

Thermodynamics-II

Spontaneous process —

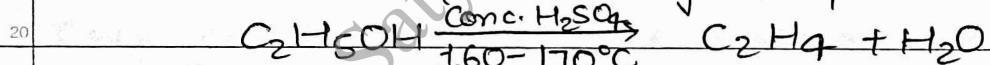
The process which proceed by their own accord without any external assistance are called spontaneous process. They are also known as positive or natural process.

10 As — ① Candle burning

Non-spontaneous process —

The process which cannot proceed by themselves are called non-spontaneous process. Such process cannot proceed without any external assistance. They are also called negative or un-natural process.

As — ① Dehydration of ethyl alcohol.



② Pumping water out of the well.

Criteria of spontaneity —

i - 25 A spontaneous reaction may be takes place rapidly or slowly or very slowly that is for a spontaneous change to occur time is no factor.

ii - 30 A spontaneous change is one way or unidirectional for reverse change to take place some work has to be done.

Second law of thermodynamics

The second law of thermodynamics has been stated in various ways. All the statements have the same meaning.

- I - All the spontaneous process occurs in one direction only and can not be reversed.
- II - The energy of universe remain constant and entropy of universe increasing.
- III - Clausius statement - It's impossible for a self acting machine unaided by an external agency to carry heat from a body at lower temperature to another at higher temperature.
- IV - Kelvin - Plank statement - It is impossible to construct a heat engine which operating in a cyclic process abstract heat from a single body and convert the whole of it into work without living in changes into working system.

Carnot's cycle

In order of demo of heat reversible cycle the system consist of node of an ideal gas as the working system which is subjected to sequence of four operation b/w temperature T_2 and T_1 both adiabatic & isothermal process are possible during the operation.

The four operation in carnot cycle are—

Isothermal reversible expansion.

Adiabatic " expansion

Isothermal " compression

Adiabatic " compression

Isothermal reversible expansion—

A gas is allow the expand isothermal at higher temperature at gas as volume increase of v_1 (state A) to v_2 (state B) so work done by the system in this operation.

From first law of thermodynamics—

$$\Delta E = Q - W$$

$0 = Q - W \quad \because \Delta E = 0$ is Isothermal process

$$W = \int_{V_1}^{V_2} P_2 dV$$

$$w_2 = \int_{v_1}^{v_2} (RT_2/v) dv \text{ we know that}$$

$$PV = RT$$

$$(P_2 = \frac{RT_2}{V})$$

$$w_1 = RT_2 \int_{v_1}^{v_2} dv/v$$

$$w_1 = RT_2 [\log v]_{v_1}^{v_2}$$

$$w_1 = RT_2 \log e \frac{v_2}{v_1}$$

Adiabatic reversible expansion—

The gas is allow as to expand adiabatically from volume v_2 (state B) to v_3 (state C) the work done w_2 by the system in this operation.

From first law thermodynamics

$$\Delta E = Q - w_2$$

$$\Delta E = -w_2 \quad (\text{since } Q \geq 0)$$

$$cvdT = -w_2$$

$$cvdT = -w_2$$

$$w_2 = - \int_{T_1}^{T_2} cvdT$$

$$w_2 = cv \int_{T_1}^{T_2} cvdT$$

$$w_2 = cv [T_2 - T_1]$$

$$w_2 = cv [T_2 - T_1]$$

Isothermal reversible compression -

The gas is compressed isothermally at lower temperature, T_1 from v_3 (state c) to before c (state d) the work done w_3 on the system in this operation

$$w_3 = q_1 RT_1 \log \frac{v_4}{v_3} \quad \text{or}$$

$$-Q = RT_1 \log \frac{v_4}{v_3}$$

Adiabatic reversible compression -

By an adiabatic and reversible compression the gas is restored to its original volume of temperature the work done w_4 on the system.

$$w_4 = -cv(T_2 - T_1)$$

$$w_4 = cv(T_1 - T_2)$$

Net work done in cauot cycle -

$$W = w_1 + w_2 + w_3 + w_4$$

$$W = RT_2 \log \frac{v_2}{v_1} + cv(T_2 - T_1) + RT_1 \log \frac{v_4}{v_3} + cv(T_1 - T_2)$$

$$w_2 = RT_2 \log \frac{v_2}{v_1} + T_2 / cr - T_1 / cr + RT_1 \log \frac{v_4}{v_3} + T_1 / cr - T_2 / cr$$

