

In this lecture, we will consider a thermodynamic property known as entropy. We will also learn about the statements of Second law based on entropy.

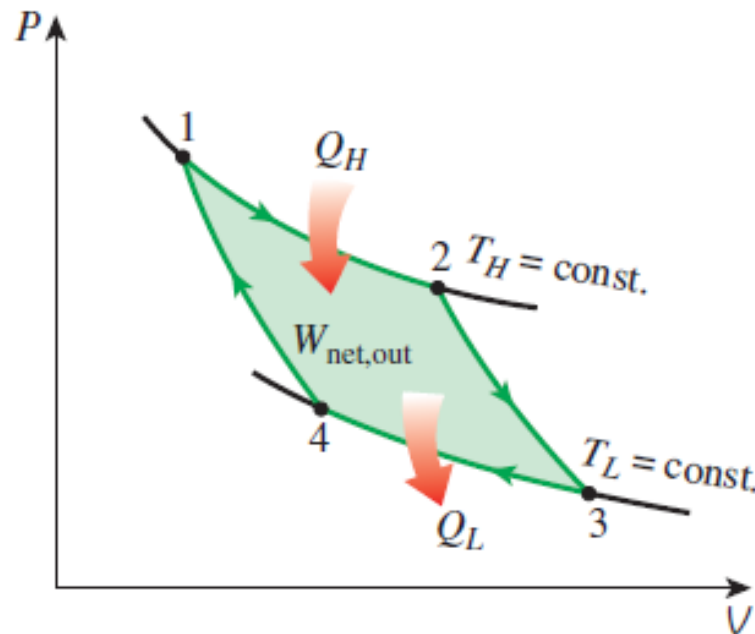
Consider the following quantity : $\left(\frac{dQ_{in}}{T}\right)_{rev}$

Here dQ_{in} is an infinitesimal amount of heat absorbed in a reversible process by a system at a uniform temperature T (as per thermodynamic temperature scale).

What is so special about the above quantity ?

To answer this, let's consider Carnot cycle.

P-V diagram (see previous lectures) for a Carnot cycle is shown below:



Integrating (adding) the differential quantity over the entire Reversible cycle, we have

$$\oint \left(\frac{dQ_{\text{in}}}{T} \right)_{\text{rev}} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

Note that here we used the following relation derived based on Carnot principle (2) (see last lecture):

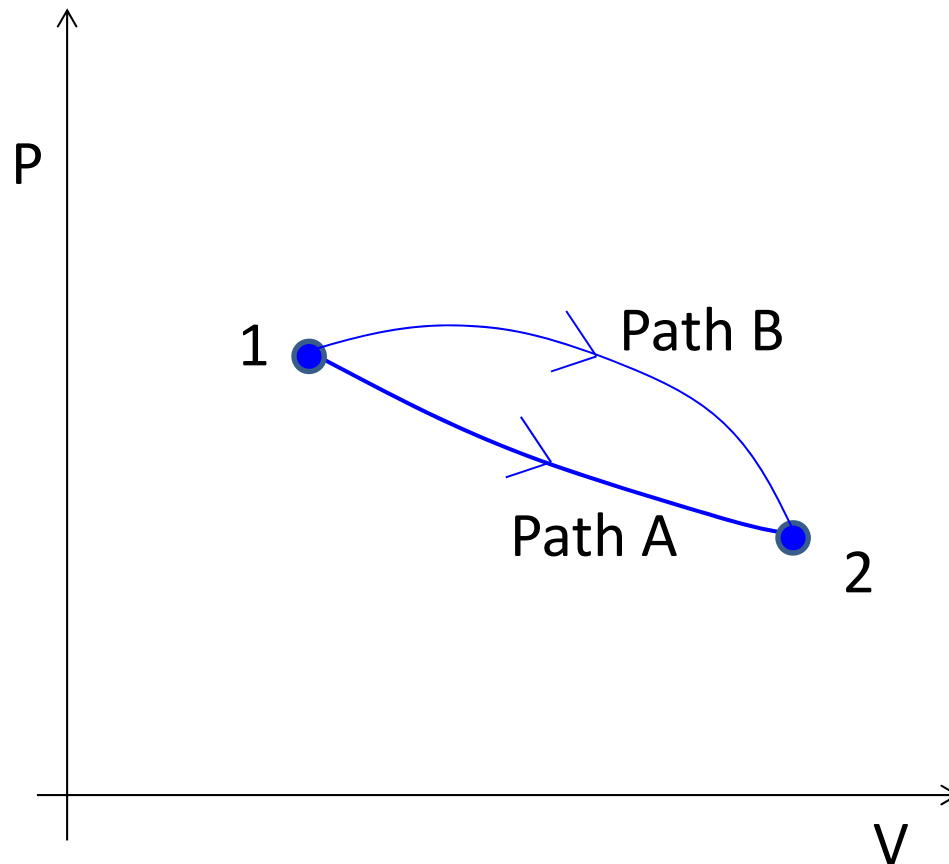
$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

