"THERMODYNAMICS"

Thermodynamics :-

Thermo :- Related to temp. or energy.

Dynamics :- Study of change due to driving forces.

\# Thermodynamics :→ It is the branch of chemistry / Physical Chemistry / Science which deals with energy changes associated with physical & chemical processes.

Or

Thermodynamics deals with energy interaction b/w two bodies and its effect on the properties of matter.

Formulation of Thermodynamics based on → 3 fundamental laws which have been established on the basis of human experience of the experimental behaviour of macroscopic aggregates of matter collected over long period of time.

Qu What is Thermochemistry?

An It is the branch of Physical chemistry which deals with the thermal or heat changes caused by Chemical reactions.

Qu Why Thermodynamics is important?

An Study of Thermodynamics tells chemists whether a particular rxn is energetically possible in the direction in which it is written and it

Gives the Composition of the rxn system at equilibrium.

Note:-> There is no any Experimental proof of any ~~three~~ law of Thermodynamics.

Application of Thermodynamics:->

- Power Generation (Thermal/Nuclear Power plant)
- Automobiles (Petrol/Diesel/LPG/CNG engines)
- Processing Industries (Steam generation, Refrigeration system)
- Gas compressors (Air compressor)

Application of Thermodynamics in Chemistry:->

- We can predict feasibity of the rxn that is two substance are mixed then the rxn between them will takes place or not.
- Help to predict the Energy changes involved during the rxn.
- Equilibrium Concentration of Different reactants & products can be calculated with thermodynamics.

Limitations of Thermodynamics:->

1. laws of thermodynamics are applicable to matter in bulk or on system as a whole, these cannot be applied on individual particles (temp, pressure ~~etc~~)

2) We cannot calculate the time taken for completion of a reaction or for attainment of chemical equilibrium.

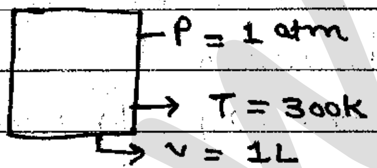
3) No theoretical proof of any law.

Basic Terminology :-

System :-> Part of the universe under investigatio

Or

Part of the universe which is under study for energy changes.

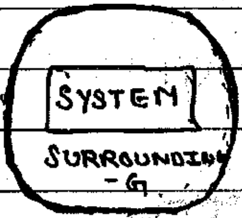


P = Pressure
T = Temp.
V = Volume.

Ex: Air in a room, water in a bottle, any living body.

Surrounding :-> Part of the universe other than system which can interact with it's known as surrounding.

Universe :- Universe = System + Surrounding



Boundary :-> Anything which seperate system & surrounding is called boundary.

It may be real or Imaginary.

- Boundary can be Fixed (Rigid) / flexible

Eg. air in balloon (flexible boundary) while air in room (fixed boundary).

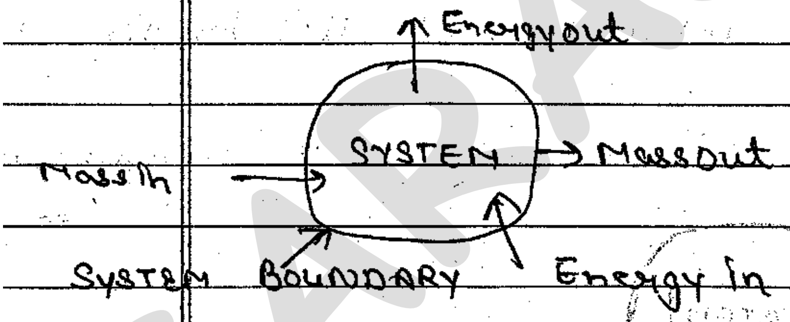
Types of System

- Open System
- Closed System
- Isolated System

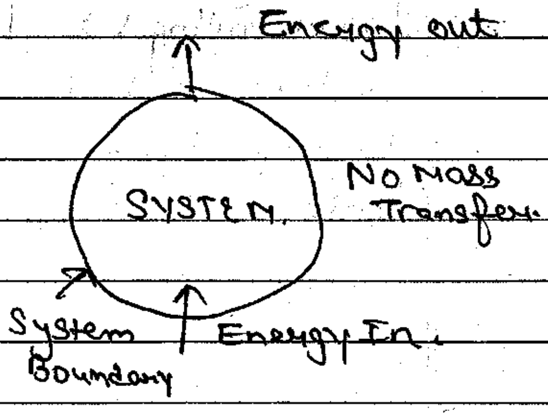
Open System :→ A system which can exchange both energy and matter with its surrounding.

Closed System → A system which permits passage of energy but not mass across its boundary. eg A certain quantity of fluid in a cylinder bounded by a piston constitutes a closed system. 2) Thermal power plant.

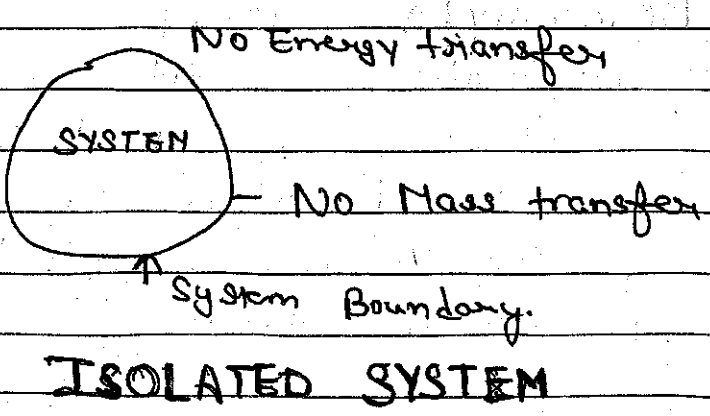
Isolated System :→ A system which can neither exchange energy nor matter with its surrounding.



OPEN SYSTEM

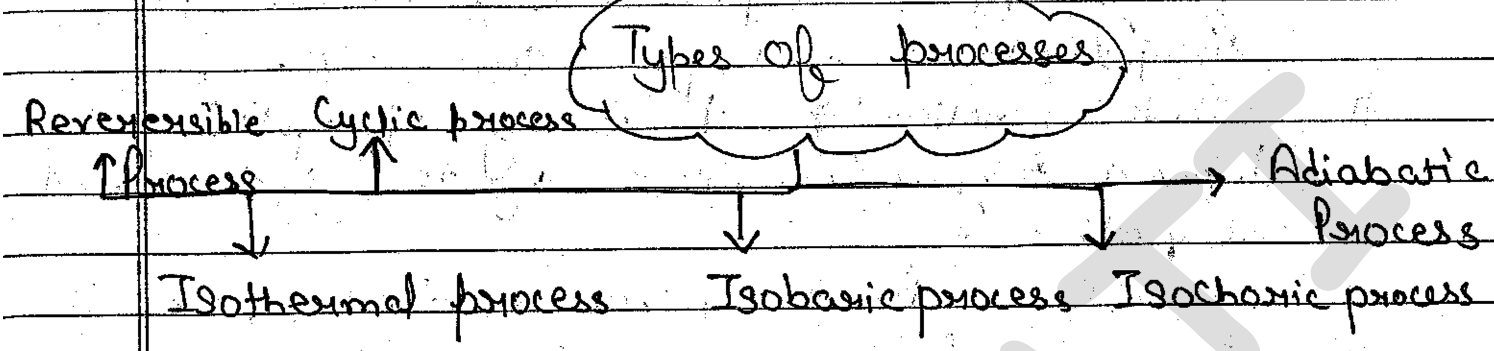


CLOSED SYSTEM



ISOLATED SYSTEM

Process → Path along which state of system changes.



