Variation of heat of reaction with temperature

(or)

** Kirchoff's eq^n :-

The dependence of heat of reaction with temperature was given by "kirchoff" by using an equation. That equation is known as Kirchoff's equation.

a) Heat of reaction at constant pressure :-

Let us consider the following reaction..

$$R \longrightarrow P$$

Heat of reaction is given by

$$\Delta H = H_P - H_R.$$

Diff the above eq^n w.r.to "T" at constant "P."

$$\frac{d[\Delta H]}{dT} = \left(\frac{dH_P}{dT}\right)_P - \left(\frac{dH_R}{dT}\right)_P$$

$$= [C_P]_P - [C_P]_R \qquad \left[\because C_P = \left(\frac{dH}{dT}\right)_P\right]$$

$$\frac{d(\Delta H)}{dT} = \Delta C_P$$

$$\Rightarrow d(\Delta H) = \Delta C_P \cdot dT$$

Integrating the above eq^n under limits ΔH_1 to ΔH_2 and T_1 to T_2.

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P \, dT$$

$$[\Delta H]_{\Delta H_1}^{\Delta H_2} = \Delta C_P [T]_{T_1}^{T_2}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_P [T_2 - T_1]$$

$$\therefore \boxed{\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta C_p}$$

- This equation is known as Kirchoff's equation at constant pressure.
- And it may defined as the change in the heat of reaction at const pressure for every degree change in the temperature is equal to the change in heat capacity at constant pressure.

b) Heat of reaction at constant volume:-

At constant volume

$$\Delta U = \Delta H$$

$$\left[\begin{array}{l} H = U + PV \\ \Delta H = \Delta U + \cancel{P\Delta V}^{0} \\ \Delta H = \Delta U \end{array} \right]$$

thus, the Kirchoff's eqn at constant volume expressed as.

$$\boxed{\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = \Delta C_V}$$

- It may be defined as the change in the heat of reaction at const volume for every degree change of temperature is equal to the change in heat capacity at constant volume.

** Second law of thermodynamics :-

Second law of thermodynamics states that "the heat flows from high temperature region to low temperature region spontaneously."

(or)

"The heat flow takes place from a system at low temperature to the other system at high temperature by applying some external work. This is called clausius statement !"
clausius

(or)

"It is not possible to construct a heat engine of 100% efficiency!"

(or)

To convert heat energy to work there must be some permanent changes in a system is required.

(or)

All the naturally occuring processes are thermodynamically irreversible.

(or)

"All the natural processes are spontaneous".

Spontaneous process :-

A process which occurs without any aid of external agency is known as a spontaneous process.

Ex:- * water flows down from hills spontaneously.

* Heat flows spontaneously from hot end to cold end.

* Electricity flows spontaneously from a point of high potential to a point of low potential.

* Carnot heat engine / carnot's cycle:-

Carnot proposed a hypothetical heat engine called "carnot engine". To show that the effeciency of heat engine which is based upon temperature between which it operates.

Carnot engine has the following features:

It consist of a cylinder containing 1 mole of an ideal gas. [working substance] fitted with a weight less, frictionless piston. So that all the operations in the cycle are carried out reversibly.

The cylinder is assumed to be insulated on all side except bottom. Thus the heat can flows from bottom side.

The engine has two heat reservoir one at high temperature T_2 [called source] and other at low temperature T_1 [called sink].

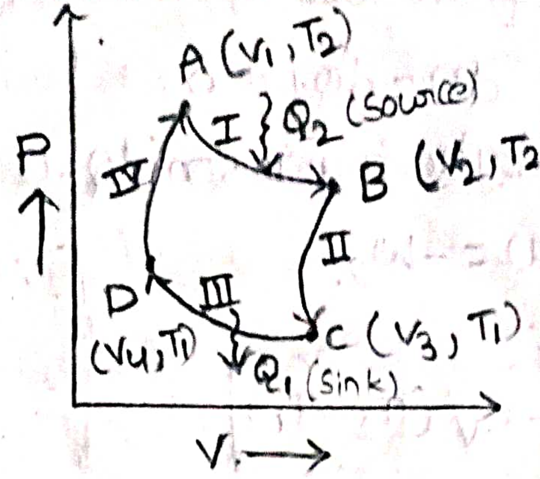
The complete carnot cycle consists of four operation (or) strokes.

