Thermodynamic System:

The term system, as used in thermodynamics, refers to a certain portion of the universe within some closed surface called the boundary of the system. Any systems which cab interchange energy or particle with a given system are called the surroundings of the system.

Systems are classified as follows:

Isolated System: If there is no interchange of energy or matter between the system and surroundings, then the system is called isolated system.

Closed System: If no energy or matter crosses the boundary, then the system is called closed system.

Open System: If there is an interchanges of energy or matter between the system and surroundings, then the system is called open system.

Thermodynamic Process:

A thermodynamic process is the energetic development of a thermodynamic system proceeding from an initial state to a final state.

Different thermodynamic processes are:

Isochoric Process: If during a process, the volume is constant then the process is called isochoric process.

Isobaric Process: If during a process, the pressure is constant then the process is called isobaric process.

Isothermal Process: If during a process, the temperature is constant then the process is called isothermal process. An isothermal process is a change of a system, in which the temperature remains constant ($\Delta T = 0$). This typically occurs when a system is in contact with an outside thermal reservoir, and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange.

Adiabatic Process: A process is called adiabatic if it is carried by a system enclosed by an adiabatic boundary; such that no flow of heat is possible across the boundary.

Reversible Process: A reversible process can be defined as one whose direction can be reversed by an infinitesimal change in some property of the system. Thus if the temperature of the system within a diathermal boundary is always slightly lower than that of its surroundings, there will be a flow of heat from the surroundings into the system whereas if the temperature of the system is

slightly greater than that of the surroundings there will be a flow of heat in the opposite direction. Such process is therefore reversible process where no dissipative force is present.

Irreversible Process: If there is a finite temperature difference between system and surroundings the direction of the heat flow can't be reversed by an infinitesimal change in temperature of the system and the process is irreversible.

First Law of Thermodynamics:

"When heat is supplied to any system then a part of that heat helps to increase the internal energy of the system and the remaining part of the energy is used by the system to do external work on the environment." .

Explanation:

Let us consider,

U_1 be the internal energy of a system. If Q amount of heat is added to the system then the internal energy of the system becomes U_2.

The change in internal energy can then be denoted as

$\Delta U = U_2 - U_1$……………………….. (1)

Thus the first law of the thermodynamics gives

$Q = \Delta U + W$ …………………….(2)

Equation (2) is the mathematical form of the first law of thermodynamics.

For an infinitesimal reversible process, the first law takes the form,

$dQ = dU + dW$

Application of First Law of Thermodynamics:

Molar Specific Heat: The amount of heat needed to increase the temperature one Kelvin of one mole gas is called molar specific heat.

$C = \dfrac{\Delta Q}{m\,\Delta T}$ or, $C = \dfrac{dQ}{m\,dT}$

Molar Specific Heat at Constant Pressure: At constant pressure, the amount of heat needed to increase the temperature one Kelvin of one mole gas is called molar specific heat at constant pressure.

$$C_P = \frac{dQ}{m \, dT}$$

Molar Specific Heat at Constant Volume: At constant volume, the amount of heat needed to increase the temperature one Kelvin of one mole gas is called molar specific heat at constant volume.

$$C_v = \frac{dQ}{m \, dT}$$

Relation between C_p and C_v:

Let us consider a cylinder containing one mole gas. A frictionless piston is attached to the cylinder. Let P be the pressure, V be the volume, T be the temperature and U be the internal energy of the gas.

If dQ amount of heat is given to the cylinder then the increase in internal energy, volume and temperature are dU, dV and dT respectively and dW is the external work then from the first law of thermodynamics, we get,

dQ = dU + dW

or, dQ = dU + pdV …………………..(1)

But, increase in internal energy dU per mole gas is equal to the product of molecular specific heat at constant volume, C_v and increase in temperature dT.

$\Box$ dU = C_v dT ……………………..(2)

We know that, the amount of heat needed to increase the temperature one Kelvin of one mole gas is called molar specific heat at constant pressure.