$$w_2 = RT_2 \log \frac{v_2}{v_1} + RT_1 \log \frac{v_4}{v_3}$$

$$W = RT_2 \log \frac{v_2}{v_1} + T_1 \log \frac{v_4}{v_3}$$

Heat absorbed in one cycle -

Let 'q' is the heat absorbed in one cycle then

$$q = q_2 - q_1$$

$$q_2 = RT_2 \log \frac{V_2}{V_1} + RT_1 \log \frac{V_4}{V_3}$$

$$q = RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_3}{V_4} \quad \textcircled{1}$$

for adiabatic changes we have

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3} \right)^{r-1} \quad \textcircled{II} \quad \left\{ \text{for adiabatic expansion} \right.$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_4} \right)^{r-1} \quad \textcircled{III} \quad \left\{ \text{for adiabatic compression} \right.$$

Comparing equation \textcircled{II} & \textcircled{III} we get

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

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

Putting the value of $\frac{V_3}{V_4}$ in equation first we get -

$$q = RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_2}{V_1}$$

$$q = R \log \frac{V_2}{V_1} (T_2 - T_1)$$

$$q = R(T_2 - T_1) \log \frac{V_2}{V_1}$$

IV

Calculate of thermodynamic efficiency -

Since the total work done in a cycle is equal to the total heat absorbed. Thus from equation IV we have

$$w = R(T_2 - T_1) \log \frac{V_2}{V_1} \quad \textcircled{IV}$$

We know that

$$q_2 = RT_2 \log \frac{V_2}{V_1} \quad \textcircled{VI}$$

Dividing equation \textcircled{IV} by \textcircled{VI} we have

$$\frac{w}{q_2} = R(T_2 - T_1) \log \frac{V_2}{V_1}$$

$$RT_2 \log \frac{V_2}{V_1}$$

$$\frac{w}{q_2} = \frac{(T_2 - T_1)}{T_2}$$

$$\frac{w}{q_2} = \left(1 - \frac{T_1}{T_2} \right)$$

$$w = q_2 \left(1 - \frac{T_1}{T_2} \right)$$

The factor w/q_2 is called thermodynamic efficiency.

Efficiency of Carnot's Engine -

The fraction of heat absorbed engine which it can convert into work is called

efficiency of Carnot engine." It is denoted by η . Thus the efficiency of a Carnot engine may be written as follows —

$$\eta = \frac{q_2 - q_1}{q_2}$$

$$\eta = \frac{RT_2 \log \frac{V_2}{V_1} - RT_1 \log \frac{V_3}{V_4}}{RT_2 \log \frac{V_2}{V_1}}$$

$$\eta = \frac{T_2 \log \frac{V_2}{V_1} - T_1 \log \frac{V_3}{V_4}}{T_2 \log \frac{V_2}{V_1}}$$

for adiabatic change —

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_3} \right)^{\gamma-1} \quad \text{--- (ii)}$$

$$\text{thus } \frac{T_1}{T_2} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad \text{--- (iii)}$$

Comparing eqn (ii) and (iii) we get

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

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

Putting the value of $\frac{V_3}{V_4}$ in eqn (i)

$$\eta = T_2 \log \frac{V_2}{V_1} - T_1 \log \frac{V_2}{V_1}$$

$$\frac{T_2 \log V_2}{V_1}$$

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

Ex- Calculate the efficiency of steam engine operating b/w 110°C and 25°C ?

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 110 + 273 = 383 \text{ K}$$

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

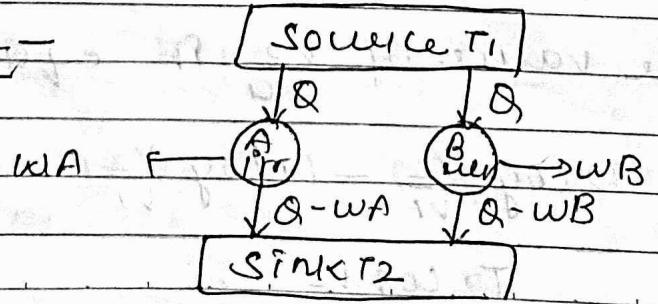
$$\eta = \frac{383 - 298}{383} = 0.222$$

$$\eta = \frac{0.222}{1} = 0.222 \text{ or } 22.2\%$$

Carnot's theorem —

No heat engine working b/w to given temperature of source, sink can be more efficient than a perfectly reversible engine working b/w the same two temperatures.

Statement —



Entropy -

The extent of disorder is expressed by a property known as entropy.

