

**ESO201A**  
**Lecture#36**  
**(Class Lecture)**

Date: 7.11.22

By  
Dr. P.S. Ghoshdastidar

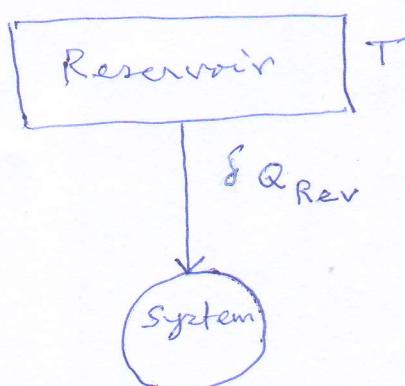
## Entropy and Reversibility

In order to understand the physical meaning of entropy and its significance, it is necessary to study all entropy changes that take place when a system undergoes a reversible process. If we calculate the entropy change of the system and add the calculated entropy change of the surroundings, then we obtain the sum of entropy changes brought about by this particular process. We may call this sum the entropy change of the universe due to the process in question.

Consider now the following two cases. During any infinitesimal portion of the process, an amount of heat  $\delta Q_{\text{rev}}$  is transferred between the system and the reservoir at  $T$ .

Case I

$\delta Q_{\text{rev}}$  is absorbed by the system.



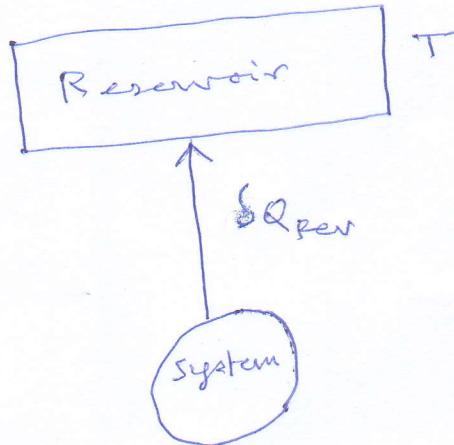
$$dS_{\text{system}} = + \frac{\delta Q_{\text{Rev}}}{T}$$

$$dS_{\text{Reservoir}} = - \frac{\delta Q_{\text{Rev}}}{T}$$

$$dS_{\text{Universe}} = dS_{\text{system}} + dS_{\text{Reservoir}}$$

$$= + \frac{\delta Q_{\text{Rev}}}{T} - \frac{\delta Q_{\text{Rev}}}{T} = 0$$

### Case II



$\delta Q_{\text{Rev}}$  is rejected by the system.

$$dS_{\text{system}} = - \frac{\delta Q_{\text{Rev}}}{T}$$

$$dS_{\text{Reservoir}} = + \frac{\delta Q_{\text{Rev}}}{T}$$

$$dS_{\text{Universe}} = dS_{\text{system}} + dS_{\text{Reservoir}}$$

$$= - \frac{\delta Q_{\text{Rev}}}{T} + \frac{\delta Q_{\text{Rev}}}{T} = 0$$

If no heat is transferred,

$$\delta Q_{\text{rev}} = 0.$$

$$dS_{\text{system}} = 0$$

$$dS_{\text{reservoir}} = 0$$

$$dS_{\text{universe}} = dS_{\text{system}} + dS_{\text{reservoir}}$$

$$= 0 + 0 = 0$$

In general,  $dS_{\text{universe}} = 0$  for a reversible process.

In other words, when a reversible process is performed, the entropy of the universe remains unchanged. That is,  $(\Delta S)_{\text{universe}} = 0$  for a reversible process. However, all natural processes are irreversible and only ideal processes are reversible.

