

ESO201A : THERMODYNAMICS

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Lecture 16

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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.

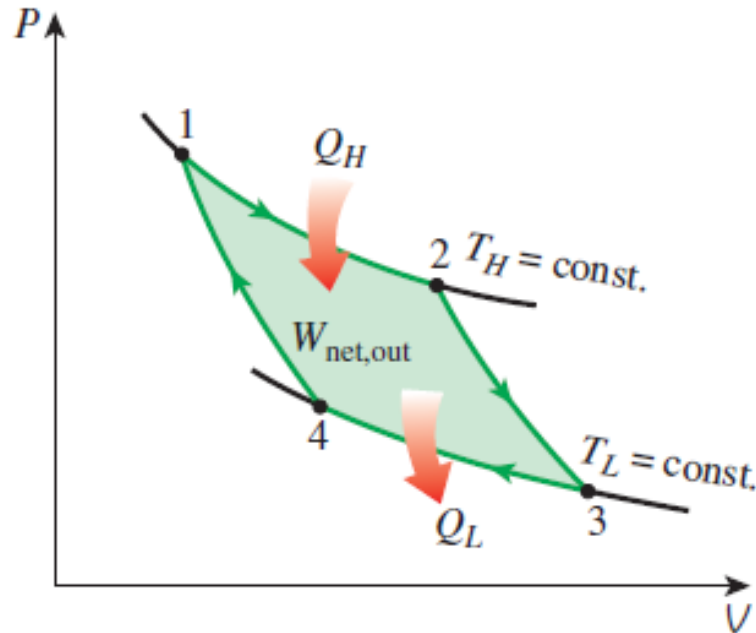
Consider the following quantity : $\left(\frac{dQ_{in}}{T}\right)_{rev}$

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):

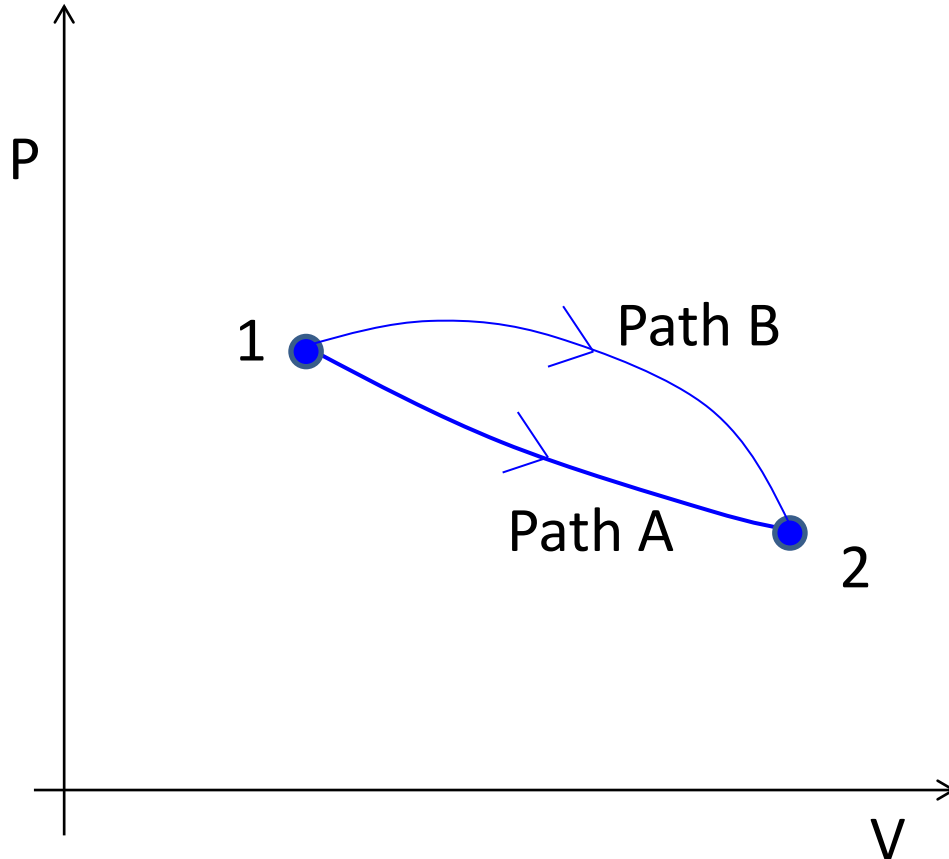
$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L}$$

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 :

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

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,

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

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:

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

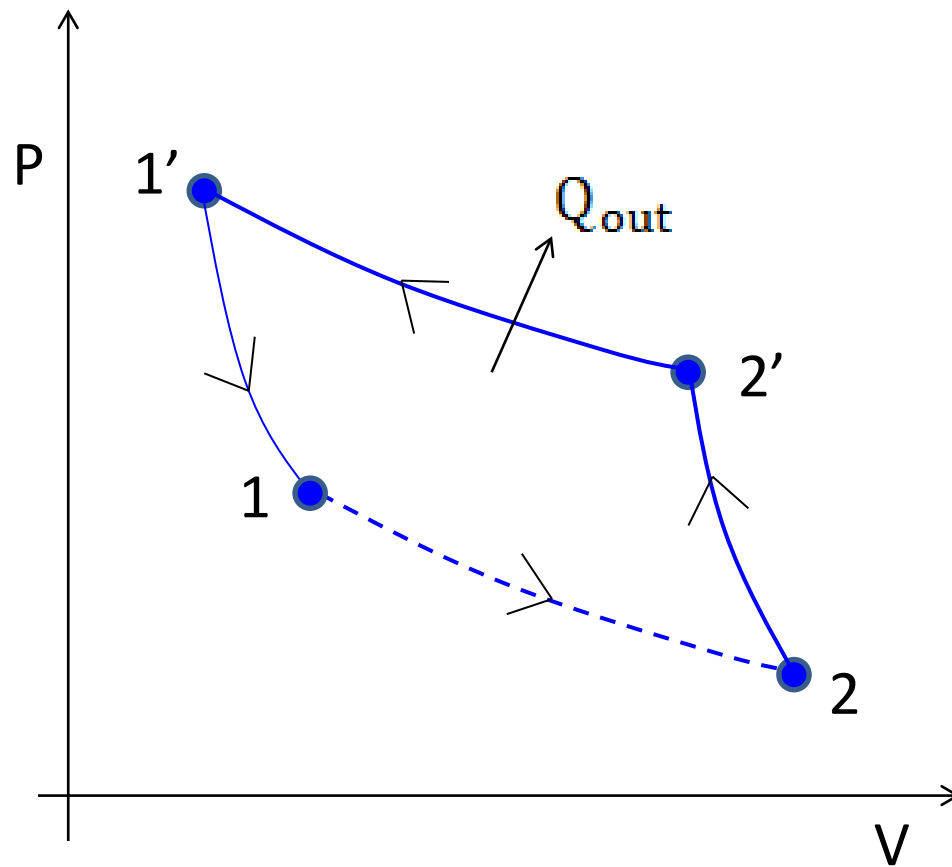
$$W_{\text{out}}^{\text{net}} < 0 \quad (\text{Net work is done on the gas})$$

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

Extension 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 certain irreversible processes as well.

Consider a system such that the state of the system is completely specified by its internal energy and volume. Since entropy is a function of state, $S = S(U,V)$, i.e., value of S is completely determined by values of U and V .

Lets consider that energy transfer to the system as work is only due to volume change. Applying first law of thermodynamics, we have

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

Extension of Clausius equation to quasi-static irreversible process :

We consider the process to be sufficiently slow so that system is in internal equilibrium which implies that temperature is uniform throughout the system and 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 .

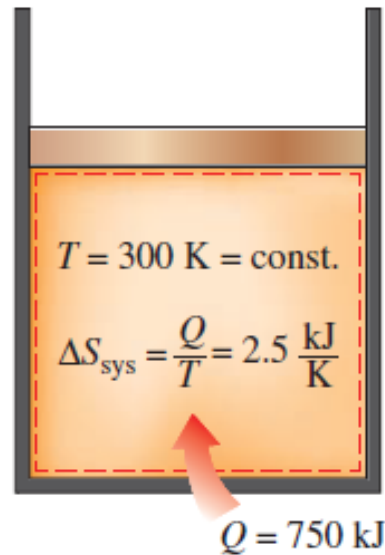
Extension of Clausius equation to quasi-static irreversible process :

(U,V) and $(U+dU, V+dV)$ determine the initial and final states of the system, respectively. Therefore, dQ_{in} (as given by last equation) depends only upon the initial and final states and is independent of path, i.e., the amount of heat transferred in a reversible and irreversible (quasi-static) process between must be same.

Since the same amount of heat must be transferred in a reversible, process between states (U,V) and $(U+dU, V+dV)$, the change in S for a quasi-static process is given by

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

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,

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