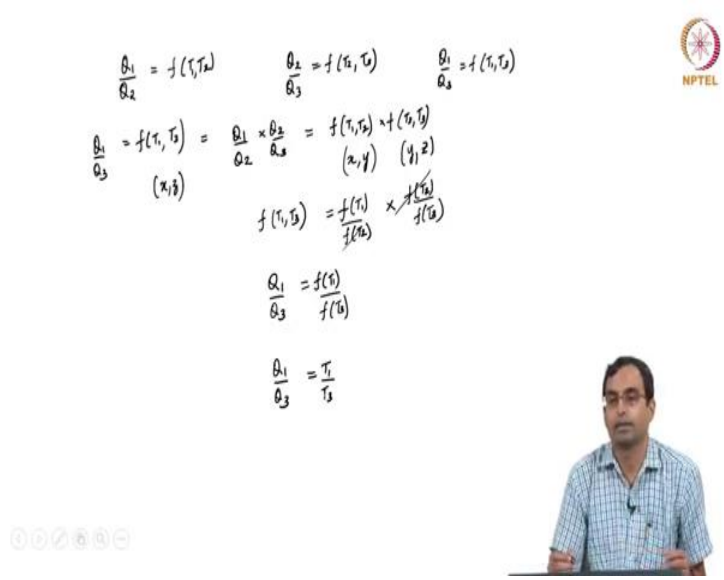


Figure 1.



The concept of the Carnot engine and the second law give us a concept of an absolute temperature scale which is essentially a temperature scale which is independent of the working substance.

Consider temperature reservoirs at temperatures T_1 and T_3 as shown in Fig. 1. We have a Carnot's engine C working between temperature reservoirs at T_1 and T_3 and producing work W_C. The engine takes in Q_1 amount of heat and gives out Q_3 amount of heat. Its efficiency is $1-\frac{Q_3}{Q_1}$.

Consider two more reversible heat engines (Carnot's engines) A and B (Fig. 1). The engine A operates between the temperature reservoirs T_1 and T_2, whereas the engine B operates between the temperature reservoirs at T_2 and T_3. The engine A takes in Q_1amount of heat and rejects Q_2 amount of heat. It also gives out W_A amount of work. The engine B takes in Q_2 amount of heat and rejects Q_3 amount of heat while giving out W_B amount of work. The efficiency of engine A is $1-\frac{Q_2}{Q_1}$ and that of B is $1-\frac{Q_3}{Q_2}$. According to the Carnot's theorem, the efficiency of a reversible engine operating between two temperature reservoirs depends only on the temperature of those reservoirs. Hence, $\frac{Q_1}{Q_2}=f(T_1,T_2), \frac{Q_2}{Q_3}=f(T_2,T_3), \frac{Q_1}{Q_3}=f(T_1,T_3)$. Now, $\frac{Q_1}{Q_2}\times\frac{Q_2}{Q_3}=f(T_1,T_2)\times f(T_2,T_3) \quad\rightarrow\quad \frac{Q_1}{Q_3}=f(T_1,T_3)=f(T_1,T_2)\times f(T_2,T_3)$. The term T_2 cancels out in the multiplication completely. Kelvin assumed the forms of these functions as $f(T_1,T_3)=\frac{f(T_1)}{f(T_3)}, f(T_1,T_2)=\frac{f(T_1)}{f(T_2)}, f(T_2,T_3)=\frac{f(T_2)}{f(T_3)}$ so that they satisfy $f(T_1,T_3)=f(T_1,T_2)\times f(T_2,T_3)$.

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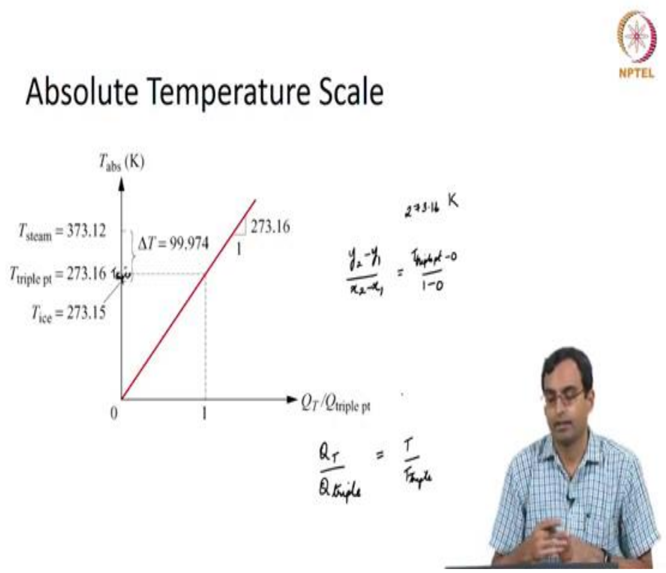
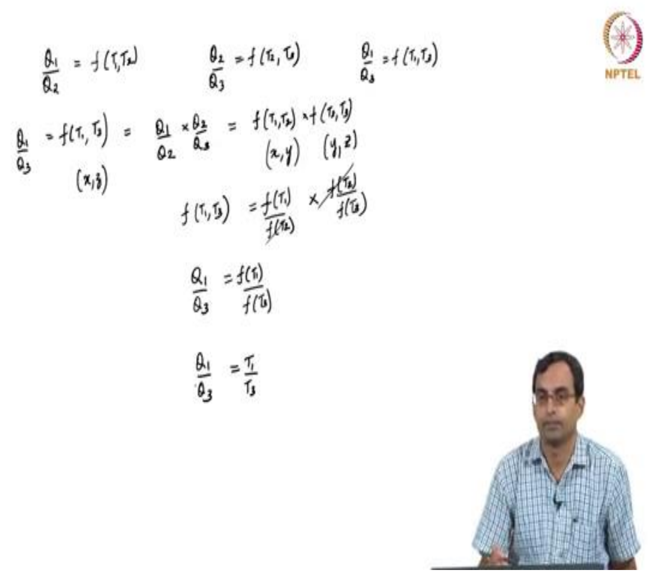