- Isothermal process → Process which takes place at constant temperature.
- Isobaric process → Process which takes place at constant pressure.
- Isochoric process → Process which takes place at constant volume.
- Adiabatic process → Process during which transfer of heat cannot takes place between system and surrounding.

Or

The system which is thermally insulated from its surrounding is called adiabatic system. it can power exchange work with the surrounding if does not it become an isolated system.

Extensive properties → Properties of a system which ~~do not~~ depend on mass of the system ie volume, energy, enthalpy, entropy ~~gd~~ mass etc.

Intensive properties → The properties of system which do not depend on mass of the system. ie Temp. pressure, density, Concentration,

\# State variable :→ The variable which are required to be defined in order to define state of any system i.e pressure, volume, mass temperature, surface area etc.

\# State function :→ Property of system which depend only on the state of the system and not path.

Example pressure, volume, temp., Internal Energy, Entropy etc.

\# Path function :→ Property of system which depend upon path of system only.

Example :→ Heat and work.

Ex #

Extensive Properties (Depend upon quantity of matter present and are additive)	Intensive properties. Do not depend upon quantity of matter present and are not additive.
Volume	Molar Volume
No. of Moles	Density
Mass	Refractive Index
Free Energy (G)	Viscosity
Entropy (H) | (S)	Free Energy per Mole.
Internal Energy (E) | (U)	Pressure
(C_p, C_v) Heat capacity.	Temp., (B.P, Freezing Point)

Cyclic process :→ Process in which system comes back to its initial state after undergoing series changes.

Reversible Process → Process during which the system always departs infinitesimally from the state equilibrium i.e.

its direction can be reversed at any moment.

State of a System :-

- It means the condition in which the system is present.
- It can be specified / defined by measuring / specifying some observable / measurable properties of the system like pressure, volume, temp, amount of sys substance, elasticity, heat capacity.

Difference B/wn State function and Path function :-

State function	Path function.
• It is a thermodynamic property whose value donot depend on the path taken to reach that specific value.	• It is a thermodynamic property whose value depend on the path taken to reach that specific value.
• It is also known as point functions	• It is also known as Process functions
• It donot depend up path or process.	• It depend upon path or process.
• It remains same regardless of the no. of steps.	• The value of path function of a single step process is different from a multiple step process.
Eg Volume, Enthalpy, Temperature, Entropy	Eg :- Heat and Mechanical Energy

Entropy (S) → It is the measure of degree of randomness or disorderness in an isolated System.

Change in Entropy $\Delta S = S_2 - S_1$
$= \Sigma S_{Products} - \Sigma S_{reactants}$.

Que Suppose there is one container having no. of atom of given type why it has greater entropy assign a reason?

Ans It self (Self - practice)

I.E

Imp: For ideal Gas at Isothermal conditions ($\Delta U/E$) $= 0$

(U) Internal Energy → Total Energy possessed by all atom, molecules, Ions in the System is known as Internal Energy of the System.

Condition for Internal Energy change.

→ **M**atter enter or leaves the System.

→ **H**eat - Passes through into or out of the System.

→ Work is done on or by System.

☆ If Energy is released by System $\Delta U = -ve$

☆ If Energy is absorbed by System $\Delta U = +ve$

For Isothermal process $\Delta U = 0$

U Change when

* Work is done on or by System.

Work :→

$W = F \times dx$

W = work
F = force
dx - distance

Work done

By System
- (-ve)
- System Loose Energy

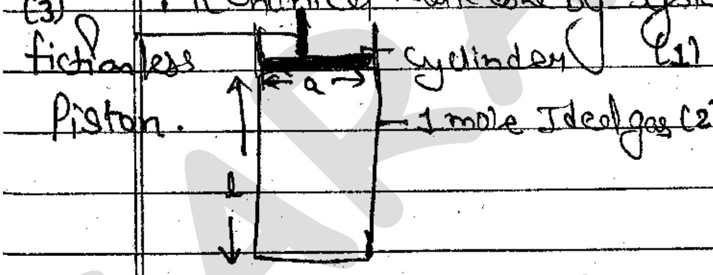
On System
- (+ve)
- System Gain Energy.

Types of Work Done

(Mechanical work done also known as PV work)

(Electrical work done)

Mechanical work done by System



Total Volume = V_t (4)

Total Pressure P (5)

P_{ex} = external pressure (6)

$P_{ex} > P$ (7)

Result Piston move inward (8) till $P = P_{ex}$

$P = P_{ex}$ Achieved by Two ways

a) Irreversible process
(Single Step process)

b) Reversible process.

EMF ∝ Quantity of Electricity

[EMF - Electromotive force]

Electric work done perform-ed with the help of immersion rod and by this we can easily find the change in Temperature

$\Delta T = T_B - T_A$.

	Reversible process :-	Irreversible process.
1	The process is carried out infinitesimally slowly.	1.) The process is carried out not infinitesimally slow It occurs rapidly.
2.)	At any stage during the process, equilibrium is not disturbed.	2.) Equilibrium may exist only after the completetion of the process.
3.)	It takes infinite time for completion.	3) It takes finite time for completion.
4.)	Work obtained in this process is maximum.	4.) Work obtained in this process is not maximum.

Heat ⇒ It is mode of energy transfer between system and surrounding. It is Represented by (q)

* Heat flowing into the system or absorb by System = +q.

* Heat flowing out of the System or Heat released by System = -q.

Internal Energy → It is total energy contained by a thermodynamic system.

It could be stored in the form P.E + M.E + K.E E.E, R.E etc.

$\Delta U = q + w$ [(Law of Conservation of Energy)]

⇓ First law of Thermodynamics

⇓

Energy of Isolated System is Constant.

P.E – Potential Energy
M.E – Mechanical Energy
K.E – Kinetic Energy.
E.E – Electrical Energy
R.E – Rotational Energy

Some Important points

* For Open System $\Delta m \neq 0$, $\Delta E \neq 0$
* For Closed System - $\Delta m = 0$ $\Delta E = 0$
* For Isolated $\Delta m = 0$, $\Delta E = 0$

m = matter
E = Energy

\# If x is any extensive property of n moles of system, the molar property of the system x_m is intensive

\# No heat is absorbed by system → boundary of system is having Adiabatic Wall.

\# When amount of heat is taken out from the system walls of system is thermally conducting.

\# $\frac{\text{Extensive property}}{\text{Extensity property}} = \text{Intensive property}$.

\# Absolute value of Internal Energy cannot be determined.)

