Thermodynamics - II

Second Law of Thermodynamics:

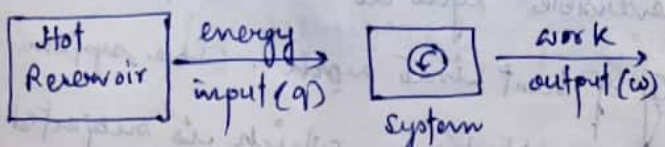
Spontaneous process: A change which occurs naturally of its own. Spontaneous processes are irreversible process. e.g. A gas expands to fill the available volume, a hot body cools at the room temperature, electricity flows spontaneously from a point of higher potential to a point of lower potential.

Non-spontaneous process: Those processes which don't occur spontaneously and must be brought about by doing some work are called non-spontaneous processes. e.g. confining a gas in a small volume.

Recognisation of spontaneous and non-spontaneous processes can be summarized by the following statements of 2nd Law of thermodynamics —

① **Kelvin Statement:** No process is possible in which the sole result is the ~~ads~~ absorption of heat from a hot reservoir and its complete conversion to work.

② **Kelvin-Planck Statement:**



It is possible for a system to undergo a cyclic process where sole effect are the flow of heat into the system from a hot reservoir and the performance of a equal

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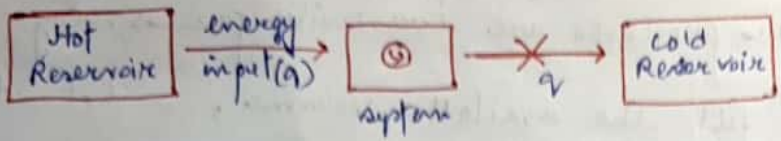
amount of work by the system on the surrounding.

③ Clausius statement:



It is impossible for a system to undergo cyclic process whose sole effects are the flow of heat from a hot reservoir into the system, or the flow of unequal amount of heat out of the system into a cold reservoir.

The Carnot Cycle:

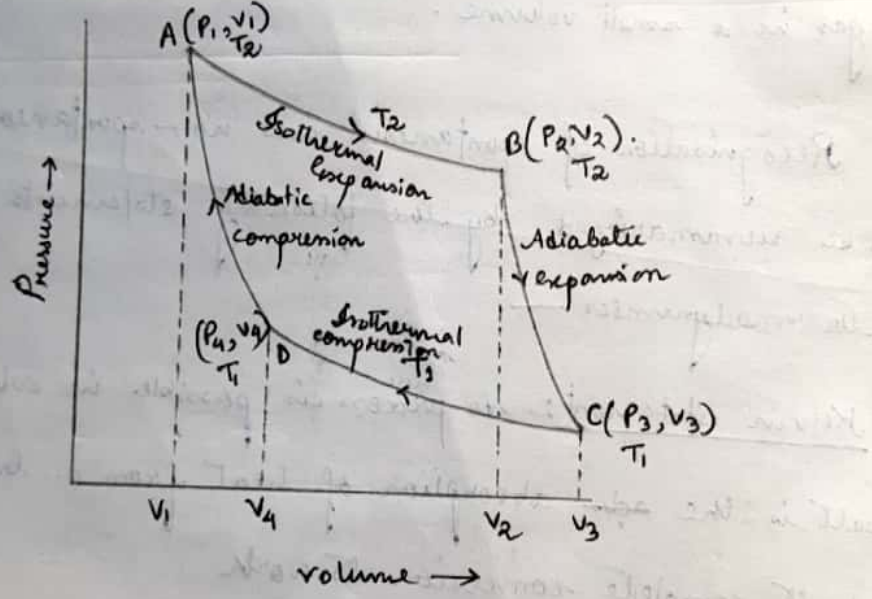


Fig: Carnot cycle

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work. The system consists of one mole of an ideal gas which is subjected to a series of four successive operations, commonly termed as four strokes as given below:—

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Stroke I: Isothermal Expansion:

