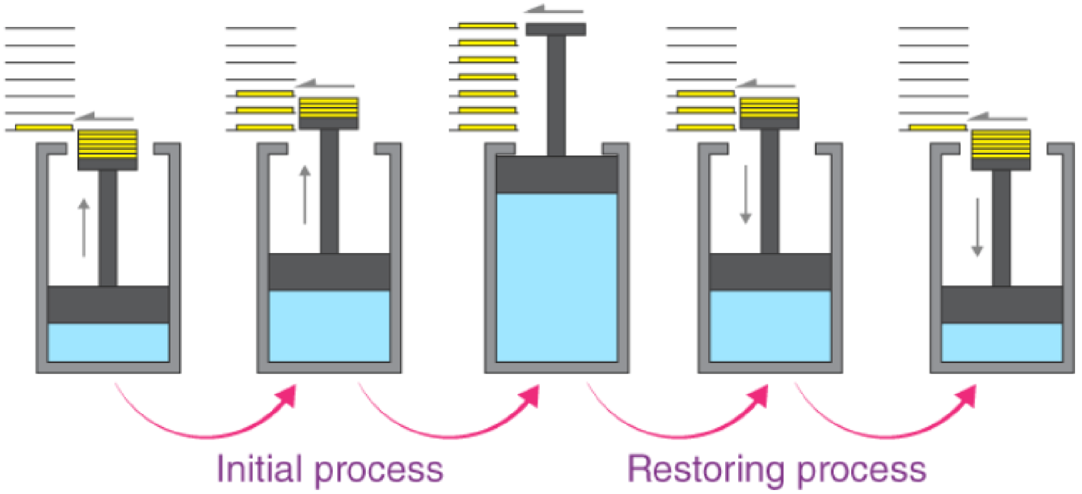
Lecture Ten

Reversible and Irreversible Processes

We see so many changes happening around us every day, such as boiling water, rusting of iron, melting ice, burning of paper, etc. In all these processes, we observe that the system in consideration goes from an initial state to a final state where some amount of heat is absorbed from the surroundings and some amount of work W is done by the system on the surrounding. Now, for how many such systems can the system and the surrounding be brought back to their initial state? With common examples such as rusting and fermentation, we can say that it is not possible in most cases. In this section, we shall learn about reversible and irreversible processes.



What Are Reversible Processes?

A thermodynamic process is said to be reversible if the process can be turned back to such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. As we know, in reality, no such processes as reversible processes can exist. Thus, reversible processes can easily be defined as idealizations or models of real processes on which the limits of the system or device are to be defined. They help us in

Email (esam.muhe@uomus.edu.iq)

incurring the maximum efficiency a system can provide in ideal working conditions and, thus, the target design that can be set.

Examples of Reversible Processes

Here, we have listed a few examples of Reversible Processes:

- extension of springs
- slow adiabatic compression or expansion of gases
- electrolysis (with no resistance in the electrolyte)
- the frictionless motion of solids
- slow isothermal compression or expansion of gases

What Are Irreversible Processes?

An irreversible process can be defined as a process in which the system and the surroundings do not return to their original condition once the process is initiated. Take an example of an automobile engine that has travelled a distance with the aid of fuel equal to an amount ‘x’. During the process, the fuel burns to provide energy to the engine, converting itself into smoke and heat energy. We cannot retrieve the energy lost by the fuel and cannot get back the original form. There are many factors due to which the irreversibility of a process occurs, namely:

1. The friction that converts the energy of the fuel to heat energy.
2. The unrestrained expansion of the fluid prevents from regaining the original form of the fuel. Heat transfer through a finite temperature, the reverse of which is not possible as the forward process, in this case, is spontaneous.
3. Mixing of two different substances that cannot be separated as the intermixing process is again spontaneous in nature, the reverse of which is not feasible.

Thus, some processes are reversible while others are irreversible in nature, depending upon their ability to return to their original state from their final state.