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Entropy is a thermodynamic state quantity which is a measure of disorder of the molecules of the system.

Note -

The entropy is a state function and depend only on the initial and final state of the system.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

for chemical reaction -

$$\Delta S = S_{\text{product}} - S_{\text{Reactants}}$$

Mathematical definition of Entropy -

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged divided by the absolute temperature is also known as entropy.

$$\Delta S = \frac{1}{T} \int \delta Q / T$$

$$\boxed{\Delta S = \frac{Q}{T}}$$

or

$$\boxed{\Delta S = \frac{Q}{T}}$$

several factors influence the amount of entropy that a system has in particular state. In general —

- (1) The value of entropy depends on the mass of the system. Hence it's an extensive property.
- (2) A liquid has a higher entropy than the solid from which it is formed.
- (3) In a solid the atoms/molecules/ions are fixed in position in the liquid these particle are free to move past one another that liquid structure is more random and the solid more ordered.

Unit of entropy—

We know that

$$\Delta S = \frac{q}{T}$$

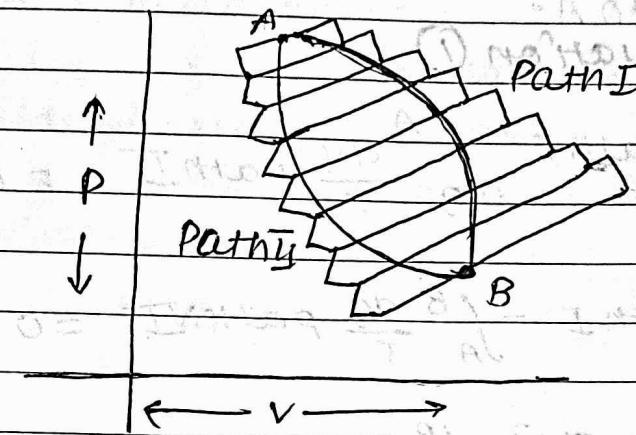
$$\Delta S = \frac{J}{K}$$

$$\boxed{\Delta S = JK^{-1}}$$

Derivation of Entropy from Carnot cycle—

In a Carnot cycle q_2 heat is taken by a hot system at higher temperature and hence has a positive value while q_1 heat is given out at lower temperature at has a negative value.

Thus thermodynamics efficiency is given by -



$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

$$\frac{q_1}{q_2} = \frac{-T_1}{T_2}$$

$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

Since heat absorbed that is q_2 is given positive sign and heat given out has negative (-) sign. Thus the above equation can be written as

$$-\frac{q_1 + q_2}{q_2} = \frac{T_1}{T_2}$$

$$\frac{q_1 + q_2}{q_2} = \frac{T_1}{T_2} \quad \text{--- (1)}$$

The cycle is followed performing A to B and then back B to A.
from equation ①

$$\int_A^B \frac{dq}{T} \text{ path I} - \int_B^A \frac{dq}{T} \text{ path II} = 0$$

$$\int_A^B \frac{dq}{T} \text{ path I} - \int_A^B \frac{dq}{T} \text{ path II} = 0$$

$$\int_A^B \frac{dq}{T} \text{ path I} = \int_A^B \frac{dq}{T} \text{ path II} \Rightarrow$$

It follows from the above that integration A to B $\frac{dq}{T}$ is a finite quantity

$$\Delta S = S_B - S_A \int_A^B \frac{dq}{T}$$

for each infinite similarly small change -

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

for finite change -

$$\boxed{\Delta S = \frac{q}{T}}$$

The entropy is defined as the change in entropy is equal to moment of heat absorbed or evolved divided by absolute temperature.

Physical significance of entropy -

Entropy and unavaiable energy →

When heat is supplied to a system a portion of it is used to do work.

This portion of heat is called
useful energy.

When reversible process is Isothermal -

Let's consider an isothermal reversible process in which the system absorbs heat q_{rev} from surroundings at temperature T . This increases the entropy of the system which is given by -

$$\Delta S_{\text{system}} = + \frac{q_{rev}}{T}$$

$$\Delta S_{\text{surrounding}} = - \frac{q_{rev}}{T}$$

Total change in entropy of the process =

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$= \left(+ \frac{q_{rev}}{T} \right) + \left(- \frac{q_{rev}}{T} \right)$$

$$= \frac{q_{rev}}{T} + \frac{q_{rev}}{T}$$

$$= 0$$

When reversible process is adiabatic -

In this process no exchange of the heat takes place with the surrounding that is $q_{rev} = 0$
hence -

$$\Delta S_{\text{system}} = \frac{q_{rev}}{T} = \frac{0}{T} = 0$$

$$\Delta S_{\text{surrounding}} = \frac{q_{rev}}{T} = \frac{0}{T} = 0$$

Total change in entropy of the process
 $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$

$$0 + 0$$

$$= 0$$

Entropy change in an irreversible or spontaneous process

Let's consider a system at higher temperature T_1 and the surroundings at lower temperature T_2 . A small quantity of heat q_{irr} passes irreversibly from system to surroundings.