## Entropy and Irreversibility

During an irreversible process, there is a different situation for the entropy change of the universe. When a system undergoes an irreversible process between an initial equilibrium state to a final equilibrium state, the irreversible process is replaced by a reversible one. This replacement is permitted when the initial and final state of the system are equilibrium states. No integration is performed over the original irreversible path, because the path is not known. The entropy change of the system is equal to

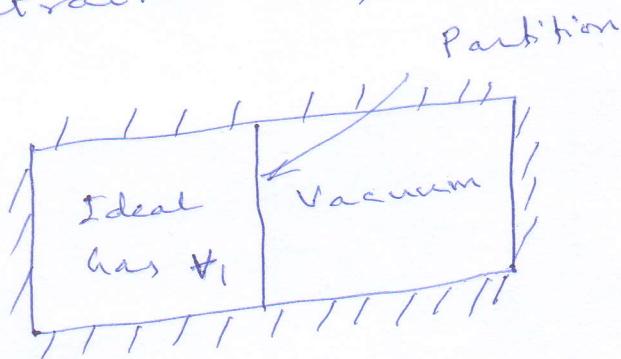
$$S_2 - S_1 = \int_{R_1}^{R_2} \frac{\delta Q}{T}$$

where  $R$  indicates any arbitrarily chosen reversible process by which the system is brought from the given initial state to the given final state of the irreversible process.

## Example

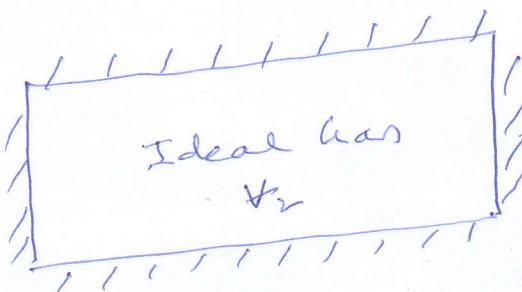
A process exhibiting internal mechanical irreversibility such as an ideal gas rushing into a vacuum (free expansion or unrestrained expansion).

Initial :  
State 1



The outside of the rigid container is insulated.

Final :  
(Partition removed)  
State 2



The entropy change of the local surroundings is zero, because there is no heat transfer through the adiabatic walls.

(43)

In order to calculate the entropy change of the system, the free expansion must be replaced by a reversible process that will take the gas from its original state (volume  $x_1$ , temperature  $T$ ) to the final state (volume  $x_2$ , temperature  $T$ ), where temperature does not change for the ideal gas during expansion. Evidently, the most convenient reversible process to replace the irreversible process for the purpose of calculation is a reversible isothermal expansion at temperature  $T$  from a volume  $x_1$  to the volume  $x_2$ . The entropy change of the system is then

$$(S_2 - S_1)_{\text{system}} = \int_{x_1}^{x_2} \frac{\delta Q}{T}$$

For an isothermal process of the ideal gas,  $\delta Q_{\text{rev}} - \delta W_{\text{rev}} = \delta U = 0$

$$\text{or } \delta Q_{\text{rev}} = P dV$$

$$\text{and } \frac{\delta Q_{\text{rev}}}{T} = \frac{P dV}{T} = \frac{N R T dV}{T} = N R \frac{dV}{T}$$

(A4)

Thus,

$$(S_2 - S_1)_{\text{system}} = N R \int_{T_1}^{T_2} \frac{dH}{V}$$

$$= N R \ln \frac{T_2}{T_1}$$

The entropy change of the universe  
is therefore,

$$(S_2 - S_1)_{\text{system}} + (S_2 - S_1)_{\text{surroundings}}$$

$$= N R \ln \frac{T_2}{T_1} + 0$$

$$= \boxed{N R \ln \frac{T_2}{T_1}}$$

which is a positive number

Hence, we see  $(\Delta S)_{\text{universe}} > 0$ ,  
even though no heat entered or  
left the system.

This result may seem puzzling,  
because entropy is defined  
in terms of the heat entering

or leaving a system. The puzzle is resolved by recognizing that the free expansion of the ideal gas within an adiabatic container is not a reversible process. During an irreversible process, the entropy change of the universe, even if the process is adiabatic, is always positive.