\# Intensive property is not additive in nature.

\# Extensive properties are additive in nature.

\# For Cyclic process - Like $A(P_1 V_1 T_1) \rightarrow B(P_2, V_2, T_2) \rightarrow C(P_3 V_3 T_3) \rightarrow A(P_1 V_1 T_1)$.

$$dE \text{ or } dU = 0 \text{ and } dH = 0$$

Reversible process:- It is ideal process here every intermediate state is in equilibrium with others.

Net work done $W_{irr} < W_{rev}$.

$q_p = \Delta H$

$\Delta U = q_v$

Ques. For Practice.

1. What kind of System is the coffee held in a cup?

Ans. Coffee held in a cup is Open System because it can exchange matter (water vapour) and energy (heat) with the Surrounding.

Que2. Give an example of an Isolated System?

Coffee held in thermos flask is an example of isolated System because it can neither exchange energy or matter with the Surrounding.

Que3. Name the different types of System?

Ans. Open System
Closed System
Isolated System,

Que4. State the first law of thermodynamics?

Ans. The first law of thermodynamics states that energy can neither be created nor be destroyed but can be transformed from one form to another.

Que5. Why the entropy of Diamonds is less than that of graphite?

Ans Diamond is more compact than graphite.

Que6. What is the limitation of the First law of Thermodynamics?

Ans It cannot tell us about the direction of process. 2.) fail to Explain how much Heat is transfered from one System to another.

Que7. Write a mathematical relationship between Heat, Internal Energy and work done on the System.

Ans $\Delta E = q + w$

ΔE - Change in Energy, q - Heat w = work.

Que8. Which of the following is a State function?

a) Height of a hill.

b) Distance travelled in climbing the hill.

c) Energy consumed in climbing the hill.

Ans Energy consumed in climbing the hill.

Que9. Name the two common modes by which a system and surrounding exchange their energy?

Ans. Heat and Work.

Que10. What will happen to Internal Energy if work is done by the System?

Ans Internal Energy of the System will decrease.

Que11 Name the State function which remains constant during isothermal change.

Ans Temperature.

Que12 When a Substance is said to be in its Standard State?

Ans When it is present at 298K and under one atmospheric pressure.

Que13 What is the entropy of the formation of an element in its Standard State?

Ans By Convention, the enthalpies (heat) of the

Que Predict the change in the internal energy for an isolated system at constant volume?

Ans There is no energy transfer as heat or work in an isolated system

$q \times w = 0 + q = 0.$

Acc. to first law of thermodynamics

$U = q + w = 0 + 0 = 0$

$\Delta U = 0.$

Que Although heat is a path function but heat absorbed by the system under certain conditions is independent of path. What are those conditions?

Ans

AT Constant Volume :-

By first law of thermodynamics

$q = \Delta U + (-w)$

$(-w) = P\Delta V$

$\Delta V = 0$ Since volume is constant

$\therefore q_v = \Delta U + 0 \Rightarrow q_V = \Delta U$ Change in I.E

(ii) At Constant pressure.

$q_p = \Delta U + P\Delta V$

But $\Delta U = P\Delta V = \Delta H$

formation of all the elements in their most stable form (Standard State) is taken as zero.

Que When is the entropy of a perfectly crystalline solid zero?

Ans At absolute zero (0° K)

Que Define Spontaneity or feasibility of a process?

Ans Spontaneity or feasibility of a process means its inherent tendency to occur on its own in a particular direction under a given set of conditions.

Que Ice is lighter than water, but the entropy of ice is less than that of water. Explain.

Ans Water is the liquid form while Ice is its solid form. Molecular motion in ice is restricted than in water ie disorder in ice is restricted than water.

Que What is the most important condition for a process to be reversible in thermodynamics?

Ans The process should be carried out infinitesimally slowly or the driving force should be infinitesimally greater than the opposing force.

Que What is Entropy? What happen when reactant is more disordered as compared to products in the chemical rxn?

Ans It is the measure of degree of randomness or disorderness in an isolated system. It is represented by symbol S.

Randomness (↑) Inc., Higher is Entropy (↑).

functionals It shows the rearrangement of atoms or ions from one pattern in the reactant to another (in the products).

* If the str. of reactant is more disordered as compared to products it results in decreased entropy.

Que What is the order of randomness or Entropy in solid, liquid and gases?

Ans Gas > Liquid > Solid

⇓ Randomness of atom is more.

⇓ Randomness of atom is quite less.

Que Write down the order of Entropy for inert gases?

NOTE → With increase in the molecular mass of atom or molecule belonging to different elements entropy of inert gases also increases.

$S_{He} < S_{Ne} < S_{Ar} < S_{Kr} < S_{Xe} < S_{Ra}$.

\# ||ar for Halogen

$S_{F_2} < S_{Cl_2} < S_{Br} < S_{I_2}$.

\# Vapourisation and fusion

Entropy Increase

Crystallisation Results dec. in Entropy.] Page 21

Que What happen with the Entropy when Egg gets boiled?

Ans Egg gets solidity on Heating | Boiling so Entropy of egg gets decrease.

Que Express the change in internal energy of a system when:

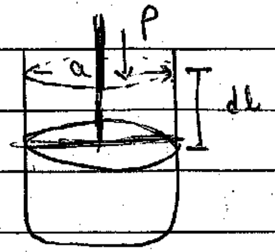
(i) W amount of work is done by the system and q amount of heat is supplied to the system. What type of system would it be?

Ans $\Delta U = q - w$ Closed System.

Applications of Work.

1. Work of Expansion or P-V (Pressure volume work).

It is the work done when the gas expands or contract against the external pressure. It's a kind of mechanical work.



Expansion of Gas.

Consider a gas in cylinder fitted with frictionless piston

a = area of cross-section

P – Pressure on the Piston.

dl – distance through which gas expand.

Pressure = force per unit area.

Force acting on piston $F = P \times a$

∴ work done by gas

$$F \times dl \Rightarrow P \times a \times dl$$

But $a \times dl = dV$

Small increase in the volume of the gas.

Hence small amount of work done by the gas.

$dw = P \times dV$

Initial volume of gas which is allowed to expand V_1

& final volume V_2.

Total workdone

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

(i) If gas expand against constant external pressure (irreversible expansion).

$$W = P \int_{V_1}^{V_2} dV \Rightarrow P(V_2 - V_1) = \boxed{P \Delta V}$$

$$\Delta V = (V_2 - V_1)$$

* If $(P)_{ext}$ is external pressure more than pressure of gas, the gas will contract.

$$\boxed{W = P_{ext} \times \Delta V}$$ for contraction

Acc. to S-I =

for Expansion ← $\boxed{W = -P\Delta V}$ For Expansion

$W = -ve$ if work done by the system.

Note :→ If Ideal gas expend against vaccum, the Irreversible expansion is called free expansion.

$P_{ext} = 0$

$$w = -P_{ext}\Delta V = 0 \times \Delta V = 0$$

$\boxed{w = 0}$ for free Expansion.

(ii) Work done in Isothermal Reversible expansion of an Ideal Gas.