The gas is allowed to expand reversibly and isothermally at temperature T_2 so that the volume increases from V_1(A) to V_2(B). Since in isothermal expansion of an ideal gas,

$$\Delta U = 0.$$

$$\therefore q = -w \quad [\text{From 1st law}].$$

i.e. The heat absorbed is equal to the work done by the system on the surrounding.

i.e.
$$\boxed{\begin{aligned} & q_2 = -w \\ \Rightarrow\ & q_2 = RT_2 \ln\left(\frac{V_2}{V_1}\right) \end{aligned}} \longrightarrow (1).$$

Stroke (II): Adiabatic Expansion:

The gas is then allowed to expand reversibly and adiabatically from the volume V_2 (B) to volume V_3 (C).

Since work is done by the system adiabatically, it is not in a position to absorb heat. The temp$^{\text{r}}$ of the system falls from T_2 to T_1.

Since, the process involves expansion of the gas, work is done by the system on the surrounding.

Again, $q = 0$

$$\Rightarrow \Delta U = -w.$$

By definition, $C_v = \left(\frac{\partial U}{\partial T}\right)_v$.

$$\Rightarrow \Delta U = C_v \cdot \Delta T.$$

$$\Rightarrow -w = C_v \cdot (T_1 - T_2).$$

$$\Rightarrow \boxed{w = C_v (T_2 - T_1).} \longrightarrow (11)$$

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Stroke III: Isothermal Compression:

After this, the gas is subjected to a reversible and isothermal compression at the lower temp T_1, so that the volume decreases from V_3 to V_4. Here work is done on the system and hence heat will be produced and given up to the surrounding.

$\because \Delta U = 0.$

$\Rightarrow w = -q.$

$\Rightarrow RT_1 \ln\left(\frac{V_4}{V_3}\right) = -q$

$\Rightarrow \boxed{q_1 = RT_1 \ln \frac{V_3}{V_4}} \longrightarrow (iii).$

Stroke IV: Adiabatic Compression:

Finally, by an adiabatic and reversible compression, the gas is restored to its original volume V_1 and temp^{re} T_2. Here, work is done by on the system, so w is positive.

$\therefore w = C_v(T_1 - T_2) \quad [\because q = 0]$

$\longrightarrow (iv).$

$\therefore$ Total work done during the process.

$|w| = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right) + C_v(T_2 - T_1) + C_v(T_1 - T_2).$

$\Rightarrow |w| = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln \frac{V_3}{V_4}. \longrightarrow (v).$

Again, for adiabatic process,

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

$\Rightarrow T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1} \longrightarrow (vi)$

And, $T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1} \longrightarrow (vii).$

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$(vi) \div (vii) \Rightarrow \frac{V_2}{V_3} = \frac{V_3}{V_4}$.

$\therefore$ Eqn (v) $\Rightarrow |W| = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_3 \ln\left(\frac{V_3}{V_4}\right)$.

$\Rightarrow |W| = R \ln\left(\frac{V_2}{V_1}\right)(T_2 - T_1)$. $\longrightarrow$ (viii).

Again, total heat absorbed. $\Rightarrow q = \cancel{nR} \cdot q_2 - q_1$.

$\Rightarrow q = RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_3}{V_4}\right)$.

$\Rightarrow q = R \ln\left(\frac{V_2}{V_1}\right)(T_2 - T_1)$. $\longrightarrow$ (ix).

$\therefore$ Eqn (viii) and (ix) implies that the net work done is equal to the net heat absorbed, the essential condition for a cyclic process is fully satisfied.

Again, Eqn (viii) $\div$ (i), we have,

$$\frac{W}{q_2} = \frac{R(T_2 - T_1)\ln\left(\frac{V_2}{V_1}\right)}{RT_2 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\Rightarrow \frac{W}{q_2} = \frac{T_2 - T_1}{T_2}.$$

$$\Rightarrow W = q_2 \frac{(T_2 - T_1)}{T_2}.$$

$\because \frac{T_2 - T_1}{T_2} < 1$.

$\therefore W < q_2$

i.e. work done is less than the heat absorbed. This means that only a part of the heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out by the system to the surroundings.