The result derived for Carnot cycle can be generalized, i.e.,

$$\oint \left(\frac{dQ_{\text{in}}}{T} \right)_{\text{rev}} = 0$$

i.e., the above cyclic integral is zero for any reversible cycle.

Consider two reversible paths 'A' and 'B' between states (1) and (2) on a P-V diagram for a gas as shown below:



Combining path 'A' from (1) \rightarrow (2) and path 'B' in reverse direction from (2) \rightarrow (1), we have a cycle for which

$$\oint \left(\frac{dQ_{in}}{T} \right)_{rev} = 0$$

Thus,

$$\int_1^2 \left(\frac{dQ_{in}}{T} \right)_{path A} + \int_2^1 \left(\frac{dQ_{in}}{T} \right)_{path B} = 0$$

$$\int_1^2 \left(\frac{dQ_{in}}{T} \right)_{path A} - \int_1^2 \left(\frac{dQ_{in}}{T} \right)_{path B} = 0$$

$$\int_1^2 \left(\frac{dQ_{in}}{T} \right)_{path A} = \int_1^2 \left(\frac{dQ_{in}}{T} \right)_{path B}$$

The above relation implies that the quantity $\int_1^2 \left(\frac{dQ_{in}}{T} \right)_{rev}$

is independent of the path. It depends only on initial and final states.

The last equation (on previous slide) implies that the quantity :

$$\int_1^2 \left(\frac{dQ_{in}}{T} \right)_{rev}$$

is independent of the path. It depends only on initial and final states.

Therefore, it must represent change in a thermodynamic property of the system. That property is called 'Entropy' and is denoted by S. Thus,

$$dS = \left(\frac{dQ_{in}}{T} \right)_{rev}$$

Here dS is the change in entropy of the system (to first order) at a uniform temperature T when it absorbs an infinitesimal amount of heat dQ_{in} in a reversible process. The above equation for change in S was proposed by Clausius.

Lets consider a gas (control mass system) enclosed in a piston-cylinder arrangement. Suppose that piston-cylinder arrangement is insulated and the gas undergoes an adiabatic irreversible expansion from state (1) to state (2).

Now consider a reversible process by which gas is brought back to the original state. During this process gas exchanges heat with a thermal energy reservoir. Combining the adiabatic irreversible process $(1) \rightarrow (2)$ and the reversible process $(2) \rightarrow (1)$, the gas undergoes a cyclic process for which

$$Q_{in} = W_{out}^{net} \quad (\text{for a cyclic process})$$

where

Q_{in} = heat absorbed from thermal energy reservoir in $(2) \rightarrow (1)$ process
 W_{out}^{net} = Net work output of the cycle

If we have the following condition,

$$Q_{\text{in}} > 0, \text{ then } W_{\text{out}}^{\text{net}} > 0$$

Then, we have a cyclic process which takes in heat from a single reservoir and converts it into a net amount of work

This violates Kelvin-Planck statement of Second law.