1. Isothermal reversible expansion

~~2. Isothermal~~

2. Adiabatic reversible expansion
3. Isothermal revesible compression.
4. Adiabatic reversible compression.

The four strokes are carried out as shown in the figure and which is represented in the indicator diagram [pv-graph] as follows.



1. Isothermal reversible expansion:-

The cylinder contains one mole of ideal gas of the volume V_1.

It expands isothermally to the volume of V_2. During this it absorbs heat Q_2 from a source.

From first law of thermodynamics

$$du = dQ \pm dw.$$

for Isothermal expansion, $du = 0$

$$0 = Q_2 - W_1$$

[Here W_1 is the expansion work]

$$\boxed{Q_2 = W_1}$$

$$\boxed{Q_2 = RT_2 \ln \frac{V_2}{V_1}}$$

Adiabatic reversible expansion:-

In this cylinder is removed from source and connected to adiabatic wall and expands adiabatically.

During this expansion the volume of gas changes from V_2 to V_3. Then the temperature of the gas changes from $T_2 \rightarrow T_1$.

From first law of thermodynamics

$$dU = dQ + dW.$$

For adiabatic expansion, $dQ = 0$

$$dU = -W_2$$ [∵ Here $-W_2$ is the expansion work]

$$\boxed{W_2 = -C_V(T_2 - T_1)}$$ [∵ $dU = C_V dT = C_V(T_2 - T_1)$]

Isothermal reversible compression:-

In this step the cylinder is connected to sink at a temp T_1. and it is compressed isothermally.

During this compression, System losses Q_1 amount of heat to a sink at T_1 temperature and the volume changes from V_3 to V_4.

From first law of thermodynamics

$$dU = dQ + dW.$$

For Isothermal compression, $dU = 0$ and $dQ = -Q_1$

$$0 = -Q_1 + W_3$$

$$\therefore Q_1 = W_3$$

$$\boxed{Q_1 = RT_1 \ln \frac{V_4}{V_3}}$$

Adiabatic reversible compression:-

In this cylinder is removed from sink and connected to adiabatic wall and compressed adiabatically.

During this compression the volume of

gas changes from V_4 to V_1, then the temperature of the gas changes from $T_1 \rightarrow T_2$.

From first law of thermodynamics

$$du = dq + dw$$

For adiabatic compression, $dq = 0$

$$du = W_4$$ [∵ Here W_4 is compressed work

$$W_4 = C_v (T_2 - T_1).$$

Net workdone in cyclic process:-

The net workdone in the ~~pro~~ cyclic process is

$$W = W_1 + W_2 + W_3 + W_4$$

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

$$W = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$$

Since V_1 and V_4 are on the same adiabatic line.

Similarly V_3 and V_2 are also on same adiabatic line.

For adiabatic process the relation between T and V is

$$TV^{\gamma-1} = \text{constant}$$

$$\therefore \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \frac{T_2}{T_1}$$

and similarly $\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1}$

Hence $\left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$

$$\frac{V_4}{V_1} = \frac{V_3}{V_2}$$

$$\boxed{\frac{V_4}{V_3} = \frac{V_1}{V_2}}$$

∴ The net work is $W = RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_4}{V_3}\right)$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) + RT_1 \ln\left(\frac{V_1}{V_2}\right)$$

$$= RT_2 \ln\left(\frac{V_2}{V_1}\right) - RT_1 \ln\left(\frac{V_2}{V_1}\right)$$

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

Calculation of efficiency of heat engine:

The efficiency of the heat engine (η) is given by

$$\eta = \frac{\text{net workdone}}{\text{Heat absorbed}} = \frac{W}{Q}$$

$$\eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}$$

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

$$\boxed{\eta = \frac{T_2 - T_1}{T_2}}$$ (or)

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

The efficiency of the carnot engine depends on the temperature difference of source (T_2) and sink (T_1)

The efficiency of the heat engine is always less than unity i.e., less than 100%.