Examples of Irreversible Processes

A few examples of Irreversible Processes are:

- Relative motion with friction
- Throttling
- Heat transfer
- Diffusion
- Electricity flow through a resistance

Exergy or Availability of energies:

Work potential of an energy source {is the amount of energy that can be extracted as useful work.

This property is exergy, which is also called the availability or available energy.

Recall that the work done during a process depends on the initial state, the final state, and the process path.

Work = f (initial state, process path, final state).

The work output is maximized when the process between two specified states is executed in a reversible manner. Therefore, all the irreversibility is disregarded in determining the work potential.

A system is said to be in the dead state when it is in thermodynamic equilibrium with the environment.

At the dead state, a system is at the temperature and pressure of its environment (in thermal and mechanical equilibrium); it has no kinetic or potential energy relative to the environment (zero velocity and zero elevation above a reference level); and it does not react with the environment (chemically inert).

Also, there are no unbalanced magnetic, electrical, and surface tension elects between the system and its surroundings, if these are relevant to the situation at hand.

The properties of a system at the dead state are denoted by subscript zero, for example, P_0, T_0, h_0, u_0, and s_0.

Distinction should be made between the surroundings, immediate surroundings, and the environment.

Surroundings are everything outside the system boundaries.

The immediate surroundings refer to the portion of the surroundings that is affected by the process, and environment refers to the region beyond the immediate surroundings whose properties are not a_ected by the process at any point.

A system delivers the maximum possible work as it undergoes a reversible process from the specified initial state to the state of its environment, that is, the dead state.

Exergy represents the upper limit on the amount of work a device can deliver without violating any thermodynamic laws.

Unavailable energy is the portion of energy that cannot be converted to work by even a reversible heat engine.

The Relationship between Internal Energy and Entropy

Because work done during the expansion of a gas depends on the opposing external pressure ($w = - P_{ext.} \Delta V$), work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$. Whether a process is reversible or irreversible, $\Delta U = q + w$. Because U is a state function, the magnitude of ΔU does not depend on reversibility and is independent of the path taken. So

$$\Delta U = q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$$

Work done in a reversible process is always equal to or greater than work done in a corresponding irreversible process: $w_{rev} \geq w_{irrev}$.

In other words, ΔU for a process is the same whether that process is carried out in a reversible manner or an irreversible one. We now return to earlier definition of entropy, using the magnitude of the heat flow for a reversible process (q_{rev}) to define entropy quantitatively.

Because the quantity of heat transferred (q_{rev}) is directly proportional to the absolute temperature of an object (T) ($q_{rev} \propto T$), the hotter the object, the greater the amount of heat transferred. Moreover, adding heat to a system increases the kinetic energy of the component atoms and molecules and hence their disorder ($\Delta S \propto q_{rev}$). Combining these relationships for any reversible process,

$$q_{rev} = T\Delta S \qquad \text{and} \qquad \Delta S = q_{rev}/T$$

Because the numerator (q_{rev}) is expressed in units of energy (joules), the units of ΔS are joules/kelvin (J/K). Recognizing that the work done in a reversible process at constant pressure is $w_{rev} = -P\Delta V$, we can express Equation above as follows:

$$\Delta U = q_{rev} + w_{rev} = T\Delta S - P\Delta V$$

Thus, the change in the internal energy of the system is related to the change in entropy, the absolute temperature, and the PV work done.

Thermodynamic Potentials and Maxwell's Relations

The energy and entropy representations:

We have noted that both S(U,V,N) and U(S,V,N) contain complete thermodynamic information (where N= number of particles).
We will use the fundamental thermodynamic identity

$$dU = TdS - pdV + \mu dN$$

as an aid to memorizing the of temperature, pressure, and chemical potential (μ) from the consideration of equilibrium conditions. by calculating the appropriate partial derivatives, we have

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T,$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P,$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,N} = \mu,$$

And
We can also write the fundamental thermodynamic identity in the entropy representation:

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

from which we find

$$\frac{\partial S}{\partial U})_{V,N} = \frac{1}{T},$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T},$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,N} = -\frac{\mu}{T},$$

Email (esam.muhe@uomus.edu.iq)

And

By calculating the second partial derivatives of these quantities we find the Maxwell relations.