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Efficiency of a heat engine:

The fraction of the heat absorbed by an engine which it can convert into work gives the efficiency (η) of the system engine.

ie. $\eta = \frac{|w|}{q_2} = \frac{\text{Amount of heat converted into work}}{\text{Total heat absorbed}}$ ⟶ (1)

$\Rightarrow \eta = \frac{nR(T_2 - T_1)\ln\left(\frac{V_2}{V_1}\right)}{nRT_2\ln\left(\frac{V_2}{V_1}\right)}$

$\Rightarrow \eta = \frac{T_2 - T_1}{T_2}$

$\Rightarrow \boxed{\eta = 1 - \frac{T_1}{T_2}}$

Again, net heat,
$q = q_2 - q_1$
∴ From 1st law,
$w = q_2 - q_1$.
∴ Eq^n (1) $\Rightarrow \eta = \frac{q_2 - q_1}{q_2}$

$\Rightarrow \boxed{\eta = 1 - \frac{q_1}{q_2}}$

*

Concept of Entropy:

The 2nd law of thermodynamics uses a state function entropy (S) to identify the spontaneity of a process. The law can be expressed in terms of entropy as —

"The entropy of an isolated system increases in the course of a spontaneous change."

ie $\Delta S_{total} > 0$

where, ΔS_{total} is the total entropy of the system and the surrounding.

Thermodynamically irreversible process are spontaneous and hence must be accompanied by increasing entropy.

Since all natural proces are spontaneous, 2nd law of thermodynamics may also be stated as "The entropy of the nature is increasing".

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Thermodynamic definition of entropy:

In thermodynamics it is the entropy change that occurs during a chemical or physical change and is based on the expression,

$$ds = \frac{dq_{rev}}{T}$$

For a measurable change between two states, initial and final, this eqⁿ integrates to $\Delta S = \int \frac{dq_{rev}}{T}$, i.e. to calculate the difference of entropy between any two ~~system~~ state of the system, we find the reversible path between them. Unit of entropy is JK^{-1}. Molar entropy is expressed in $JK^{-1}mol^{-1}$.

Entropy change for the isothermal expansion of an ideal gas:

From 1st law, we have $dU = dq + dw$.

For isothermal process, $dU = 0$.

$\therefore dq = -dw$.

Now, the work done when 'n' moles of a gas expands reversibly and isothermally from volume V_1 to V_2 at constant T is,

$$w = -nRT\ln\left(\frac{V_2}{V_1}\right).$$

$$\Rightarrow q = nRT\ln\left(\frac{V_2}{V_1}\right).$$

By definition, $$ds = \frac{dq}{T} = \frac{dnRT\ln\left(\frac{V_2}{V_1}\right)}{T}$$

$$\Rightarrow \boxed{ds = nR\ln\left(\frac{V_2}{V_1}\right)}$$

$\because V \propto \frac{1}{P}$ at const T.

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore \boxed{ds = nR\ln\left(\frac{P_1}{P_2}\right)}$$

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Entropy is a state function:

Entropy is a state function which implies that the change of entropy in a process is the same irrespective of the manner in which the change is brought about.

Let us consider a Carnot cycle in which an ideal gas is subjected to a series of four operations as follows —

(a) Isothermal Expansion: The gas is allowed to expand reversibly and isothermally at temperature T_2. If the heat absorbed from the hot source is q_2, then the entropy change of the system would be $\frac{q_2}{T_2}$.

(b) Adiabatic Expansion: Since the gas expands adiabatically, $dq = 0$. Hence entropy is zero.

(c) Isothermal compression: The gas is subjected to isothermal compression at temp T_1 such that $T_1 < T_2$. Here, some heat could be given to the sink. If this heat is q_1, then the change of entropy of the system is $-\frac{q_1}{T_1}$.

(d) Adiabatic compression: Since the gas undergoes adiabatic compression, $dq = 0$, hence entropy is zero.