Decrease in entropy of system - $- \frac{q_{\text{irr}}}{T_1}$

Increase in entropy of surrounding - $+ \frac{q_{\text{irr}}}{T_2}$

Total change in entropy of the process -

$$- \frac{q_{\text{irr}}}{T_1} + \frac{q_{\text{irr}}}{T_2}$$

$$\textcircled{1} \quad \text{Sign of } q_{\text{irr}} \text{ is negative} \Rightarrow q_{\text{irr}} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

but $T_1 > T_2$ hence $T_1 - T_2$ is a positive quantity

Entropy change for ideal gas with change P, V and T -

a- When T and V are variables

Entropy is state function and it's value depends upon volume, pressure and temperature since temperature is take a one of the variable and second variable may be pressure and volume. Thus variables are either volume and temperature or pressure and temperature.

From definition of Entropy,

$$dS = \frac{dQ}{T} \quad \textcircled{1}$$

From first law of thermodynamics -

$$dQ = dE + PdV \quad \textcircled{11}$$

We know that

$$PV = RT$$

$$P = \frac{RT}{V}$$

$$\text{Again } - dE = C_V dT$$

Putting the value of P & dE in eqn. $\textcircled{11}$

$$dS = \frac{dE + PdV}{T}$$

$$dS = C_V dT + \frac{RT dV}{V}$$

$$ds = \frac{cv}{T} dT + \frac{R}{v} dv$$

Integrating above eqn with limits S_1 to S_2 , T_1 to T_2 and v_1 to v_2 .

$$\int_{S_1}^{S_2} ds = cv \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{v_1}^{v_2} \frac{dv}{v}$$

$$[S]_{S_1}^{S_2} = cv [\log T]_{T_1}^{T_2} + R [\log v]_{v_1}^{v_2}$$

$$S_2 - S_1 = cv [\log T_2 - \log T_1] + R [\log v_2 - \log v_1]$$

$$\Delta S = cv \log \frac{T_2}{T_1} + R \log \frac{v_2}{v_1}$$

$$\boxed{\Delta S = 2.303 cv \log_{10} \frac{T_2}{T_1} + 2.303 R \log_{10} \frac{v_2}{v_1}}$$

For n moles of gas

$$\Delta S = 2.303 ncv \log_{10} \frac{T_2}{T_1} + 2.303 nR \log \frac{v_2}{v_1}$$

when T and P are variables —

Suppose P_1 is the pressure of an ideal gas in the initial state and P_2 in the final state then —

We know that

$$\Delta S = ncv \log_e \frac{T_2}{T_1} + nR \log_e \frac{v_2}{v_1} \quad \text{--- (1)}$$

from gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \frac{v_2}{v_1} = \frac{P_1 T_2}{T_1 P_2}$$

Putting the value of $\frac{V_2}{V_1}$ in equation ①
we get

$$\Delta S = nC_V \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1 T_2}{T_1 P_2}$$

$$\Delta S = nC_V \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2} + nR \log_e \frac{T_2}{T_1}$$

$$\Delta S = n(C_V + R) \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2}$$

$$\Delta S = nC_P \log_e \frac{T_2}{T_1} + nR \log_e \frac{P_1}{P_2} \quad \{ \text{from } C_P = C_V + R \}$$

$$\Delta S = 2.303 nC_P \log_{10} \frac{T_2}{T_1} + 2.303 nR \log_{10} \frac{P_1}{P_2} \quad ①$$

for 1 mole of the ideal gas $n=1$ hence

$$\Delta S = 2.303 C_P \log_{10} \frac{T_2}{T_1} + 2.303 R \log_{10} \frac{P_1}{P_2}$$

From equ ① and ② evident that entropy change in an ideal gas depends upon the initial and final temperatures as well as on pressure.

