**Thermodynamics**

*Zeroth law of thermodynamics, first law of thermodynamics, brief discussion on application of 1st law, second law of thermodynamics and concept of Engine, entropy, change in entropy in reversible and irreversible processes, third law of thermodynamics*

**Terminology**

There are certain terms in thermodynamics which are used with specific connotation. It is necessary for us to acquaint with these terms before we embark on the study of thermodynamics.

**System**

The principles of thermodynamics are usually stated with reference to a well-defined system. A system is defined in thermodynamics as a quantity of matter of fixed mass and identity.

**State**

Thethermodynamics state of a system is described with the macroscopic quantities such as pressure and volume. The physical quantities which unambiguously determine the state of a body are called thermodynamics variables.

**Thermodynamics Equilibrium**

In mechanics, equilibrium means a state of rest. In thermodynamics the concept is somewhat broader. A system is said to be in thermodynamics equilibrium if none of the thermodynamics variables determining its state changes with time.

Thermodynamics is the science that deal with the rules according to which bodies exchange energy. In the early stages, thermodynamics was concerned with the relationship between mechanical and heat energy. Further developments turned thermodynamics into a science that is concerned with relationships between heat and all other kind of energy such as chemical, electrical etc.

**Concept of temperature**

The concept of temperature originated from or subjective sense of hot and cold. We use these words to denote the degree of heating to which a body is subjected. The quantity that characterizes the degree of heating to which a body is subjected is termed the temperature of that body.

In technical terms, the bodies are said to be in thermal equilibrium. Thus, if the temperatures of two bodies are equal, no heat exchange takes place between them and the energy of each body remains constant we may therefore define temperature as a quantity indicating the direction of heat exchange.

The concept of thermal equilibrium leads us to the Zeroth law of thermodynamics. It may be stated formally as follows:

‘Two bodies, A and B, each in thermal equilibrium with a third body C are in thermal equilibrium. With each other”

This law is implies that equality of temperature is necessary and sufficient to ensure thermal equilibrium.

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**First law of thermodynamics**

Thermodynamics is concerned with three general formal of energy, namely heat, work and internal energy. Heat is the energy transferred by virtue of temperature difference, thermodynamics work is energy ( exclusive of heat ) transferred between a system and surroundings, and internal energy is energy stored within a system If the state of a system such as the one described in Fig16.2 change as a result of supplying a quantity of heat Q to it, and as a consequence the system does the work w , then the law of conservation of energy state that the quantity of heat supplied to the system will beequal to the sum of the work performed by the system and the and the change in the internal energy of the system. That is,

Net heat transfer = work + Change in internal energy

Or mathematically, Q= W+

This is known as the first law of thermodynamics. It is in effect a statement of the conservation of energy . The net change in the internal energy of the system is always equal to the net transfer of energy as heat and work across the boundary of the system.

While the quantities Q and w are path – dependent, the internal energy does not depend on the path of the process.

**Application of the first law**

Let us now study some special processes and the application of the first law to them.

1. Isolated system : An isolated system does not interact with its surroundings. Therefore, there is no heat flow and the work done is zero. That is Q = 0 and w = 0. It follows from equ.(16.6) that

U2  - U1  = 0 or

U2 = U1 Isolated system (16.8)

Equ ( 16.8) means that the internal energy of an isolated system remains constant.

2 Cyclic process: In a cyclic process, the initial and find state of the system are the same. Thus,

U2 = U1

3 Adiabatic process: A process in which no heat is absorbed or ejected by the system is called an adiabatic process. Thus Q = 0

4 Isothermal process: When a substance – undergoes a process in which the volume remains unchanged, the process is called isochoric. If the volume of a system remains contant, it can do no work. Thus, W= 0 and the first law gives

Isochoric process ( 16.11)

In this case, the heat that entered the system is stored as internal energy.

5 A process taking place at constant temperature is said to be isothermal. In an isothermal process, the quantities, Q, W and are in general nonzero.

6 Isobaric process: A process taking place at constant pressure is called an isobaric process.

As the pressure is constant,

W = - )

Isobaric process (16.12)

7 Isothermal expansion of an ideal gas: Let an ideal gas allowed to expand quasistatically at constant temperature by placing the gas in good thermal contact with a heat reservoir at the same temperature.