∴ The total change in entropy around the cycle is,

$$\Delta S = \oint dS = \frac{q_2}{T_2} - \frac{q_1}{T_1}.$$

$$\Rightarrow \oint dS = 0 \qquad \left[\because \frac{q_2}{T_2} = \frac{q_1}{T_1}\right]$$

i.e. When the material of the system reaches the original state, $\Delta S = 0$. Thus, entropy is a state function.

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* Thermodynamic Scale of Temperature:

We know, efficiency of a heat engine,

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \longrightarrow (1)$$

where, q_2 = amount of heat absorbed at the temp^r of source (T_2).

q_1 = amount of heat absorbed at the temp^r of sink (T_1).

Eq^n (1) $\Rightarrow$ $\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$

$\Rightarrow 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$.

$\Rightarrow \boxed{\frac{q_1}{q_2} = \frac{T_1}{T_2}}$.

$\Rightarrow \boxed{\frac{q_1}{T_1} = \frac{q_2}{T_2}}$.

If Temp^r of the sink, i.e. $T_1 = 0$., then efficiency of the heat engine,

$$\eta = 1 - \frac{T_1}{T_2} = 1.$$

i.e. as the efficiency of heat engine can't be greater than 1, i.e. 100%, thus temp^r can't be below zero. This Kelvin scale of temp^r is known as Thermodynamic scale of temp^r and zero of this scale matches with the absolute zero of gas scale. It depends upon the thermodynamic nature of the cycle that is reversible. If degree celsius and degree Kelvin have to be same, then.

$$0^\circ C = 273.16\ K.$$

which is the melting point of water at 1 atm pressure.

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Entropy change accompanying change of phase:

(a) From solid phase to liquid phase:

Let us consider a case when a solid changes into liquid state at its fusion point, the process requires absorption of heat called heat of fusion and it is a reversible process.

$$\text{Solid} \underset{}{\overset{T_f}{\rightleftharpoons}} \text{Liquid}.$$

ΔH_f is molar heat of fusion, and when this much heat is supplied, it is absorbed to increase the randomness of molecules from solid to ~~that of~~ liquid state.

$\therefore$ Entropy of fusion, $\Delta S_f = \frac{\Delta H_f}{T_f}$.

Where, T_f is the melting point.

(b) From liquid phase to vapour phase:

Let, one mole of a substance changes from liquid to vapour state reversibly at its boiling point T_b, under a constant pressure. If ΔH_v is the molar heat of vapourisation then the entropy of vapourisation is given by,

$$\Delta S_v = \frac{\Delta H_v}{T_b}.$$

Trouton's Rule:

It is an empirical observation that for a wide range of liquid, the standard enthalpy of vapourisation (ΔH_v) is approximately the same which is $88\ J K^{-1} mol^{-1}$. It is called Trouton's Rule.

i.e. $\frac{\Delta H_v}{T_b} \simeq 88\ J\ mol^{-1} K^{-1}$.

The quantity $\frac{\Delta H_v}{T_b}$ is called entropy of vaporisation, ΔS_v.

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Entropy change of an ideal gas with pressure, volume and temperature:

(a) When Temp^{e} and vol^{m} are variables:

For an infinitesimally small change,

$$dS = \frac{dq_{rev}}{T}$$

From 1st law,

$$dU = dq + dw.$$

$$\Rightarrow dq_{rev} = dU - dw.$$

For a system involving only expansion work,

$$dw = -pdV.$$

Again, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

$$\Rightarrow dU = C_V.dT.$$

$$\therefore dq_{rev} = C_V.dT + pdV.$$

ie. For 1 mole of a ideal gas,

$$dq_{rev} = C_V.dT + RT.\frac{dV}{V} \quad \left[\because pV = RT \Rightarrow p = \frac{RT}{V}\right].$$

$$\Rightarrow dq_{rev} = dS = C_V.\frac{dT}{T} + R.\frac{dV}{V}.$$

For a finite change of a state of a system, the entropy change ΔS may be obtained by integrating the above eq^{n} within the limits of initial state 1 and final state 2. Assuming C_V to be constant within the temperature range T_1 and T_2. for one mole of gas, we have,

$$\Delta S = S_2 - S_1.$$

$$\Rightarrow \Delta S = C_V \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}.$$

$$\Rightarrow \boxed{\Delta S = C_V.\ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)}$$

For n. moles, $\boxed{\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)}$.