Calculate entropy change when one mole an ideal gas are allow to expand reversibly at 25°C . from a pressure of 1 atm to 500 mm of mercury at 0°C . $C_P = \frac{3}{2}R$

Given that -

$$n = 1 \text{ mole}$$

$$T_1 = 25 + 273 \\ = 298$$

$$T_2 = 0 + 273$$

$$P_1 = 1 \text{ atm} \quad 760 \text{ mm}$$

$$P_2 = 500 \text{ mm}$$

$$R = 0.314$$

$$CP = CV + R$$

$$\frac{3}{2}R + R$$

$$2.5R$$

$$2.5 \times 0.314 \text{ Joule/degree mole}$$

$$\Delta S = 2.303 n CP \log \frac{T_2}{T_1} + 2.303 n R \log \frac{P_1}{P_2}$$

$$\Delta S = 2.303 \times 1 \times 2.5 \times 0.314 \log \frac{273}{298} + 2.303 \times 1 \times 0.314 \log \frac{760}{500}$$

$$\Delta S = 2.303 \times 0.314 [2.5 \times (\log_{10} 273 - \log_{10} 298) + (\log_{10} 38 - \log_{10} 25)]$$

$$\Delta S = 1.67 \text{ J/degree mole}$$

Entropy change of an ideal gas in different process —

We consider the following three types of process —

(A) Isothermal process —

$$\Delta S_T = 2.303 n R \log_{10} \frac{V_2}{V_1}$$

$$\boxed{\Delta S_T = 2.303 n R \log_{10} \frac{P_1}{P_2}}$$

II- Isobaric process -

$$\Delta S_p = 2.303 ncp \log_{10} \frac{T_2}{T_1}$$

III- Isochoric process -

$$\Delta S_V = 2.303 ncv \log_{10} \frac{T_2}{T_1}$$

X Entropy of a mixture of ideal gases X

Entropy change in physical change -

Physical
change taking place at constant temperature
and pressure are as follows -

Solid \rightarrow Liquid (melting)

Liquid \rightarrow Vapour (vapourisation)

Solid \rightarrow Vapour (sublimation)

Solid (A) \rightarrow Solid (B) (transition)

① From solid to vapour phase -

$$1) \quad \Delta S_f = \frac{\Delta H_f}{T_f}$$

where,

T_f = Temperature of fusion

ΔH_f = Enthalpy change in fusion

ΔS_f = Entropy " " " "

calculate the entropy change in the melting of 1 gm of ice at 0°C in calories as well as in S.I. units. Heat of fusion of ice is equal to 80 calory/gm.

$$\Delta H_f = 80$$

$$T_f = 0 + 273$$

$$\therefore \Delta S_f = \frac{\Delta H_f}{T_f} = \frac{80}{273} \text{ cal/kmole}$$

$$\Delta S_f = \frac{80}{273} = 0.29 \text{ cal/kmole}$$

$$\Delta S_f = \frac{80}{273} = 0.29 \text{ cal/kmole}$$

$$= 0.29 \text{ cal/kmole}$$

$$\Delta H_f = 80 \text{ cal/gm}$$

$$M_f = 80 \times 4.2 \times 1000$$

$$\Delta H_f = 336000 \text{ J/kg}^{-1}$$

$$\Delta S_f = \frac{\Delta H_f}{T_f} = \frac{336000}{273} \text{ J/kg}^{-1} \text{ K}^{-1}$$

$$\Delta S_f = \frac{336000}{273} = 1226.7 \text{ J/K}$$

$$\Delta S_f = \boxed{1226.7 \text{ J/K}}$$

From liquid phase to vapour phase -

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

III

From one crystalline form to another -

$$\Delta S_f = \frac{\Delta H_f}{T}$$

standard entropy - (S°) -

Entropy of 1 mole of a pure substance at 1 atm pressure and 25°C temperature is called the standard entropy. It is denoted by ' S° '.

standard entropy change -

In a chemical reaction, in which all the reactants and products are in their standard state, the entropy change is called the standard entropy change of the reaction - It is represented by ' ΔS° '. The standard entropy change of the any reaction is given by -



$$\Delta S^\circ = S^\circ_{\text{product}} - S^\circ_{\text{reactant}}$$

standard entropy of formation - (ΔS_f°) -

The entropy change when 1 mole of a compound is formed from its elements under standard condition is called the standard entropy of formation. It is denoted by ' ΔS_f° '.

$$\Delta S_f^\circ = S^\circ_{\text{compound}} - \sum S^\circ_{\text{element}}$$

Helmholtz free energy or work Function(A)