Therefore,

$$\Delta S_{\text{universe}} \geq 0$$

where the equality sign refers to reversible processes and the inequality sign to irreversible processes.

The above equation is a succinct statement of the second law of thermodynamics. It is also known as the principle of increase of entropy.

(46)

(38)

## Entropy Change of a Control Mass During an Irreversible Process

Consider a control mass that undergoes the cycles shown in Fig. 1. The cycle is made up of the reversible processes A and B in a reversible cycle. Therefore, we can write

$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B = 0 \quad (1)$$

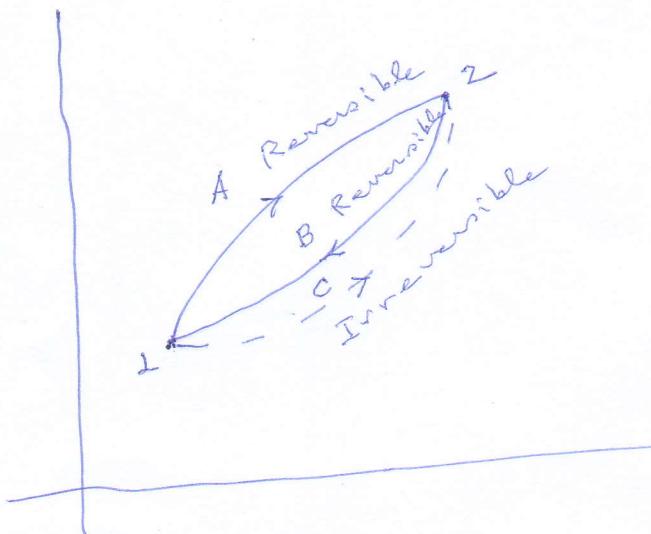


Fig. 1 Entropy change of a control mass during an irreversible process

(47)

(39)

The cycle made up of the irreversible process  $c$  and the reversible process  $B$  is an irreversible cycle. Therefore, for this cycle the inequality of Clausius may be applied, giving the result

$$\oint \frac{\delta Q}{T} = \int_1^2 \left( \frac{\delta Q}{T} \right)_c + \int_2^1 \left( \frac{\delta Q}{T} \right)_B < 0 \quad (2)$$

Subtracting eq. (2) from eq. (1),

$$\begin{aligned} \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \cancel{\frac{\delta Q}{T}} \right)_B - \int_1^2 \left( \frac{\delta Q}{T} \right)_c \\ - \int_2^1 \left( \cancel{\frac{\delta Q}{T}} \right)_B > 0 \\ \Rightarrow \int_1^2 \left( \frac{\delta Q}{T} \right)_A - \int_1^2 \left( \frac{\delta Q}{T} \right)_c > 0 \\ \Rightarrow \int_1^2 \left( \frac{\delta Q}{T} \right)_A > \int_1^2 \left( \frac{\delta Q}{T} \right)_c \end{aligned} \quad (3)$$

Since path A is reversible, and since entropy is a property,

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 dS_A = \int_1^2 dS_c$$

Therefore,  $\int_1^2 dS_c > \int_1^2 \left( \frac{\delta Q}{T} \right)_c$  (4)

As path c is arbitrary, the general result is

$$dS \geq \frac{\delta Q}{T}$$

or 
$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

The equality holds for a reversible process and the inequality for an irreversible process.