Maxwell relations can be used to relate partial derivatives that are easily measurable to those that are not. Starting from

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T, \quad and \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P,$$

We can calculate

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_{S,N} and \frac{\partial^2 U}{\partial S \partial V} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

Now since under appropriate conditions

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

Then

$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

This result is called a Maxwell relation. By considering the other second partial derivatives, we find two other Maxwell relations from the energy representation of the fundamental thermodynamic
identity. These are:

$$\left(\frac{\partial T}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial S}\right)_{V,N} \quad \text{and} -\left(\frac{\partial P}{\partial N}\right)_{S,V} = \left(\frac{\partial \mu}{\partial V}\right)_{S,N}$$

Similarly, in the entropy representation, starting from

$$dS = \frac{dU}{T} + \frac{P}{T} dV - \frac{\mu}{T} dN$$

and the results

$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}, \quad \left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{P}{T}, \quad \left(\frac{\partial S}{\partial N}\right)_{U,N} = -\frac{\mu}{T},$$

We find the Maxwell relations:

$$\left(\frac{\partial(\frac{1}{T})}{\partial V}\right)_{U,N} = \left(\frac{\partial(\frac{P}{T})}{\partial U}\right)_{V,N}, \left(\frac{\partial(\frac{1}{T})}{\partial N}\right)_{U,V} = -\left(\frac{\partial(\frac{\mu}{T})}{\partial U}\right)_{V,N} \text{ and } \left(\frac{\partial(\frac{P}{T})}{\partial N}\right)_{U,V} = -\left(\frac{\partial(\frac{\mu}{T})}{\partial V}\right)_{U,N}$$

Email (esam.muhe@uomus.edu.iq)

Enthalpy H(S,p,N):

We have already defined enthalpy as $H = U + pV$. We can calculate its differential and combine it with the fundamental thermodynamic identity to show that the natural variables of H *are* S, p, *and* N.

$$H = U + pV$$

$$\text{we have} \quad dH = dU + d(pV) = dU + pdV + V dp,$$

$$\text{and so inserting} \quad dU = TdS - pdV + \mu dN$$

$$\text{we have} \quad dH = TdS - pdV + \mu dN + pdV + V dp$$

$$\text{resulting in} \quad dH = TdS + V dp + \mu dN.$$

Thus, we can see that we can write $H = H(S, p,N)$, and as already noted $S, p,$ *and* N *are the natural variables of* H. We can continue as above to generate the definitions

$$(\frac{\partial H}{\partial S})_{P,N} = T, (\frac{\partial H}{\partial P})_{S,N} = V, (\frac{\partial H}{\partial N})_{S,P} = \mu$$

And the Maxwell relations

$$(\frac{\partial T}{\partial P})_{S,N} = (\frac{\partial V}{\partial S})_{P,N} \quad , (\frac{\partial T}{\partial N})_{S,P} = (\frac{\partial \mu}{\partial S})_{P,N} \quad and \quad (\frac{\partial V}{\partial N})_{S,P} = (\frac{\partial \mu}{\partial P})_{S,N}$$

In the above, as we transformed from U to H, we changed independent variables, *i.e.*, we replaced the variable V with its conjugate p. (Variables x and y that are related through the partial derivative of some function ξ such that $\frac{\partial \xi}{\partial x} = y$ are called conjugate variables). This is an example of a *Legendre transform*. In a Legendre transform, to replace one independent variable with its conjugate, a new function ξ is defined by the addition or subtraction of the product of the conjugates x and y. In other words, we define ξ = ξ ± xy. In the case of enthalpy we added pV , as we shall see, this was due to the presence of the term ?pdV in the fundamental thermodynamic identity. To eliminate the variables S and N in terms of their conjugates, it will be necessary to subtract the products of the conjugate variables, as we shall soon see.