The quantity ($E - TS$) is called helmholtz free energy or work function. It is represented by A :

$$[A = E - TS]$$

where,

A = work function

T = absolute temperature

S = Entropy

E = Internal energy

(a) change of work junction for an Isothermal process

Consider an Isothermal change at temperature T from initial state (I) to final state (II) so that

$$\text{For Initial state (I)} \quad A_1 = E_1 - TS_1$$

$$\text{For Final state (II)} \quad A_2 = E_2 - TS_2$$

$$A_2 - A_1 = (E_2 - TS_2) - (E_1 - TS_1)$$

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$

$$[\Delta A = \Delta E - T\Delta S] \quad \textcircled{1}$$

where,

ΔA = change in work function

ΔE = change in internal energy

ΔS = change in entropy.

$$\text{since } \Delta S = \frac{\Delta Q}{T}$$

$$\Delta Q = T \Delta S$$

Putting the value $T \Delta S$ in equation (i) we get

$$\Delta A = \Delta E - Q \quad \text{(ii)}$$

From 1st law of thermodynamics

$$Q = \Delta E + W \quad \text{(iii)}$$

From equ (i) & (iii) we get

$$\boxed{-\Delta A = W}$$

(b) variation of work function with temperature and volume -

We know that

$A = E - TS$
differentiating above equation with respect to T

$$\frac{dA}{dT} = \frac{dE}{dT} - \left[T \frac{ds}{dT} + S \frac{d(T)}{dT} \right]$$

$$\frac{dA}{dT} = \frac{dE}{dT} - \left[T \frac{ds}{dT} + S \right]$$

$$\Delta A = \Delta E - T \Delta S - S \Delta T \quad \text{(i)}$$

$$\text{Since } \Delta S = \frac{\Delta Q}{T}$$

$$\Delta Q = T \Delta S \quad \text{(ii)}$$

$$\Delta Q = \Delta E + P \Delta V \quad \text{(iii)}$$

Comparing (ii) and (iii) we get

$$Tds = dE + PdV$$

putting the value of Tds in equ ①

$$\partial A = dE - (dE + PdV) - SdT$$

$$\partial A = dE - dE + PdV - SdT$$

$$\boxed{\partial A = -PdV - SdT}$$

$$\boxed{\partial A = -(PdV + SdT)}$$

IV

Variation

equation no IV represent the variation of work function with change in volume and temperature.

Case I - At constant volume

$$dV = 0$$

From equation IV

$$\partial A = -(PdV + SdT)$$

$$\partial A = -SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

Case II - At constant Temperature -

$$dT = 0$$

From equation IV

$$\partial A = -(PdV + SdT)$$

$$\partial A = -(PdV + S \times 0)$$

$$\partial A = -PdV$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -P}$$

case III - At constant temperature and constant volume

$$dT = 0, dV = 0$$

from equation (iv)

$$dA = -(PdV + SdT)$$

$$dA = -(P\Delta V + S\Delta T)$$

$$dA = 0$$

$$(dA)_{T, V=0}$$

Note - (i) From case Ist we get

$$dA = -SdT \quad (i)$$

From case IInd

$$dA = -PdV \quad (ii)$$

Comparing equation (i) and (ii) we get

$$dA = -PdV \quad (iii)$$

From ideal gas equation

$$PV = nRT \quad (IV)$$

$$P = \frac{nRT}{V}$$

Putting the value of P in equation (iii) we get

$$dA = -nRT \frac{dV}{V}$$

on integrating we get

$$\int_{A_1}^{A_2} dA = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$[A_2 - A_1] = nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$[A_2 - A_1] = nRT \left[\ln V \right]_{V_1}^{V_2}$$

$$\Delta A = NRT \ln \frac{V_1}{V_2}$$

$$\Delta A = 2.303 NRT \log_{10} \frac{V_1}{V_2}$$

Gibb's Free energy Function -

The quantity $H - TS$ or $E + PV - TS$ is called ^{Gibb's} free energy function. It is represented by 'G'.

$$G = H - TS$$

$$\{ \because H = E + PV \}$$

$$G = E + PV - TS$$

where, H = Enthalpy

T = absolute temperature

S = Entropy

Change in Free energy Function -

let's consider isothermal process at constant temperature. The initial state represented by step-I, and final state is represented by step-II.

hence

$$\text{for initial state, } G_1 = H_1 - TS_1 \quad \text{--- (1)}$$

$$\text{for final state, } G_2 = H_2 - TS_2 \quad \text{--- (2)}$$

from (2) - (1) we get

$$G_2 - G_1 = (H_2 - TS_2) - (H_1 - TS_1)$$

$$\Delta G = (H_2 - H_1) - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S$$