$\Box$ $C_p = \frac{dQ}{dT}$

or, dQ = C_p dT …………………(3)

If R is the molar gas constant, then for one mole gas we get,

pV = RT

Differentiating with respect to T,

$$\frac{d}{dT}(pV) = \frac{d}{dT}(RT)$$

or, $p\frac{dV}{dT} = R$

∴ pdV = RdT ……………………(4)

Putting the values of dU, dQ and pdV from equation (2), (3) and (4) into equation (1), we get,

$C_p dT = C_v dT + R\ dT$

or, $C_p = C_v + R$

or, $C_p - C_v = R$

Here, Molar gas constant R is universal constant and is a positive quantity. So C_p is always greater than C_v.

In Case of Adiabatic Change for an Ideal Gas PV$^\gamma$ = constant:

Let us consider a cylinder containing one mole gas. A frictionless piston is attached to the cylinder. Let P be the pressure, V be the volume, T be the temperature and U be the internal energy of the gas.

If dQ amount of heat is given to the cylinder then the increase in internal energy, volume and temperature are dU, dV and dT respectively and dW is the external work then from the first law of thermodynamics, we get,

dQ = dU + dW

or, dQ = dU + pdV …………………..(1)

But, increase in internal energy dU per mole gas is equal to the product of molecular specific heat at constant volume, C_v and increase in temperature dT.

∴ $dU = C_v\ dT$

Now from equation (1)

$dQ = C_v\ dT + pdV$

At adiabatic process, dQ = 0

∴ $C_v\ dT + pdV = 0$ …………………..(2)

Again we know for one mole gas,

pV = RT

Differentiating with respect to T,

$\frac{d}{dT}(pV) = \frac{d}{dT}(RT)$

or, $p\frac{dV}{dT} + V\frac{dp}{dT} = R$

or, $pdV + Vdp = RdT$

$\therefore dT = \frac{pdV + Vdp}{R}$ ………………….(3)

Substituting equation (3) in equation (2) we get,

$C_v(\frac{pdV + Vdp}{R}) + pdV = 0$

or, $C_v\,pdV + C_v\,Vdp + R\,pdV = 0$

or, $C_v\,pdV + C_v\,Vdp + (C_p - C_v)\,pdV = 0$

or, $C_v\,Vdp + C_p\,pdV = 0$

or, $Vdp + (C_p/C_v)\,pdV = 0$

or, $Vdp + \gamma\,pdV = 0$ [where, $\gamma = (C_p/C_v)$]

$\therefore \frac{dp}{p} + \gamma\frac{dV}{V} = 0$

Integrating above equation we get,

$\int\frac{dp}{p} + \gamma\int\frac{dV}{V} = $ constant

or, $\ln p + \gamma\,\ln V = $ constant

or, $\ln p + \ln V^\gamma = $ constant

or, $\ln(pV^\gamma) = $ constant

$\therefore pV^\gamma = $ constant

Second Law of Thermodynamics:

Different scientist have stated the law in different forms:

Carnot's Statement: *No engine can be built which can extract a fixed amount of heat and will convert totally into work.*

Clasius's Statement: *It is impossible for a self acting machine, unaided by external agency, convey heat from one body at a lower temperature to another body at a higher temperature.*

Planck's Statement: *It is impossible to construct an engine which can extract heat continuously from a source of heat and completely transforms into work.*

Kelvin's Statement: *Continuous flow of energy can't be obtained from an object cooling it than the coolest part of its surroundings.*

Heat Engine and Efficiency of Heat Engine:

Heat Engine: Any mechanism for the conversion of heat into mechanical power is called a heat engine or any suitable device which can convert heat into mechanical work is called heat engine.

Efficiency of Heat Engine: The efficiency of heat engine is defined as the ratio of work done during a cycle to the heat absorbed during the cycle.

Thus if W be the amount of work obtained from heat engine in one cycle at the expense of amount of heat, then its efficiency η is defined as,

$$\eta = \frac{W}{Q}$$

$$= (Q_1 - Q_2) / Q_1$$

$$= 1 - (Q_2 / Q_1)$$

Carnot's Heat Engine and It's Efficiency:

A Carnot heat engine is a hypothetical engine that operates on the reversible carnot cycle. The basic model for this engine was developed by Sadi Carnot in 1824.

A system carried through a Carnot cycle is the prototype of all cyclic heat engines. The feature that is common to all such devices is that, they receive an input of heat at one or more higher temperatures, do mechanical work on their surroundings and reject at some lower temperature.