The Small amount of work done δw, when the gas expands through a small volume dV against the external pressure P.

$$\delta w = -PdV$$

∴ Total work done (when gas expand) V_1 to V_2

$$w = -\int_{V_1}^{V_2} PdV$$

for Ideal gas $PV = nRT$

P = Pressure
V = Volume
n = no. of moles
R = Universal gas constant
T = Temp.

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

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

for Isothermal expansion ; T = Constant

$$w = -nRT \int \frac{1}{V} dV \Rightarrow -nRT \ln \frac{V_2}{V_1}$$

or

#. Units of Work.

1 atm Litre = 101.3 Joule

1 Bar Litre = 100 Joule

1×10^7 erg = 1 Joule.

1 Calories – 4.18 Joule.

for Free expansion :-

$P_{ex} = 0$ so $W = 0$.

Or

$$W = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303\, nRT \log \frac{P_1}{P_2}$$

At constant Temp $P_1V_1 = P_2V_2$

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

Que 5.2 mol of Ideal gas at 3 atm and 25°C Expands isothermally to 3 times of its Original volume against the external pressure of 1 atm. calculate the work done.

(ii) If the Same gas expands isothermally in a reversible manner, then what will be the value of work done?

A $W = -P_{ex}(V_2 - V_1)$

Now initial volume $V_1 = \frac{nRT}{P}$

$= 5.2 \times 0.082 = 42.35\ L,$

final volume $V_2 = 42.35^3 \times 3 = 127.05.$

Now $W = -1\,(127.05 - 42.35)$

$= 84.7$

$= -84.7 \times 101.325 = 8582.22\ J.$

(ii) for Isothermal reversible expansion of Ideal gas.

$$W_{rev} = -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303 \times 5.2 \times 8.314 \times 298 \log \left(\frac{127.05}{42.35} \right)$$

$= 14156.38\ J.$

Que Calculate the work done when 2 moles of an ideal gas expands reversibly and isothermally from a volume of 500ml to a volume of 2L at 25°C and normal pressure.

$n = 2$ moles
$V_i = 500ml = 0.5$ lit.
$V_f = 2$ lit.
$T = 25°C = 298K$.
$w = -2.303 nRT \log (V_f - V_i)$

$W = -2.303 \times 2 \times 8.314 \times 298 \times \log(2/0.5)$
$W = -2.303 \times 2 \times 8.314 \times 298 \times \log 4$.

$W = -6871 J$
$w = -6.871 KJ$.

Enthalpy :→ (H) → Heat at constant pressure is known as enthalpy change $q_p = dH$.

* Heat at constant pressure is known as enthalpy change = $q_p = dH$.

* State function.
* Absolute value (H) = not countable.
* Change of Enthalpy (dH) = countable.

* $H = f(T)$ for ideal gas, Enthalpy of system only depend up on temp. for ideal gas.

Imp. $\boxed{H = \text{Internal Energy} + \text{Product of } P \cdot V \text{ work}}$

$$\boxed{H = \Delta U + p\Delta V} \quad -①$$

units of H = Kcal | KJ mol

H = Enthalpy
ΔU = Change Internal Energy
p - pressure
ΔV - Change in volume.

Suppose a System absorb heat, q_p at constant pressure and Its volume changes from V_1 to V_2.

The work done by the System.

$$W = -P(V_2 - V_1) = -P\Delta V$$

Apply First law of thermodynamics

$$\Delta U = q_p - P(V_2 - V_1) \quad (U_2 - U_1) = q_p - P(V_2 - V_1)$$

or $(U_2 + PV_2) - (U_1 + PV_1) = q_p$ -(2)

We know

$U + pV = H$ (Enthalpy of System)

$(U_2 + PV_2) = H_2$ and $U_1 + PV_1) = H_1$

Put these value in eq (2).

$$H_2 - H_1 = q_p$$

or

$$\boxed{\Delta H = q_p}$$

$$\boxed{\Delta U = P\Delta V = \Delta H}$$

Difference between Enthalpy change and Internal energy Change :-

Enthalpy Change	Internal Energy Change
↓	↓
Heat Supplied at Constant pressure.	Heat Supplied at Constant volume.

ΔH

+ve	−ve
(For Endothermic Rxns)	(for exothermic Rxns)
↓	
absorb Heat from Surrounding.)	(: Evolve Heat during Rxns]

\# At Constant volume ($\Delta V = 0$)

$$\Delta H = \Delta U = q_v$$

$$H = U + PV$$

$$\boxed{dH = dU + d(PV)}$$

Change in Enthalpy

P = Constant

$$\boxed{dH = dU + PdV}$$

P = variable
V constant.

$$\boxed{dH = dU + P_f V_f - P_i V_i}$$

ΔH - At constant P.

$[dH]^r$

- No Chemical Rxn
  No Phase Change
  only temp. change
  $\boxed{dH = dU + nRdT}$
- Chemical rxn occur
  Phase Change
  $\boxed{dH = dU + \Delta n_g RT}$
- Solid or Liquid
  $\boxed{\Delta H = dU}$

$V_f - V_i$ where Δn_g total mole of gaseous products - total mole of gaseous reactant. ⇐ Reason

- $\Delta n_g = 0$ ⇓ $dH = dU$
- $\Delta n_g = +ve$ ⇓ $dH > dU$
- $\Delta n_g = -ve$ ⇓ $dH < dU$

Eg $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$

$$\boxed{dH - dU = \Delta n_g RT}$$

⇓ Heat at Constant pressure

↓ Heat at Constant Volume.

Eg $RCOOR + H_2O \rightarrow RCOOH + ROH$.

Relationship between ΔH and ΔU

Suppose a chemical rxn is going on :-

$\boxed{A}$ Reactant $\longrightarrow$ products, $\boxed{B}$

If P and T are constant

- V_A is Total volume of gaseous Reactants
- V_B = Total volume of the gaseous products
- n_A → Total no. of moles of reactant
- n_B = Total no. of moles of products.

From ideal gas Equation:- $[PV = nRT)$

For reactants - $PV_A = n_ART$

For Products - $PV_B = n_BRT$

$$PV_B - PV_A = n_BRT - n_ART$$
$$P(V_B - V_A) = (n_B - n_A)RT$$

$$P\Delta V = \Delta n_gRT \quad - ①$$

Δn_g = Total no. of moles of gaseous products minus the total no. of moles of gaseous reactant

$$\Delta n_g = n_p - n_R$$

Put the value $P\Delta V$ from eq ① in expression of Enthalpy change

$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = \Delta U + \Delta n_gRT$$

Cases

$\Delta n_g = 0$ then	$\Delta n_g < 0$	$\Delta n_g > 0$
$\Delta H = \Delta U$	$\Delta H < \Delta U$	$\Delta H > \Delta U$

Numericals related to Internal Energy, Work done, Enthalpy change and Heat.

1. Calculate the internal energy change in each of the following cases.

a) A system absorb 15KJ of Heat and does 5KJ of work.

Soln: Here $q = +15kJ$

Acc. to first law of thermodynamics

$$\Delta U = q + w$$

$$= 15 + (-5) = 10kJ$$

Thus internal energy of the System increas by = 10kJ.