Figure 2.



This gives us the absolute temperature scale (Kelvin scale). We know that for a reversible heat engine operating between a heat source at T_1 and a heat sink at T_2, the ratio of the heat received (Q_1) from the heat source and the heat rejected (Q_2) to the heat sink equals the ratio of temperatures, i.e., $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$. For the Kelvin scale, the triple point of water is taken as the standard reference point. For the Carnot's engine operating between the temperature reservoirs at T and the triple point (T_{triple}), $\frac{Q_T}{Q_{triple}} = \frac{T}{T_{triple}}$. The triple point of water is arbitrarily taken as $T_{triple} =$

$273.16\,K$ in the Kelvin scale. Hence, the plot of T (in Kelvin) versus $\frac{Q_T}{Q_{triple}}$ is a straight line passing through the origin because $T = T_{triple}\frac{Q_T}{Q_{triple}} = 273.16\frac{Q_T}{Q_{triple}}$ (see Fig. 2). Thus, any temperature T can be determined by running the Carnot's engine between the reservoir at that temperature (T) and the reservoir at T_{triple} and measuring the heat transfers. The smallest possible value of Q_T is 0, and the corresponding temperature is the absolute 0, i.e., T = 0 K. On this scale, the melting point of water is 273.15 K and the boiling point of water is 373.15 K. The conversion between the Celsius scale and the Kelvin scale takes place according to $T\,(K) = T\,(°\mathrm{C}) + 273.15$. The Kelvin scale is independent of peculiar characteristics of any particular substance. However, measuring temperature in this way is difficult as making Carnot's engine is difficult. Hence, practically, ideas gases are used to make a scale which is also fairly close to the Kelvin scale, i.e., absolute temperature scale.

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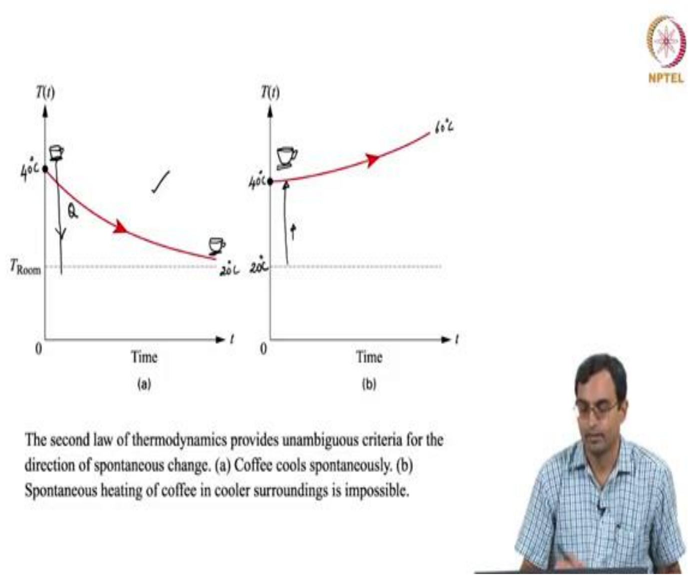

Figure 3.

All the processes satisfy the first law irrespective of whether the process is possible or not. The first law can be used to calculate work or heat transfers involved in a process.

The coffee at 40 °C, when kept in an atmosphere of 20 °C, cools down to 20 °C after some time, spontaneously (i.e., on its own or naturally). The coffee cannot attain 60 °C spontaneously. The coffee can attain 60 ℃ if some work is done on it according to the Clausius statement of the second law of thermodynamics. The second law of thermodynamics provides unambiguous criteria for the direction of spontaneous change, for example, hot coffee cools spontaneously and spontaneous heating of coffee in cooler surroundings is impossible. The first law, on the other hand, is applicable to the process of hot coffee getting cooled spontaneously and the spontaneous heating of the coffee in cooler surroundings. The time, which flows in only one direction, is linked to the second law.