* Carnot's theorem :-

This theorem states that "the efficiency of the heat engine is independent on the nature of working substance used."

Concept of entropy :-

The efficiency of the heat engine is

$$\eta = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$1 - \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}.$$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$\boxed{\frac{Q_1}{T_1} = \frac{Q_2}{T_2}}$$

Hence $\frac{Q}{T}$ = constant

where Q_1, Q_2 are the heat evolved and heat absorbed by the system.

Thus, $\frac{-Q_1}{T_1} = \frac{+Q_2}{T_2}$.

$$\therefore \boxed{\frac{Q_2}{T_2} + \frac{Q_1}{T_1} = 0}$$

$$\boxed{\Sigma \frac{Q}{T} = 0}$$

This is for cyclic process.

This change in thermodynamic parameter $\frac{Q}{T}$ is named as entropy change by clausius.

Therefore, the entropy change $\boxed{\Delta S = \frac{q_{Rev}}{T}}$

For infinite changes $\boxed{dS = \frac{dQ_{rev}}{T}}$

The entropy change is defined as the ratio of amount of heat changed to the absolute temperature.

Significance :-

It is the measure of randomness or the disorderness of a system.

It is the measure of dispersion of energy of a system.

It is the extensive and state property.

* If ΔS = positive (+ve) then the process is spontaneous

* If ΔS = -ve then the process is non-spontaneous.

* Entropy change in a reversible process:-

Let us consider a process occurring in under completely reversible condition. i.e., heat absorbed by the system heat lossed by the surroundings reversibly.

If Q_{rev} heat is absorbed by the system reversibly then heat lossed by the surroundings reversibly will be Q_{rev}.

The entropy change in the surroundings is

$$\therefore \Delta S_{surr} = \frac{-Q_{rev}}{T}$$

The entropy change in the system is

$$\therefore \Delta S_{rev} = +\frac{Q_{rev}}{T}$$

∴ The total entropy change in reversible Process is

$$\Delta S_{Tot} = \Delta S_{sys} + \Delta S_{surr}$$

$$= +\frac{Q_{rev}}{T} - \frac{Q_{rev}}{T}$$

$$\boxed{\Delta S = 0}$$

Thus in a reversible process the net entropy change for the combined system and surroundings is zero.

(or)

In a thermodynamically reversible process the entropy of the system and surroundings remains constant.

Entropy change in irreversible process :-

[Spontaneous process]:-

Let us consider an irreversible process in which the heat exchanged by the system and surroundings irreversibly.

If the system is at high temperature T_2 and the surroundings is at low temperature T_1 then heat lossed by system to surroundings spontaneously.

∴ The change in entropy of system is

$$\Delta S_{sys} = \frac{-Q}{T_2}$$

The change in entropy of surroundings is

$$\Delta S_{surr} = \frac{+Q}{T_1}$$

∴ Total change of entropy in Irreversible process is given by

$$\Delta S_{Tot} = \Delta S_{sys} + \Delta S_{surr}$$

~~Here~~ ~~Q~~

$$= \frac{-Q}{T_2} + \frac{Q}{T_1}$$

$$= Q\left[\frac{-1}{T_2} + \frac{1}{T_1}\right]$$

$$\boxed{\Delta S_{Tot} = Q\left[\frac{T_2 - T_1}{T_1 T_2}\right]} \Rightarrow$$

Here $T_2 > T_1$

∴ $T_2 - T_1 > 0$

∴ $\boxed{\Delta S > 0}$ (or) $\Delta S = +ve$

$\boxed{\Delta S \geq 0}$

Thus in irreversible process the entropy of system and surrounding increases.