This is one of the most important equations of thermodynamics. It is used to develop a number of concepts and definitions. In essence, this equation states the influence

For an isentropic process, in general, we have

$dS = 0$

Hence,  $\frac{\delta Q}{T} \leq 0$  for an ~~isentropic~~ isentropic process, therefore, either  $\delta Q = 0$  (reversible)  $\delta Q < 0$  (irreversible)

49 50 51

of irreversibility on the entropy of a control mass. Thus, if an amount of heat  $\delta Q$  is transferred to a control mass at temperature  $T$  in a reversible process, the change of entropy is given by the relation

$$dS = \left( \frac{\delta Q}{T} \right)_{rev} \quad (6)$$

If any irreversible effects occur while the amount of heat  $\delta Q$  is transferred to the control mass at temperature  $T$ , however, the change of entropy will be greater than for the reversible process. We would then write

$$dS > \left( \frac{\delta Q}{T} \right)_{rev} \quad (7)$$

Equation (5) holds when  $\delta Q = 0$ , when  $\delta Q < 0$ , and when  $\delta Q > 0$ .

If  $\delta Q$  is negative, the entropy will tend to decrease as a result of heat transfer. However, the

(50)

(42)

influence of irreversibilities is still to increase the entropy of the mass, and from the absolute numerical perspective we can still write for

(8)

$$dS \geq \frac{dq}{T}$$

### Entropy Generation

The conclusion from the previous exercise is that the entropy change in an irreversible process is larger than the change in a reversible process for the same  $dq$  and  $T$ . This can be written out in a common form as an equality

$$dS = \frac{dq}{T} + S_{gen} \quad (9)$$

provided that the last term is positive.

(10)

$$\text{Thus, } S_{gen} \geq 0$$

The amount of entropy,  $\delta S_{gen}$ , is the entropy generation in the process due to irreversibilities occurring inside the system. This internal generation can be caused by the processes such as friction, unrestrained expansions, and the internal transfer of energy over a finite temperature difference. In addition to this internal entropy generation, external irreversibilities are possible by heat transfer over finite temperature differences as the  $\delta Q$  is transferred from a reservoir or by the mechanical transfer of work.

Equation (10) is then valid with the equal sign for a reversible process and the greater than sign for an irreversible process. Since the entropy generation is always positive and is zero for a reversible process, we may deduce some limits for the heat transfer and work terms.

(52)

(44)

Consider a reversible process, for which the entropy generation is zero, and the heat transfer and work terms therefore are

(11)

$$\delta Q = T dS$$

(12)

$$\text{and } \delta W = P dV$$

For an irreversible process with a nonzero entropy generation, the heat transfer, from eq. (9) becomes

(13)

$$\delta Q_{\text{irrev}} = T dS - T \delta S_{\text{gen}}$$

$$dS = \frac{\delta Q_{\text{irrev}}}{T} + \delta S_{\text{gen}}$$

and thus is smaller than that for the reversible case for the same change of state,  $dS$  (compare eq. (11) with eq. (13)).

We also note that for the irreversible process, the work is no longer equal to  $P dV$  but is smaller.

Furthermore, since the first law is

$$\delta Q_{\text{irrev}} = dU + \delta W_{\text{irrev}} \quad (14)$$

Since the states 1 and 2 are the same for irreversible and reversible processes,  $dU$  is same for both.

and the following property relation

$$TdS = dU + P dV$$

is valid for a reversible process,

(15)

(53) (54)

it is found from eqs. (13), (14) and (15) that

$$\delta W_{\text{inner}} = P dV - T \delta S_{\text{gen}} \quad (16)$$

[Derivation: Putting eq. (14) into eq. (13),

$$T dS - T \delta S_{\text{gen}} = dU + \delta W_{\text{inner}}$$

Substituting eq. (15) into the above equation,

$$dU + P dV - T \delta S_{\text{gen}} = dU + \delta W_{\text{inner}}$$

$$\Rightarrow \delta W_{\text{inner}} = P dV - T \delta S_{\text{gen}}]$$

Equation (16) shows that the work is reduced by an amount proportional to the entropy generation. For this reason the term  $T \delta S_{\text{gen}}$  is often called lost work, although it is not a real work or energy quantity lost but rather a lost opportunity to extract work.