When any working substance is carried through a cyclic process, there is no change in its internal energy in any complete cycle and from the first law the net flow of heat Q into the substance in any complete cycle is equal to the workdone W by the engine per cycle,

$W = Q_1 - Q_2 = Q$

Where,

Q_1 is the heat flowing in the system and Q_2 is the heat flowing out of the system per cycle.

The thermal efficiency η of heat engine is defined as,

$$\eta = \frac{work\ output}{heat\ input}$$

$$= \frac{heat\ converted\ into\ work\ per\ cycle}{heat\ drawn\ from\ the\ heat\ source\ into\ the\ system\ per\ cycle}$$

$= W / Q_1$

$= (Q_1 - Q_2) / Q_1$

$= 1 - (Q_2 / Q_1)$ ………………..(1)

For Carnot's engine the heat flowing in or out of the system is proportional to the temperature to the heat reservoir,

$Q \times T$

or, $\frac{Q}{T}$ = constant

If T_1 and T_2 are the temperature of the source and sink respectively, then

$(Q_1 / T_1) = (Q_2 / T_2)$

$\square\ (Q_2 / Q_1) = (T_2 / T_1)$

Then from equation (1) we get,

$\eta = 1 - (Q_2 / Q_1)$

$= 1 - (T_2 / T_1)$

$= (T_2 - T_1) / T_1$

But efficiency is expressed in term of percentage.

So, $\eta = \{(T_2 - T_1) / T_1\} \times 100\%$

Entropy:

The disability of converting energy of a system or unavailability of energy to convert into work is entropy.

In thermodynamics, entropy is a measure of the number of specific ways in which a thermodynamic system may be arranged often taken to be a measure of disorder, or a measure of progressing towards thermodynamic equilibrium.

Explanation:

It has not yet been possible to measure the absolute magnitude of entropy. If any body absorbs or rejects heat then its entropy is changed.

The change of entropy is measured by the rate of absorption or rejection of heat by the system with respect to temperature.

If any system absorbs or rejects dQ amount of heat at temperature T, then the change of entropy

$$dS = \frac{dQ}{T}$$

Change of Entropy:

Change of Entropy in Reversible Adiabatic Process:

By definition, the heat absorbed in a reversible adiabatic process is zero,

$dQ_r = 0$

Hence for such a process entropy change is given by,

$dS = dQ_r / T = 0$

☐ S = constant

Thus the entropy of a reversible adiabatic process is constant and such process is called isentropic.

Change of Entropy in Reversible Isothermal Process:

In a reversible isothermal process the temperature remains constant and for such a process

$$S = \int \frac{dQ}{T}$$

$$= \frac{1}{T} \int dQ$$

$$= Q_r / T$$

That is, the change of entropy in a reversible isothermal process is equal to the heat absorbed or given out by the system dividing by the thermodynamic temperature of the system.

If the heat flows into the system Q is positive and entropy increases. If the heat flows out of the system Q is negative and entropy decreases.

Change of Entropy in Irreversible Process:

Let two objects completely isolated from the environment are in contact with each other. The temperatures of two objects are respectively T_1 and T_2. If $T_1 > T_2$ then heat will flow from the warm object to the cold object. Let within a very short period of time dQ amount of heat is transferred from the warm one to the cold one. That is the warm object looses dQ amount of heat and the cold object gains dQ amount of heat.

Therefore,

- dQ/ T_1 = Decrease of entropy of the warm object.

And

 dQ/ T_2 = Increase of entropy of the cold object.

Therefore, the change of entropy of the system,

dS = (- dQ/ T_1) + (dQ/ T_2)

It is observed from the above equation that

Since $T_1 > T_2$

□ dS > 0

That is the change of entropy is always positive.

Heat Death of The Universe:

Everything in nature tries to acquire the state of equilibrium. As a system goes towards equilibrium the possibility of getting work from the system reduces and when it attains the equilibrium no work is found from it. This disability of converting the entropy is known as entropy. As the systems proceed towards the equilibrium their entropy also increases. The entropy of a system becomes maximum when we do not get any work from it. All spontaneous changes are directed towards the equilibrium. Therefore in case of all spontaneous change the

entropy is increased. Since everything in nature wants to attain equilibrium so the entropy of nature is gradually increasing. When the entropy of the universe will reach at the highest point then everything will attain the same temperature. As a result heat energy will not be possible to convert into mechanical energy. This state of the universe is so called heat death of the universe.