Therefore, the (2) \rightarrow (1) process must be such that gas rejects heat:

$$Q_{\text{in}} < 0 \quad (\text{heat is lost by the gas to the thermal energy reservoir})$$

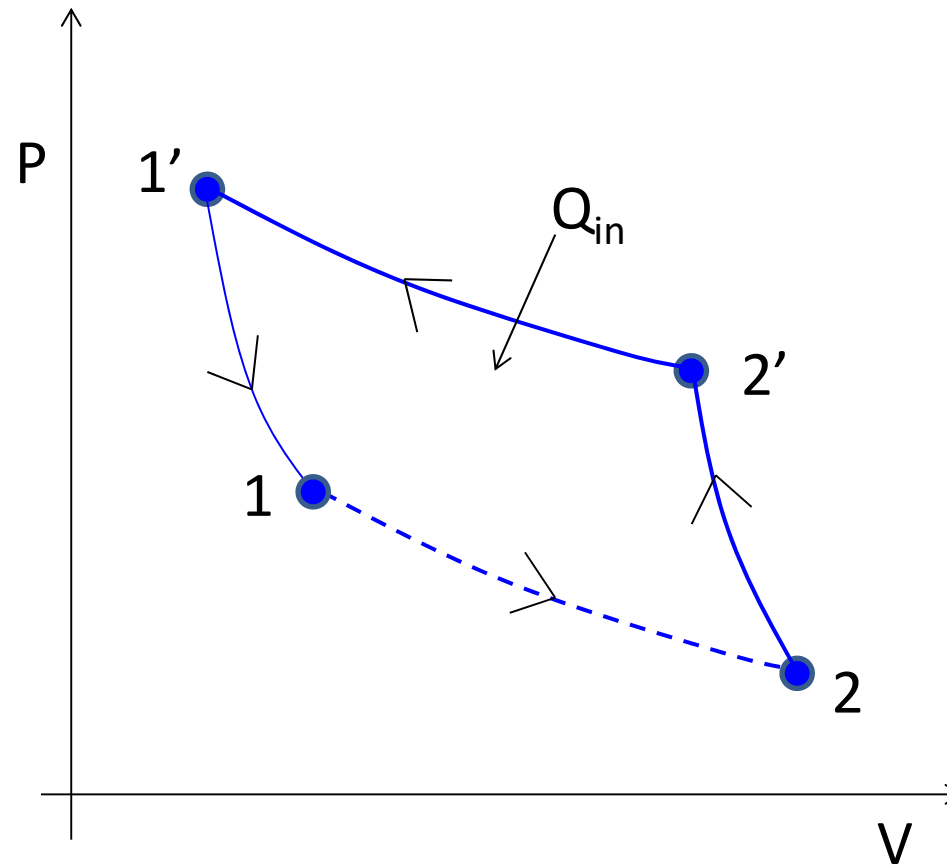
$$W_{\text{out}}^{\text{net}} < 0 \quad (\text{Net work is done on the gas})$$

Denoting Q_{out} as the heat lost by the gas, we have the condition

$$Q_{\text{out}} = -Q_{\text{in}} > 0$$

Lets consider
the cyclic
process of the gas
(see previous
slides)

The reversible
process $(2) \rightarrow (1)$
consists of three
parts



$1 \rightarrow 2$: Adiabatic irreversible path

$2 \rightarrow 2'$: Adiabatic reversible process

$2' \rightarrow 1'$: Isothermal reversible process

$1' \rightarrow 1$: Adiabatic reversible process

Applying Clausius equation for entropy (see sixth slide) to the reversible process $(2) \rightarrow (1)$, we have

$$\begin{aligned} S_1 - S_2 &= (S_{2'} - S_2) + (S_{1'} - S_{2'}) + (S_1 - S_{1'}) \\ &= 0 + \int_{2'}^{1'} \left(\frac{dQ_{\text{in}}}{T_g} \right)_{\text{rev}} + 0 \\ &= -\frac{Q_{\text{out}}}{T} \end{aligned}$$