Equation (9) can be integrated between initial and final states to

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q}{T} + S_{1-2, \text{gen}} \quad (17)$$

$ds = \frac{\delta Q}{T} + \delta S_{\text{gen}}$

(54)

(55)

Thus, we have an expression for the change of entropy for an irreversible process as an equality; whereas in the previous section we had an inequality.

Equation (17) is now the entropy balance equation for a control mass. The equation can also be written in the general form

$$\Delta \text{Entropy} = +\text{in} - \text{out} + \text{gen}$$

stating that we can generate but not destroy entropy. This is in contrast to energy, which we can neither generate nor destroy.

Some important conclusions can be drawn from eqs. (9) - (17). First,

there are two ways in which the entropy of a system can be increased

— by transferring heat to it, and

— by having an irreversible process.

Since the entropy generation cannot be less than zero, there is only one

way in which the entropy of a system can be decreased, and

that is to transfer heat from the system. These changes are illustrated

55 47

in a T-s diagram in Fig. 2 showing the half plane into which the state moves due to a heat transfer or an entropy generation.

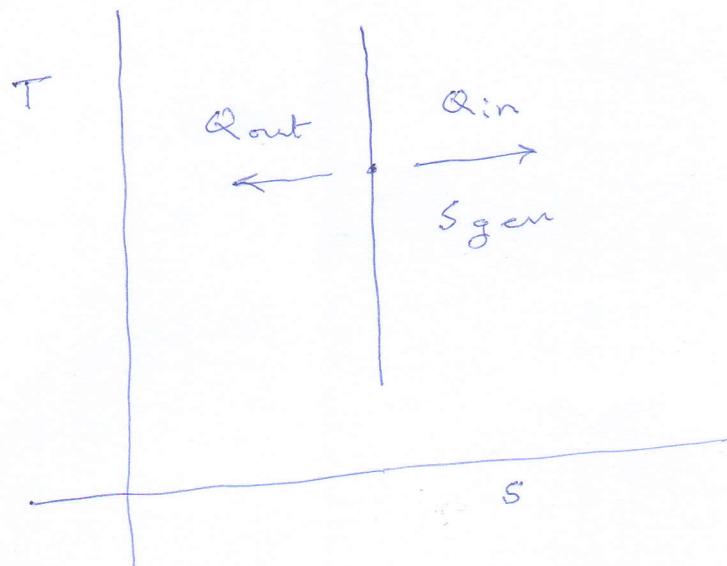


Fig. 2 Change of entropy due to heat transfer and entropy generation

Second, since for an adiabatic process  $\delta Q = 0$ , there is an increase in entropy which is always associated with irreversibilities.

Third, the presence of irreversibilities will cause the work (more specifically, the expansion work) to be smaller than the reversible work. On the other hand, the work will be greater than the reversible work in a compression process.

(56)

(48)

Finally, it should be emphasized that the change in 's' associated with the heat transfer is a transfer across the control surface. So, a gain for the control volume is accompanied by a loss of the same magnitude outside the control volume. This is in contrast to the generation term that expresses all the entropy generated inside the control volume due to any irreversible process.

One other point concerning the representation of irreversible processes on  $P-V$  and  $T-s$  diagrams should be made. The work for an irreversible process is not equal to  $\int p dV$ , and the heat transfer is not equal to  $\int T dS$ . Therefore, the area underneath the path does not represent work and heat on the  $P-V$  and  $T-s$  diagrams, respectively. In fact, in many situations we are not certain of the exact state through which a system passes when it undergoes an irreversible process. For this reason it is advantageous to show irreversible

(SF) ~~AT~~

processes as dashed lines and reversible processes as solid lines. Thus, the area underneath the dashed line will never represent work or heat. Figure 3(a) shows an irreversible process, and, because the heat transfer and work for this process are zero (for example, unrestrained expansion in a rigid insulated container), the area underneath the dashed line has no significance. Figure 3(b) shows the reversible process, and area 1-2-b-a-1 represents the work on the P-V diagram and the heat transfer on the T-S diagram.