W =

W= nRT

W =nRTn()

(8) Adiabatic expansion of an ideal gas: Let us find the relation between p and v for an adiabatic process carried out on an ideal gas. According to equ. (16.10),

For an ideal gas (at constant volume)

The work done during the process is given by w = pdv

Pdv =- ndT

WE CAN WROTE THE EQUATION OF THE STATE OF the gas in differential form as

d(PV) = d(nRT)

PdV + VdP = nRdT

Using equ.(16.14) into equ.(16.15), we get

VdP = ndT

Taking the ratio between equ.(16.16) and equ(16.14), we get

= -

= -

Integrating on both sides of the above equation, we get

=-

Or

In =-

=

Or P= Constant (16.18)

**Second Law of Thermodynamics**

The second law of thermodynamics comes in more than one form, but let's state in a way that makes it obviously true, based on what you've observed from simply being alive.

The second law states that heat flows naturally from regions of higher temperature to regions of lower temperature, but that it will not flow naturally the other way.

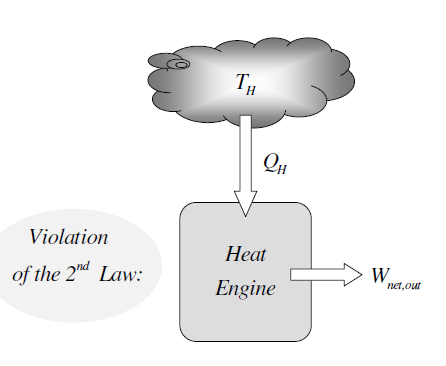
Heat can be made to flow from a colder region to a hotter region, which is exactly what happens in an air conditioner, but heat only does this when it is forced. On the other hand, heat flows from hot to cold spontaneously.

There are two classical statement of the second law of thermodynamics, they are known as the kelvin – Planck statement and the Clausius statement.

**Kelvin – Planck statement**

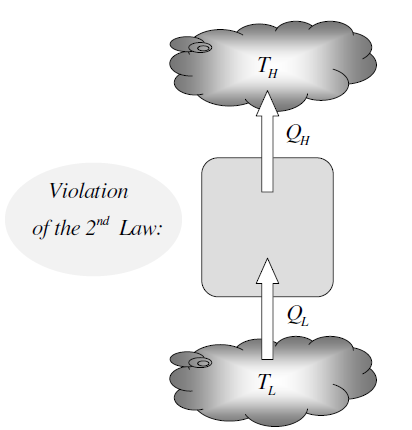
*It is impossible for any device that operates on a cycle to receive heat from a single reservoir and*

*produce a net amount of work*



**Clausius Statement:**

*No device can operate on a cycle and produce effect that is solely the heat transfer froma lower-temperature body to a higher-temperature body*



An analysis of operation of heat engines led William Thomson (later Lord Kelvin) and Planck to arrive at the following conclusion:

It is impossible to construct a heat enegine with 100% efficiency cycle and which will receive a given amount of heat from a high – temperature reservoir and does an equal amount of work.

It is impossible to construct a device that operates in a cycle and produces no effect other them the transfer of heat from a cold body to a hot body. In effect, it is impossible to construct a refrigerator that operates without an input of work.

The first law of thermodynamics is a general statement of the conservation of energy. It makes no distinction between the different forms of energy. The second law of thermodynamics assert that between the different from all other forms of energy. Various forms of energy can be converted into thermal energy spontaneously and completely, whereas the reverse transformation is never complete. The impossibility of converting heat completely into mechanical energy forms the basis of Kelvin – Planck’s statement of second law. The fact that work may be dissipated completely into heat whereas heat may be converted entirely into work expresses the essential one sidedness of nature.

**Heat engines**

We'll move on to look at heat engines, which are devices that use heat to do work. A basic heat engine consists of a gas confined by a piston in a cylinder. If the gas is heated, it expands, moving the piston. This wouldn't be a particularly practical engine, though, because once the gas reaches equilibrium the motion would stop. A practical engine goes through cycles; the piston has to move back and forth. Once the gas is heated, moving the piston up, it can be cooled and the piston will move back down. A cycle of heating and cooling will move the piston up and down.

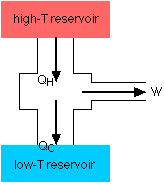
A necessary component of a heat engine, then, is that two temperatures are involved. At one stage the system is heated, at another it is cooled.

In a full cycle of a heat engine, three things happen:

1. Heat is added. This is at a relatively high temperature, so the heat can be called QH.
2. Some of the energy from that input heat is used to perform work (W).
3. The rest of the heat is removed at a relatively cold temperature (QC).

http://buphy.bu.edu/~duffy/PY105/31f.GIF

The following diagram is a representation of a heat engine, showing the energy flow:



An important measure of a heat engine is its efficiency: how much of the input energy ends up doing useful work? The efficiency is calculated as a fraction (although it is often stated as a percentage):

http://buphy.bu.edu/~duffy/PY105/31g.GIF

Work is just the input heat minus the rejected heat, so:

http://buphy.bu.edu/~duffy/PY105/31h.GIF

Note that this is the maximum possible efficiency for an engine. In reality there will be other losses (to friction, for example) that will reduce the efficiency.