(3)

since

$$\Delta H = \Delta E + P\Delta V$$

$$\therefore \Delta S = \frac{Q}{T}$$

$$Q = T\Delta S$$

from 1st law of thermodynamics

$$Q = \Delta E + W$$

From equation (ii)

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = \Delta E + P\Delta V - T\Delta S \quad \left\{ \because \Delta H = \Delta E + P\Delta V \right\}$$

$$\Delta G = \Delta E + P\Delta V - (\Delta E + W) \quad \left\{ T\Delta S = \Delta E + W \right\}$$

$$\Delta G = P\Delta V - W$$

$$\Delta G = P\Delta V - W$$

$$-\Delta G = W - P\Delta V$$

Variation of free energy function with temp and pressure

according to variation of free energy function,

$$G = H - TS$$

$$G = E + PV - TS \quad \left\{ H = E + PV \right\}$$

Differentiating above equation w.r.t, T -

$$dG = dE + PdV + VdP - TdS - SdT \quad (1)$$

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

$$(12 - T)dT = (14 - 14) \quad \text{--- (2)}$$

$$dQ = dST \quad (11)$$

$$dQ = dE + PdV - \textcircled{III}$$

Comparing equation \textcircled{II} and \textcircled{III} we get

$$dS\tau = dE + PdV - \textcircled{IV}$$

putting the value of $dS\tau$ in eqn \textcircled{I}

$$dG = dE + PdV + VdP - TdS - SdT$$

$$dG = dE + PdV + VdP - (dE + PdV) - SdT$$

$$dG = VdP + VdP - dE - PdV - SdT$$

$$\boxed{dG = VdP - SdT} \quad \textcircled{V}$$

equation \textcircled{V} represents variation of free energy function (G) with temperature and pressure.
The following three cases are shown—

Case I — At constant pressure

$$dP = 0$$

from equation \textcircled{V}

$$dG = VdP - SdT$$

$$dG = 0 - SdT$$

$$dG = - SdT$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S}$$

Case II — At constant temperature

$$dT = 0$$

from equation \textcircled{V}

$$dG = VdP - SdT$$

$$dG = VdP - 0$$

$$dG = VdP$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_T = S}$$

Case III - At constant temperature and pressure

$$dT = 0 \Rightarrow dP = 0$$

$$\Delta G = v dP - s dT$$

$$\Delta G = 0$$

$$\boxed{\frac{\partial G}{\partial P}_{T,P} = 0}$$

Note - From case I -

$$\Delta G = -s dT \quad \textcircled{1}$$

From case II

$$\Delta G = -v dV \quad \textcircled{2}$$

Comparing eqn \textcircled{1} and \textcircled{2}

$$\Delta G = v dP$$

$$\Delta G = v dP$$

$$\int_{G_1}^{G_2} dG = v \int_{P_1}^{P_2} dP \quad \textcircled{3}$$

From 1 mole of an ideal gas

$$PV = RT$$

$$V = \frac{RT}{P}$$

Putting the value of V in eqn \textcircled{3}

$$\int_{G_1}^{G_2} dG = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$[G_2]_{G_1}^{G_2} = RT \left[\ln P_2 - \ln P_1 \right]$$

$$G_2 - G_1 = RT \left[\ln P_2 - \ln P_1 \right]$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

$$\boxed{\Delta G = 2.303 RT \log_{10} \frac{P_2}{P_1}}$$

Date _____

To calculate mole of an ideal gas

$$\Delta G = 2.303 nRT \log_{10} \frac{P_2}{P_1}$$

Since T constant

$$P_1 V_1 = P_2 V_2$$

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

$$\Delta G = 2.303 nRT \log_{10} \frac{V_1}{V_2}$$

Imp

Gibb's-Helmholtz Equations —

There are two equations which were derived by Gibb's and Helmholtz. These equations are known as Gibb's-Helmholtz equation.

One equation can be expressed in terms of change of free energy (ΔG) and enthalpy (ΔH) while the other can be expressed in terms of change of work function (ΔA) and internal energy (ΔE).