The Third Law of Thermodynamics:

The third law of thermodynamics is sometimes stated as follows, (regarding the properties of closed systems in thermodynamic equilibrium):

"The entropy of a system approaches a constant value as its temperature approaches absolute zero".

This constant value cannot depend on any other parameters characterizing the closed system, such as pressure or applied magnetic field. At absolute zero (zero kelvin) the system must be in a state with the minimum possible energy. Entropy is related to the number of accessible microstates, and there is typically one unique state (called the ground state) with minimum energy. In such a case, the entropy at absolute zero will be exactly zero. If the system does not have a well-defined order (if its order is glassy, for example), then there may remain some finite entropy as the system is brought to very low temperatures, either because the system becomes locked into a configuration with non-minimal energy or because the minimum energy state is non-unique. The constant value is called the residual entropy of the system.

The Nernst–Simon statement of the third law of thermodynamics concerns thermodynamic processes at a fixed, low temperature:

The entropy change associated with any condensed system undergoing a reversible isothermal process approaches zero as the temperature at which it is performed approaches 0 K.

Here a condensed system refers to liquids and solids.

Problem 1:

A quantity of air at 27 C and atmospheric pressure is suddenly compressed to half its original volume. Find the final pressure and temperature.

Solution:

Here,

Initial pressure, $P_1 = 1$ atm

Initial temperature, $T_1 = 27$ C $= (27+273)$ K

$\gamma = 1.4$

Let,

Initial volume, $V_1 = V$

☐ Final volume, $V_2 = V/2$

Final pressure, $P_2 = ?$

Final Temperature, $T_2 = ?$

We know that,

During sudden compression the process is adiabatic.

Hence,

$$P_1 \, V_1^{\gamma} = P_2 \, V_2^{\gamma}$$

or, $P_2 = P_1 \, (V_1 / V_2)^{\gamma}$

or, $P_2 = 1 \times (2)^{1.4}$

☐ $P_2 = 2.636$ atm

Again,

$$T_1 V_1{}^{\gamma-1} = T_2 V_2{}^{\gamma-1}$$

$$\text{or, } T_2 = T_1 \left(V_1 / V_2 \right)^{\gamma-1}$$

$$\Box \; T_2 = 300 \times (2)^{1.4-1} = 395.9 \text{ K} = 122.9 \text{ C}$$

Problem 2:

Find the efficiency of the Carnot's engine working between the steam point and the ice point.

Solution:

Here,

Initial Temperature (Steam point), $T_1 = 100C = (100 + 273) \text{ K} = 373 \text{ K}$

Final Temperature (Ice Point), $T_2 = 0C = (0+273) \text{ K} = 273K$

Efficiency, $\eta = ?$

We know that,

$$\eta = 1 - (T_2 / T_1)$$

$$= 1 - (273/373)$$

$$= 100 / 373$$

$$= (100 / 373) \times 100\%$$

$$= 26.81\%$$

Problem 3:

A Carnot's engine whose temperature of the source is 400K takes 200 calories of heat at this temperature and rejects 150 calories of heat to the sink. What is the temperature of sink? Also calculate the efficiency of the engine?

Solution:

Here,

Initial Heat, $Q_1 = 200$ cal

Final Heat, $Q_2 = 150$ cal

Initial Temperature, $T_1 = 400K$

Final Temperature, $T_2 = ?$

Efficiency, η = ?

We know that,

$$Q_1 / Q_2 = T_1 / T_2$$

$$\text{or, } T_2 = (Q_2 / Q_1) \times T_1$$

$$\text{or, } T_2 = (150\text{cal} / 200\text{cal}) \times 400 \text{ K}$$

$$\square\ T_2 = 300\text{K}$$

Again,

$$\eta = 1 - (T_2 / T_1)$$

$$= 1 - (300 \text{ K} / 400\text{K})$$

$$= 0.25$$

$$= 0.25 \times 100\%$$

$$= 25\%$$

Problem 4:

If a system absorbs 1100J heat and work is done 300J on the system, Find the internal energy of the system.

Solution:

Here,

Heat, Q = 1100J

Work done, W = 300J

I   nternal energy, U = ?

We know that,

$$U = Q - W$$

$\Delta U = 1100J - 300J = 800\ J$