(b) 5KJ of work is done on the System and 15 KJ of heat is given out by the System.

Soln: Here $w = +5kJ$

$q = -5KJ$

∴ Acc. to first law of thermodynamics

$$\Delta U = q + w = -15 + (+5) = -10kJ$$

Thus internal Energy of the System deco by 10KJ.

Note! → For isothermal irreversible process work done is $P\Delta V$ and for isothermal reversible process $-2.303\, nRT \log \frac{V_2}{V_1}$

Que Calculate the amount of workdone in each of the following cases.

(i) One mole of an ideal gas contained in the bulb of 10L capacity at 1 atm is allowed to enter into an evacuated bulb of 100 Litre capacity?

Soln $\Rightarrow P_{ext} = 0$

$W = -P_{ext} \Delta V$

$0 \times \Delta V = 0.$

$W = 0.$

(ii) one mole of gas is allowed to expand from a volume of 1 litre to a volume of 5 litre against a constant external pressure at 1 atm

★ [(1 Litre atm = 101.3 J)]

$W = -P_{ext} \Delta V$

Change in $V = (\underset{V_f - V_i}{5 - 1})$

$W = (-1) \times 4 \Rightarrow -4 \times 101.3 \rightarrow -405.2$

$\boxed{1 \text{ atm} = 101.33 \text{ J}}$

R into atm = 0.821

R into Bar = .831

R into Joule - 8.34

Que 5 ml cylinder contain 10 mole of O_2 gas at 27°C is leaked through hole O_2 expand from cylinder at 1 atm pressure. Calculate the work done by the gas?

Soln. $V_{internal} = 5ml$

$T = 27 + 273 = 300K$.

$V_{final} = \frac{nRT}{P}$ (from $PV = nRT$)

$= \frac{10 \times 0.0821 \times 300}{1}$

$= 246.3$

$\Delta V = V_f - V_{initial}$

$= 246.3 - 5$

$= 241.3L$

$W_{exp} = -P\Delta V$

$= -1 \times 241.3 = -241.3$ atm

$= -2413 \times 101.3$

$\boxed{w_{exp} = -24443.7 J.}$

Que Calculate the work done in Joule when 3 moles of an ideal gas at 27°C expands isothermally and reversibly from 10 atm to 1 atm (1 atm $= 1.013 \times 10^5 Nm^{-2}$) What will be the work done of the expansion against the constant pressure of 1 atm?

Soln. $n = 3$ moles

$T = 27°C = 300K$

$P_1 = 10$ atm, $P_2 = 1$ atm

Work done in Isothermal reversible process

$$W = -2.303 nRT \log (P_1/P_2)$$

$$= -2.303 \times 3 \times 8.314 \times 300 \log\left(\frac{10}{1}\right)$$

$$= 5744.14 \text{ J.}$$

Work done against constant pressure of 1 atm

$$P_{opp} (V_f - V_i)$$

$$= -1 \text{atm} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$-1 \times 3 \times 8.314 \times 300 \left(\frac{1}{10} - \frac{1}{10}\right)$$

$$= 6734.34 \text{ J.}$$

Qu The rxn of ~~cyanide~~ Cyanamide $NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter and ΔU was found to be -742.7 kJ mol^{-1} at 298K

Que Calculate the enthalpy change from the rxn at 298K

$R = 8.314 \times 10^{-3}\ KJ K^{-1} mol^{-1}$.

$$NH_2CN(s) + \frac{3}{2} O_2(g) \rightarrow N_2(g) + CO_2 + H_2O(l).$$

Soln. Balance chemical equation

$$NH_2CN\ (s) + \frac{3}{2} O_2(g) \rightarrow N_2(g) + CO_2 + H_2O(l)$$

Step 2. Calculate - Δn_g.

Difference of moles of gaseous products and reactants

$$\Delta n_g = n_p - n_r$$

$$2 - \frac{3}{2} = \frac{1}{2} = 0.5 mol.$$

Calculate ΔH by using the formula.

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = -742.7\ KJ mol^{-1} + (0.5 mol \times 8.314 \times 10^{-3}\ KJ mol^{-1} K^{-1} \times 298 K)$$

$$= -741.46\ KJ mol^{-1}.$$

Note 1→ During calculations always remb. the units of different quantities ΔH, ΔU and R must be same.

Que Calculate the Δn_g for following rxn.

$$\underset{(g)}{CH_4} + \underset{(g)}{2O_2} \longrightarrow \underset{(g)}{CO_2} + \underset{(l)}{2H_2O}$$

Soln. $\Delta n_g = n_p - n_R$

$1 - 3 = -2$

$\Delta n_g -2.$

Que In a process 701 J of ~~Energy~~ Heat is absorbed by a System and 394 J of work is done by the System What is the Change in Internal energy for the process?

Ans. Heat absorbed by the System

$q = 701 J.$

Work done by the system = $-394J$

Change in internal energy (ΔU)

$q + w = 701 - (394) = 307 J.$

Que. Why is the difference between ΔH and ΔU not significant for solids and Liquids?

Ans The difference between ΔH and ΔU is not Significant for solids or Liquids because system made up entirely of Solids / Liquids do not experience significant volume changes when heated, the difference between and is usually insignificant.

[Summary of first law of Thermodynamics.)]

$$\boxed{\begin{aligned} dU &= q + w = q - P_{ext}\,dV \\ &= q - P_{ext}(V_f - V_i) \end{aligned}}$$

$dU = q - P_{ext}V$

Isothermal Process – T = constant
$dT = 0$
$dU = 0$ for ideal gas.

$0 = q + w$

$\boxed{q = -w}$ or $\boxed{P_{ext}\,dV}$

⇒ Isochoric Process $V =$ constant, $dV = 0$
$w = 0$

$dU = q + \overset{(0)}{w} \Rightarrow q$

$\boxed{dU = -q_v}$

Heat at Constant Volume ($q_v = dU$) is called Internal Energy Change.

* Heat of Constant volume ($q_v = dU$) = State function

Isobaric Process P constant $dp = 0$

$\boxed{dU = q - P_{ext}V}$

Adiabatic process $q = 0$ $dq = 0$

$dU = q + w = w$

$\boxed{dU = w}$ Work done of Adiabatic process is a State function.

Cyclic process

$dU = 0$ State function.

$\boxed{q = -w}$.

Heat Capacity

(Extensive property)

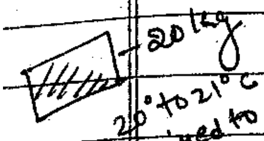
Que Define Heat Capacity ? (C)

Ans. Heat capacity is the quantity of heat required to raise the temp. of a system by 1° celcius (or one kelvin).

$$q = \text{coefficient} \times \Delta T$$

$$q = C\Delta T \quad \text{or} \quad \boxed{C = \frac{\Delta \text{Heat}}{\Delta \text{Temp}}}$$

C is known as Heat Capacity.



20° to 21°C
Heat Required to raise 1°C temp. of object.