In terms of change of free energy and enthalpy

We know that

$$G = H - TS$$

$$G = E + PV - TS \quad \{ \because H = E + PV \}$$

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Differentiating above equation w.r.t T we get

$$\Delta G = \Delta E + P\Delta V + V\Delta P - S\Delta T - T\Delta S$$

$$\Delta G = dq + V\Delta P - S\Delta T - T\Delta S \quad \{ \text{from first law of thermodynamics} \}$$

$$\Delta G = dq + V\Delta P - S\Delta T - (dq) \quad \{ \because T\Delta S = dq \}$$

$$\Delta G = V\Delta P - S\Delta T$$

At constant pressure

$$dP = 0$$

$$\Delta G = -S\Delta T$$

For initial state - I

$$\Delta G_1 = -S_1\Delta T \quad \textcircled{I}$$

For final state

$$\Delta G_2 = -S_2\Delta T \quad \textcircled{II}$$

Change

$$\Delta G_2 - \Delta G_1 = (-S_2\Delta T) - (-S_1\Delta T)$$

$$d\Delta G = -(S_2 - S_1)\Delta T$$

$$d(\Delta G) = -S\Delta T$$

$$\left(\frac{\partial(\Delta G)}{\partial T} \right)_P = -S \quad \textcircled{III}$$

We know that

$$\Delta G = \Delta H - T\Delta S \quad \textcircled{IV}$$

Putting the value of ΔS in equation \textcircled{IV} we get -

$$\boxed{\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_P}$$

This equation is called Gibbs-Helmholtz equation in terms of free energy and enthalpy change at constant pressure.

⑥ In terms of change of work function and internal energy -

we know that -

$$A = E - TS \quad \text{--- (1)}$$

for initial state - I -

$$A_1 = E_1 - TS_1 \quad \text{--- (II)}$$

for final state - II -

$$A_2 = E_2 - TS_2 \quad \text{--- (III)}$$

for change -

$$\Delta A = (E_2 - TS_2) - (E_1 - TS_1)$$

$$\Delta A = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E = T\Delta S \quad \text{--- (IV)}$$

From eqn (1)

$$A = E - TS$$

Differentiating equation (1) wrt, T -

$$dA = dE - TdS - SdT \quad \text{--- (V)}$$

from first law of F.D -

$$dq = dE + PdV$$

thus second law of F.D

$$dq = TdS$$

$$TdS = dE + PdV$$

Putting the value of TdS in equation (V)

$$dA = dE + (TdS - SdT) \quad \text{--- (VI)}$$

$$dA = -PdV - SdT$$

At constant volume

$$dV = 0$$

$$dA = -SdT$$

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_V = -S}$$

for initial state I

$$\left[\frac{\partial A_1}{\partial T} \right]_V = -S_1 \quad \text{--- (VI)}$$

for final state II -

$$\left[\frac{\partial A_2}{\partial T} \right]_V = -S_2 \quad \text{--- (VII)}$$

for change

$$\left[\frac{\partial A_2}{\partial T} \right]_V - \left[\frac{\partial A_1}{\partial T} \right]_V = (S_2 - S_1) = \Delta S$$

$$\left[\frac{\partial (\Delta A)}{\partial T} \right]_V = -\Delta S \quad \text{--- (VIII)}$$

We know that

$$\frac{\Delta A - \Delta E}{T} = -\Delta S \quad \text{--- (IX)}$$

$$\frac{\Delta A - \Delta E}{T} = \left[\frac{\partial (\Delta A)}{\partial T} \right]_V$$

$$\boxed{\Delta A = \Delta E + T \left[\frac{\partial (\Delta A)}{\partial T} \right]_V}$$

Menzel's Heat theorem -

Menzel's heat equation theorem is used to find out the condition which lead chemical reaction to completion.

According to Gibbs-Helmholz equation -

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T} \right]_P$$

If $\left[\frac{\partial(\Delta G)}{\partial T} \right]_P$ is a finite quantity, then at absolute zero, $T = 0 \text{ Kelvin}$

$$\Delta G = \Delta H$$

In other words

$$\lim_{T \rightarrow 0} \Delta G = \lim_{T \rightarrow 0} \Delta H$$

$$\left[\lim_{T \rightarrow 0} \Delta G - \lim_{T \rightarrow 0} \Delta H \right] = 0$$

This equation shows that ΔG and ΔH are equal. Increases with lowering of temperature and becomes zero at 0 Kelvin. This statement is known as Neel's Heat theorem.

Mathematically this theorem expressed at -

$$\left[\lim_{T \rightarrow 0} \left[\frac{\partial(\Delta G)}{\partial T} \right]_P = \lim_{T \rightarrow 0} \left[\frac{\partial(\Delta H)}{\partial T} \right]_P = 0 \right]$$

Consequences of Neel's Heat theorem -

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