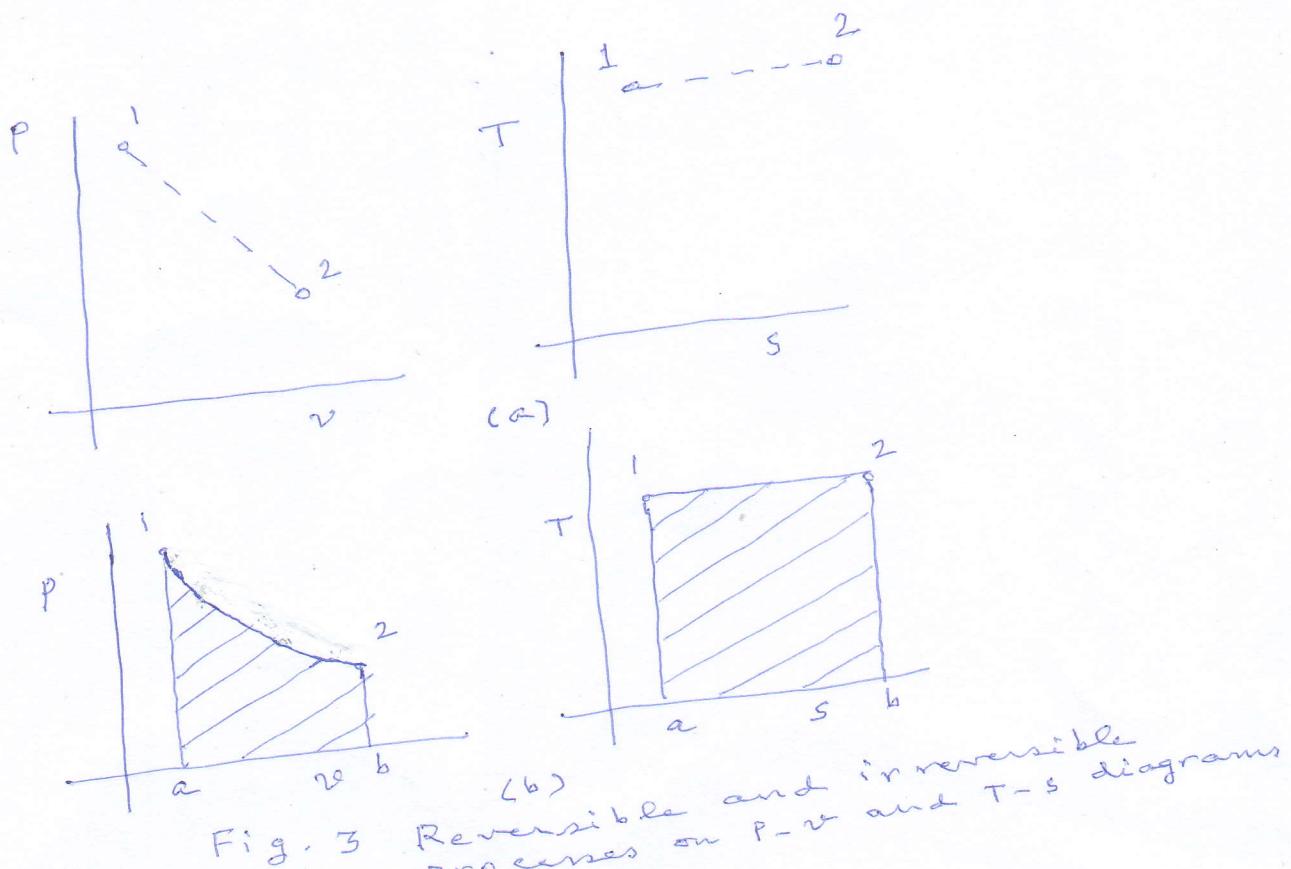


Fig. 3 Reversible and irreversible processes on P-V and T-S diagrams