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(b) When Temp^{r} and Pressure are variables:

If P_1 is the pressure of the ideal gas in the initial state and P_2 in the final state, then,

$$P_1V_1 = RT_1 \text{ and } P_2V_2 = RT_2$$

$$\therefore \frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}.$$

$$\because \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right).$$

$$\Rightarrow \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{P_1T_2}{P_2T_1}\right).$$

$$\Rightarrow \Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right).$$

$$\Rightarrow \Delta S = (C_V + R)\ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right).$$

$$\Rightarrow \boxed{\Delta S = C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)} \quad [\because C_P - C_V = R].$$

$$\Rightarrow \boxed{\Delta S = nC_P \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{P_2}{P_1}\right)} \text{ for } n \text{ moles of the gas.}$$

Entropy changes of an ideal gas in different processes:

(a) Isothermal process: Here, T is constant.

$$\therefore \Delta S_T = R\ln\left(\frac{V_2}{V_1}\right) = -R\ln\left(\frac{P_2}{P_1}\right) = R\ln\left(\frac{P_1}{P_2}\right).$$

If $V_2 > V_1$, ΔS_T will be positive.

i.e. Isothermal expansion is accompanied by increase in entropy while isothermal compression is accompanied by decrease in entropy.

(b) Isobaric Process: Here, pressure is constant.

$$\therefore \Delta S_P = C_P \ln\left(\frac{T_2}{T_1}\right).$$

ie At constant P, increase in T will increase the entropy.

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© Isochoric process: Here, V of the gas is constant.

$$\therefore \Delta S_V = C_V \ln\left(\frac{T_2}{T_1}\right).$$

i.e. At constant volume, increase in T, increases the entropy.

Molecular and Statistical Interpretation of Entropy:

The molecules in a system at high temp^r are highly disorganised either in terms of their location or in terms of occupation in their available translational, rotational and vibrational energy state. Therefore, a small additional transfer of energy will result in relatively small additional disorder. In contrast, the molecules in a system at low temperature have access to fewer energy states and the same quantity of heat will have a pronounced effect on the degree of disorderness. Hence, the change in energy when a given quantity of heat is transferred is more when it is transferred to a cold body than when it is transferred to a hot body, i.e. the change in entropy is inversely proportional to the temp^r in which transfer takes place.

Boltzmann gave a relationship between entropy (S) and the thermodynamic probability ω of the state of the system, as,

$$S = k \ln \omega + \text{constant}. \longrightarrow (1).$$

where k is Boltzmann constant. $k = \frac{R}{N_A}$.

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Boltzmann defined thermodynamic probability of a system as the ratio of the probability of the actual state to the probability of the state in which there is complete order for the same energy and volume.

Again, according to Planck, the constant in eqn ① is zero. $\therefore S = k \ln \omega$.

This eqn is called Boltzmann entropy eqn.

Clausius Inequality :

Let us consider a system in thermal and mechanical contact with the surrounding at the temp T. Any change of state is accompanied by a change in entropy of the system (dS_{sys}) and the surrounding (dS_{surr}). If an irreversible process occurs in the system, the total entropy will increase.

$$\therefore dS_{sys} + dS_{surr} \geq 0$$

$$\Rightarrow dS_{sys} \geq -dS_{surr}$$

Again, $dS_{surr} = -\frac{dq}{T}$, where dq is the heat supplied to the system during the process.

Also, $dq_{surr} = -dq$, because the heat supplied to the system comes from the surrounding.

$$\therefore \boxed{dS_{sys} \geq \frac{dq}{T}}$$. This expression is called Clausius Inequality.

When the system is isolated from the

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surrounding, then $dq = 0$ and Clausius inequality will be $dS_{sys} \geq 0$ i.e. In an isolated, the entropy can't decrease when spontaneous change takes place.

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