Magnitude of Heat Capacity is large
↓ less rise in temp. by given amount of Heat.

eg Heat capacity of H_2O is large, large amount of heat required to raise its temp.

- C depends upon
  a) size b) composition c) nature of system.

⇒ $\boxed{C \propto \text{amount of Substance}}$

\# Specific Heat Capacity :→ The Heat required to raise the temp. of one unit mass by 1 degree (either celcius or kelvin). $\boxed{q = c \times m \times \Delta T}$

⇒ [Note Specific Heat Capacity is Intensive Property]

Que Give the Mathematical Expression of Heat Capacity?

Ans. $q = mc\Delta T$

If

$m = 1 \quad q = C\Delta T.$

Que Define Molar Heat Capacity? (C_m)

The Heat required to raise the temp. of 1 mole of substance by 1° Celcius or kelvin.

Molar Heat Capacity - Intensive Property.

If C is the heat capacity of n mole of the system, then its molar heat capacity C_m

$$C_m = C/n$$

Heat Capacity at Constant Volume (C_v)

It is defined as amount of Heat required to raise the temp. of one mole of gas by 1°C/K when volume of gas is kept constant.

Heat Capacity at Constant Pressure (C_p)

It is defined as the amount of heat required to raise the temp. of 1 mole of gas by one degree when Pressure of gas kept Constent.

Prove or Derive an Expression $\boxed{C_p - C_v = R}$?

Ans from Heat Capacity Equation.

$$\boxed{q = C\Delta T}$$

q = Heat
C = Coefficient
ΔT = Change in temp.

or

$$q = nC\Delta T \quad ①$$

At constant pressure equation (1) is written as

$$q_p = nc_p\Delta T = \Delta H$$

(This value is equal to the change in enthalpy)

||ary at constant volume,

$$q_v = nC_v\Delta T$$

This value is equal to change in Internal Energy

$$\therefore \boxed{q_v = \Delta U}$$

$\therefore nC_V\Delta T = \Delta U$

we know that for one mole (n=1) of an ideal gas

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + \Delta(RT)$$
$$= \Delta U + R\Delta T$$

Therefore $\Delta H = \Delta U + R\Delta T$

Substituting the values of ΔH and ΔU from above in the former equation

$$C_P\Delta T = C_V\Delta T + R\Delta T$$
$$C_P = C_V + R$$
$$\boxed{C_P - C_V = R}$$

Que What is Calorimetry and Calorimeter?

Ans Calorimetry → This is experimental technique which is used to measure the all energy changes occuring during various physical or chemical processes is called Calorimetry.

Calorimeter:- The vessel which is used to carry out the process is called Calorimeter.

The Calorimeter is immersed in a known Volume of liquid, (C) of which is known by measuring the temp. changes and using the heat capacity of liquid and heat capacity of the Calorimeter, it is possible to measure the heat change occuring during the process.

Note 1→ Energy Changes in Calorimeter's measured under two Condition.

a) at Cp Constant Pressure

b) at (Cv) Constant Volume.

ΔH Measurements 1→ Bomb Calorimeter.)

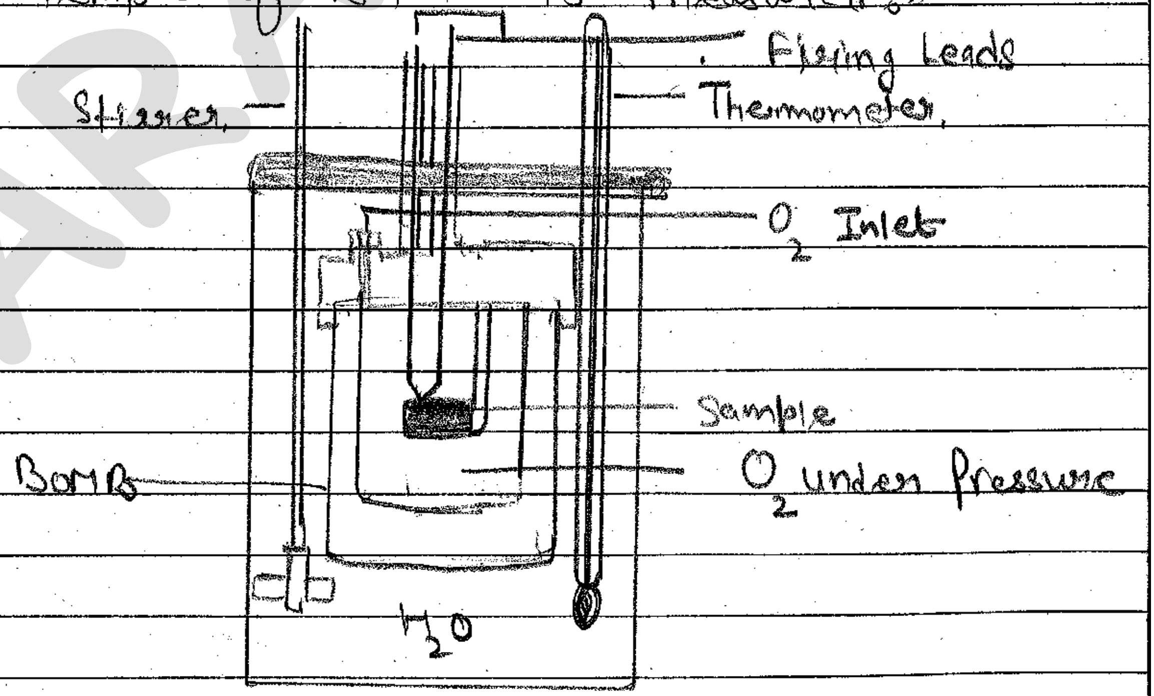
Bomb Calorimeter 1→ It's type of Calorimeter in which heat changes measured at Constant Volume in which steel vessel called bomb is immersed in a water bath.

* use of water bath → ensure no heat lose to the Surrounding.

* In Bomb (Steel Vessel) in pure dioxygen combustile Substance is burnt. during this evolved heat transfered to the water bath.

* Temp. of water is measured.

D/G



BOMB CALORIMETER

Since Bomb Calorimeter is sealed its volume remains same

$$\Delta V = 0$$

$$W = 0$$

no work done on or by the System,

from temp. change.

$$q_v = C \cdot m \cdot \Delta T = C\Delta T$$

$$\boxed{\Delta U = \frac{C \cdot \Delta T \cdot M}{m_i}}$$

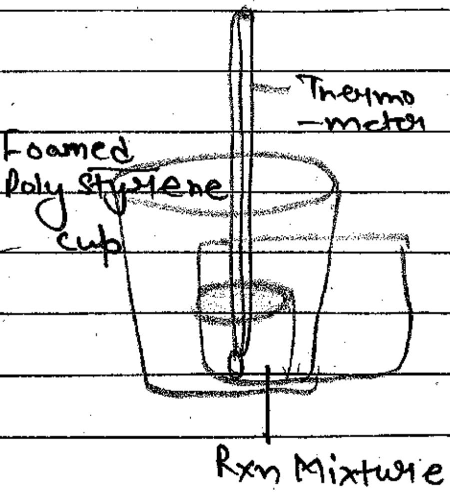
M = Molar mass

m_i = mass.