Here Q_{out} is the heat lost by the gas during reversible isothermal compression $(2') \rightarrow (1')$ (see previous slide). In the last step above, we have made use of the fact that during $(2') \rightarrow (1')$ process the temperature of the gas must be same as temperature of thermal energy reservoir since it is a reversible process. That is :

$$T_g = T = \text{constant}$$

Thus we have the condition : $S_1 - S_2 < 0$

(OR)

$$S_2 > S_1$$

This shows that entropy increases in an adiabatic irreversible process (1) \rightarrow (2). This leads to another Statement of Second law :

Statement (5) of Second law :

Entropy of a body (control mass system) increases in an adiabatic irreversible (natural or spontaneous) process and remains constant in an adiabatic reversible process.

Note that 4 statements of Second law that we learnt earlier are (1) Kelvin-Planck (2) Clausius (3) Carnot principle 1 (4) Carnot principle 2

Application of Clausius equation to quasi-static (irreversible) process :

Note that Clausius equation (see first slide) is valid for a reversible process. However we can apply this relation to irreversible processes under certain conditions. We describe these conditions below.

Lets consider a process in which volume change is the only form of work. Applying first law of thermodynamics, we have

$$dU = dQ_{\text{in}} - P_{\text{ext}}dV$$

Application of Clausius equation to quasi-static (irreversible) process :

We consider the process to be sufficiently slow so that internal pressure (P) is same as external pressure, i.e.,

$$P_{\text{ext}} = P$$

Substituting this in the first law equation (see last slide), we get

$$dU = dQ_{\text{in}} - P dV$$

As per the above equation, the amount of heat transferred depends upon the initial and final values of U and V.

Application of Clausius equation to quasi-static (irreversible) process :

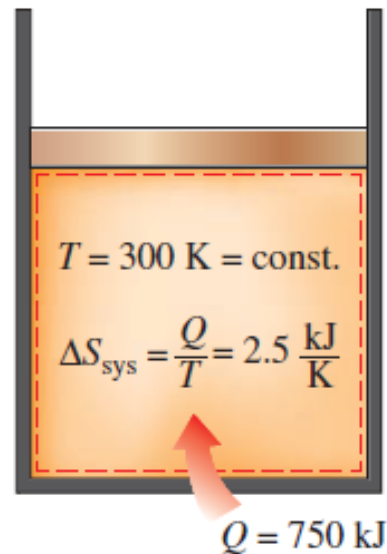
(U,V) and $(U+dU, V+dV)$ completely determine the initial and final states of the system, respectively (provided that there are no irreversible changes in composition). Such a process is called quasi-static which implies that system is in internal equilibrium at any given time which implies that pressure and temperature are uniform throughout the system. Therefore, dQ_{in} (as given by last equation), i.e., the amount of heat transferred in a irreversible (quasi-static) processes must be same as a reversible process (between the same two states) .

$$(dQ_{in})_{rev.} = (dQ_{in})_{quasi-static}$$

Therefore, the change in S for a quasi-static process between states (U,V) and $(U+dU, V+dV)$, is given by

$$dS = \left(\frac{dQ_{in}}{T} \right)_{rev.} = \left(\frac{dQ_{in}}{T} \right)_{quasi-static}$$

A piston–cylinder device contains a liquid–vapor mixture of water at 300 K. During a constant-pressure process, 750 kJ of heat is transferred to the water. As a result, part of the liquid in the cylinder vaporizes. Determine the entropy change of the water during this process.



Solution : Assuming that water undergoes a quasi-static process in which water is in internal equilibrium throughout the process, we can apply the Clausius equation for a quasi-static process (See last slide).

The entropy change of water is then given by,

$$\begin{aligned}\Delta S &= \int_1^2 \left(\frac{dQ_{\text{in}}}{T} \right)_{\text{Quasi-static}} \\ &= \frac{Q_{\text{in}}}{T} \\ &= \frac{750 \text{ kJ}}{300 \text{ K}} = 2.5 \text{ kJ/K}\end{aligned}$$