**Entropy**

The differential form of the first law of thermodynamics is written as

dQ = dU + dw

The work dw done depends on the path of process and therefore it is not a function of the state. The same is the case with dQ, the quantity of quantity of heat supplied or taken away. The work dw can be expressed in terms of thermodynamics variables and their changes. For instance, we have expressed dw in equ.( 16.2) as

dw = Pdv

It is found that dQ can also be expressed in a similar fashion, in case of reversible processes. We write

dQ = Tds

where dS is called the change in entropy and T is the temperature. Now we define the change in entropy as

dS = Reversible process (16.38)

the total entropy change in a reversible process may be obtained by integrating equ,(16.38). Thus

=

Where and are the entropies of the initial and final states of the system.

=

Thus, Isothermal Process The units of entropy and entropy change are J/k.

In practice, The value of entropy S is not of much interest. We have to Know the change in entropy when the system changes from one state to another.

These consideration led Clausius to reformulate the second law of thermodynamics in terms of entropy. According to it, The entropy of an isolate system always tends to increase. Mathematically, It is expressed as

**Some Interesting Points**

**1 The net change in entropy in any reversible cycle is Zero.**

Let us take the case of Carnot cycle as an example. There is no change in entropy of the working substance during the two adiabatic paths. Either during adiabatic expansion or compression, Q = 0

Therefore, S = 0 However, there is an increase in entropy during isothermal expansion, as heat

Is added at a constant temperature TH. The consequent increases in entropy = . There is a decrease in entropy during the isothermal compression in which heat Ql  is rejected at a temperature TL . Thus , = -

The net change in entropy is given by

+ = -

But =

**2 Entropy increases in all irreversible processes.**

It is proved that there is a net increase in the entropy during irreversible processes.. since all real processes taking place in the universe are irreversible, there is a continuous increase in its entropy. For this reasons, entropy is not conserved . In this respect entropy differs from energy.

We can illustrate this by taking a simple example. Suppose a small quantity of heat dQ is radiated away from a hot body A,at a temperature TH , to a cold body B at a temperature Tc Let dQ be so small that TH  and Tc are not altered appreciable, due to the exchange of heat. However, the entropy of A decreases by –dQ/TH where as that of B increases by dQ/Tc in this process.

=

As TH Tc (16.43)

3 Entropy indicates the direction in which proceed in nature.

All natural processes are irreversible. They proceed in the direction of increasing entropy.

**Third Law Of Thermodynamics**

With a decreases in temperature, in temperature, a greater degree of prevail in any system. If we could cool a system to 0K, the maximum conceivable order would be established in the system and the minimum entropy would correspond to this state. Now, suppose we apply a pressure on the system at 0k. what does happen to the entropy of the system? On the basis of experiments conducted at low temperatures, W. Nernst conclude that “at 0k, any change in the state of a system takes place without a change in the entropy”. This is called Nernst’s theorem. It is also called the third law of thermodynamics. Third law of thermodynamics is sometimes Known as the principle of unattainability of absolute zero. It is stated as follows:

**It is impossible to attain a temperature of 0K.**

**WORK**

**Let us examine the work done in a thermodynamics process. Consider a thermodynamics system such** as a gas contained in a cylinder fitted with a movable piston, 16.10(a). in equilibrium the gas occupies a volume V and exerts a uniform pressure P on the piston and the walls of the cylinder. If the cross- sectional area of the piston is A, the force exerted by the gas on the piston is

Now, let us assume that the gas expands quasistatically. As the piston move up a distance, the work done by the gas on piston is

But Ady = dV, the increase in the volume of the gas. Therefore,

The relation (16.2) expresses the work solely in terms of the thermodynamic variables of the system. The nature of the external force and other characteristics of the surrounding do not appear in this relation. The work

Is often called thermodynamic work. In practice,

We refer to it simply as work.

The total work done by the gas as its volume changes from V1 to V2 can be found by integrating equ.( 16.2). Thus,

W1W2 = = (16.3)

In the process represented in Fig16.13(a) the pressure of the gas is first reduced from P1 to P2 by cooling it at a constant volume V1. Next, the gas is allowed to expand V1 to V2 at constant pressure P2. The work done along this path is WA = P2(V2-V1).

In the process represented in fig.16.13(b), the gas is first allowed to expand fromV1 to V2 at constant pressure P1 and then the pressure is reduced to P2 at constant volume V2. The work done along this path is W**B = P1 (V2 –V1).**