ΔH Measurement :→

In this $\boxed{q_p = \Delta H.}$

∴ Heat absorbed or evolved q_p at constant pressure is also called Heat of rxn or Enthalpy of rxn $\Delta_r H$.



Rxn maybe

Exothermic
↓
Heat evolve
$q_p = -ve$
$\Delta_r H = -ve.$

Endothermic.
↓
Heat involve
$q_p = +ve.$
$\Delta_r H = +ve$

Que When 1 mole of benzene is burnt in a bomb Calorimeter 3263.0 KJ was liberated Calculate the heat of Combustion of benzene at Constant pressure?

rxn

$$C_6H_6(l) + \frac{15}{2} O_2(g) \rightleftharpoons 6CO_2(g) + 3H_2O(l).$$

In this rxn O_2 is the only gaseous reactant and CO_2 is the only gaseous product.

$$\therefore \Delta n_g = n_p - n_r = 6 - \frac{15}{2} = -3/2$$

also given that

$$\Delta U = -3263.9 \text{ kJmol}^{-1}$$

$$T = 25°C$$

$$= 25 + 273 = 298K$$

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

we know

$$\Delta H = \Delta U + \Delta n_g RT$$

$$\Delta H = -3263.9 - 3/2 \times 8.314 \times 10^{-3} \times 298$$

$$\Delta H = -3263.9 - 3.7$$

$$\boxed{\Delta H = -3267.6 \text{ kJmol}^{-1}}$$

Que Heat Capacity (C_p) is an extensive property but specific Heat (C) is an intensive property. What will be relation between C_p and C for 1 mole of water?

As for water, Molar Heat Capacity

$C_p = 18 \times$ Specific Heat, c

Specific heat $c = 4.18\ J g^{-1} K^{-1}$ (for water)

Heat capacity $C_p = 18 \times 4.18\ J K^{-1}$

$= 75.24\ J K^{-1}$.

$\Delta_r H$ = (Sum of Enthalpies of products) − (Sum of enthalpies of reactants)

$= \sum_i a_i H_{products} - \sum_i b_i H_{reactants}$

Eg $CH_4(g) + 2H_2O \rightarrow CO_2(g) + 2H_2O(l)$

$= [H_m(O_2), g) + 2H_m(H_2O, l)] - [H_m(CH_4), g)$

$+ 2H_m(O_2, g)]$.

H_m = molar enthalpy

Uses / Application of Enthalpy Change is

1. Need to plan the heating or cooling required to maintain an industrial / chemical rxn at constant temp.
2.) Required to calculate temp. dependent Equilibrium Constant.

⇒ Standard Enthalpy of rxn is

The Standard Enthalpy of rxn is the enthalpy change for a rxn when all the participating substance are in their Standard States. (Pure form at 1 bar)

It is denoted as $\Delta H^\ominus$

Different types of Enthalpies

- **Standard Enthalpy of formation ($\Delta_f H^\circ$) :-**

Enthalpy change accompanying the formation of one mole of a substance from its constituent elements under standard condition of temp. (298K) and pressure (1 bar).

$$2C\,(\text{graphite}) + 2H_2\,(g) \rightarrow CH_4\,(g)$$

$$\Delta_f H^\ominus = -74.81\ \text{KJ mol}^{-1}$$

Reference State :→

The most stable state of aggregation of an element at 25°C and at 1 bar pressure is called Reference state.

Standard Enthalpy of Combustion ($\Delta_c H^\circ$) :-

Enthalpy change accompanying the complete combustion of one mole of a substance under standard conditions (298K, 1bar).

Enthalpy of fusion $\Delta_{fus} H^\ominus$ →

The enthalpy change occurring when 1 mole of a solid substance in its standard state melts completely into its liquid form is called standard or molar enthalpy of fusion.

$$H_2O(s) \rightarrow H_2O(l)$$

$$\Delta_{fus} H^\ominus = 6.00\ \text{KJ mol}^{-1}$$

$\Delta_{freezing}H$ is $-ve$ (Exothermic).

Enthalpy of Vaporisation :-

The enthalpy change when one mole of Liquid is converted into vapours at its boiling temp. and under Standard pressure (1 bar) is called enthalpy of vaporisation ($\Delta_{vap}H$) or Molar Enthalpy of vaporisation.

Eg $H_2O(l) \rightarrow H_2O(g)$ $\Delta_{vap}H^\ominus = +40.79\,kJ\,mol^{-1}$.

Enthalpy of Sublimation :-

The process of conversion of a solid into its vapours without coming in the Liquid state is called Sublimation.

The Enthalpy change when one mole of a Solid Substance Sublimes i.e. converted into its vapours without melting at a temp. below its M.P is called Enthalpy of Sublimation. ($\Delta_{sub}H^\ominus$.

$$\Delta_{s}H^\ominus = \Delta_{Fus}H^\ominus + \Delta_{vap}H^\ominus.$$

Que When 1g of Liquid naphthalene ($C_{10}H_8$) solidifies 149J of Heat is evolved. Calculate the heat of fusion of naphthalene.

Ans Molecular Mass of naphthalene

$C_{10}H_8 = 10 \times 12 + 8 \times 1 = 128\,mol^{-1}$

for Solidification rxn.

$$C_{10}H_8(l) \longrightarrow C_{10}H_8(s)$$

Heat Evolved when 1 g napthalene solidifies 149 J.

Heat evolved when 128 g of naphthalene solidify

149 × 128 = 19072 J.

As solidification is reverse of fusion ∴ enthalpy of fusion will have same magnitude as that of enthalpy of solidification but with opposite sign

$C_{10}H_8(s) \rightarrow C_{10}H_8(l)$ $\Delta_{fus}H^\ominus$ = −19070 J.

$\Delta_{fus}H^\ominus$ = +19072 J.

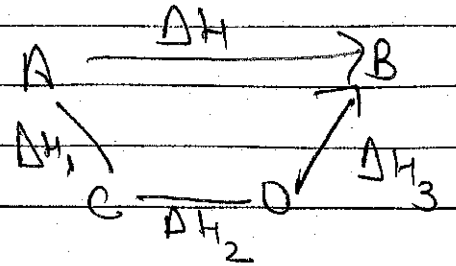
\# **Hess's Law of Constant Heat Summation** :-

Acc. to this law "the total heat change (ΔH) accompanying a chemical rxn is the same whether the rxn takes place in one or more steps.

Eg

Suppose enthalpy change for direct conversion $A \rightarrow B$ is ΔH,

B can also be performed from A through intermediate C and D for which enthalpy changes are ΔH_1, ΔH_2, & ΔH_3 "



Acc. to Hess's Law

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

Applications of Hess's law:-

1. For the determination of Enthalpies of formation of compounds.
2. For the determination of Enthalpies of extremely slow rxn.
3. for the determination of bond energies.

$$\Delta H_{rxn} = \Sigma \text{ Bond energies of Reactant} - \Sigma \text{ bond energies of products.}$$

Calorific Value:→

The amount of heat produced in Calorie or Joule when 1 gram of substance (food/fuel) is completely burnt or oxidised is called Calorific value.

$$\text{Calorific value} = \frac{\Delta_c H}{\text{mass}}$$

Numericals related to
Heat capacity,

1. Calculate the Heat Capacity when you supplied 5000J Energy to the System and Change in temp. 38 to 50°C is observed?

Sol'n Change in temp. $(T_f - T_i)$

$= 50°C$ to $30°$

$= 20°C$

$C = \frac{5000}{20} = 250 J/C°$

2.) A piece of Al metal weighing 3g requires 5.4 J of heat ~~capacity~~, raise the temp. from 298K to 300K Then.

Heat Capacity of the piece of Al

$\frac{5.4 J}{2k} = 2.7 kJ^{-1}$

Specific Heat capacity of Al

$\frac{5.4J}{3g \times 2k} = 0.9 J g^{-1} K^{-1}$

Molar Heat capacity of Al

$\frac{5.4}{3 \times 2} \times 27 = 24.3 J\ mol^{-1} K^{-1}$

3. Specific Heat Capacity of H_2O is 1cal $g^{-1} K^{-1}$ or $4.18 J g^{-1} K^{-1}$.

Notes- for Heat Capacity

$$C = \frac{\Delta Heat}{\Delta T} \qquad C_p = \frac{q_p}{\Delta T} = \frac{\Delta H}{\Delta T}$$

$$C_v = \frac{q_v}{\Delta T} = \frac{\Delta U}{\Delta T}$$

$$\Delta H = \Delta U + \Delta n_g RT$$

if $n_g = 1$

$$\frac{\Delta H}{T} = \frac{\Delta U}{T} + \frac{RT}{T}$$

$$\boxed{C_p - C_v = R}$$

Qu: $\Delta_f U^\ominus$ of formation of $CH_4(g)$ at certain temp is -393 kJ mol^{-1}. The value of $\Delta_f H^\ominus$ is.

Sol: $< \Delta_f U^\ominus$.

Rxn $CH_4(g) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2O(l)$,

$$\Delta n_g = (n_p - n_R)_g = 1 - 3 = -2$$

$$\Delta_f H^\ominus = \Delta_f U^\ominus + \Delta n_g RT$$

$$\Delta n_g = -2$$

$$\therefore \Delta_f H^\ominus < \Delta_f U^\ominus$$

Qu: Calculate the no. of kJ heat necessary to raise the temp. of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 J mol^{-1}K^{-1}. Molar Mass of Al = 27 g mol^{-1}.

Ans Mass Al = 60.0g

Molar mass of Al = 27 g mol⁻¹

Molar heat capacity $C = 24 J mol^{-1} K^{-1}$

Heat $q = n \cdot C \cdot \Delta T$

$$q = \frac{60}{27} \times 24 J mol^{-1} K^{-1} \times 20K \left(n = \frac{60}{27} mol\right)$$

$= 1066.66 J = 1.067 kJ$

Que Show that for an isothermal expansion of an ideal gas (i) $\Delta U = 0$ and $\Delta H = 0$

Sol. for one mole of an Ideal Gas

$$C_V = (\Delta U / \Delta T)_V$$

$$\Delta U = C_V \Delta T$$

for an isothermal process T=0 (Constant)

$\therefore \Delta U = 0$

(ii) $\Delta H = \Delta U + \Delta(PV)$

for an ideal gas $PV = RT$

$$\Delta H = \Delta U + \Delta(RT) = \Delta U + R\Delta T$$

Since T is Constant $\Delta T = 0$

$$\Delta H = 0$$

Que Although heat is path function but heat absorbed by the System under certain specific condition is Independent of path What are those conditions? Explain.

Ans. The two conditions under which heat ~~absorbed~~ becomes independent of path are

(i) when volume remains constant.
(ii) when pressure remains constant.

At constant volume:

By first law of thermodynamics,

$\Delta U = q + W$

$q = \Delta U - W$

But $W = -P\Delta V$

Hence $q = \Delta U + P\Delta V$

$\Delta V = 0$

∴ $q_v = \Delta U$ But ΔU is state function.

q_v is state function.

b) At constant pressure.

$q_p = \Delta U + P\Delta V$

But $\Delta U + P\Delta V = H$

∴ $q_p = \Delta H$

As ΔH is state function therefore q_p is state function.

Que. Calculate the enthalpy change on freezing of 1.0 mole of water at 10.0°C to ice at −10.0°C

$\Delta_{fus} H = 6.03\ kJ\ mol^{-1} K^{-1}$

$C_p[(H_2O)\ l] = 75.3\ J\ mol^{-1} K^{-1}$

$C_p[H_2O\ (s)] = 36.8\ J\ mol^{-1} K^{-1}$

- Conversion of 1 mole of water at 10°C to ice at = −10°C involves the following steps.

• Conversion of 1 mole of H_2O at 10°C,

• 1 mole H_2O at 10°C → 1 Mol H_2O l at 0°C

$\Delta H_1 = C_p H_2O_{(l)} \times \Delta T_1$

• 1 mol $H_2O(l)$ at 0°C → 1 mol $H_2O(s)$ at -10°C,

$\Delta H_2 = \Delta H$ freezing.

• 1 mol H_2O (s) at 0°C → 1 Mol H_2O (s) at -10°C

$\Delta H_3 = C_p H_2O(s) \times \Delta T$.

ΔT = 10k and we know that according to Hess's law total Enthalpy change.

$\Delta H = H_1 + H_2 + H_3$

so first calculate $\Delta H_1 + \Delta H_2$, ΔH_3 & ΔH.

Sol.

$\Delta H_1 = C_p H_2O_{(l)} \times \Delta T$

$= -75.3 \text{ J mol}^{-1} \text{k}^{-1} \times 10 \text{k}$

$= 753 \text{ J mol}^{-1} = 0.753 \text{ kJ mol}^{-1}$

Enthalpy of fusion

$\Delta H_2 = \Delta H$ freezing $- \Delta H$ fusion

$= -6.03 \text{ kJ mol}^{-1}$.

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at 10°C.

$\Delta H_3 = C_{p\,H_2O(s)} \times \Delta T$

$= -36.8\ J\,mol^{-1}K^{-1} \times 10\,K.$

$= -368\ J\,mol^{-1} = 0.368\ kJ\,mol^{-1}$

$\Delta H_{total} = -(0.735 + 6.03 - 0.368)\ kJ\,mol^{-1}$

$= -7.151\ kJ\,mol^{-1}$

Qu. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data.

$CH_3OH(l) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta_r H^\ominus = -726\ kJ\,mol^{-1}$

$C(graphite) + O_2(g) \rightarrow CO_2(g);\ \Delta_c H^\ominus = -393\ kJ\,mol^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta_f H^\ominus = -286\ kJ\,mol^{-1}.$

Soln:

On Reversing the first equation we get,

$CO_2(g) + 2H_2O(l) \rightarrow CH_3OH(l) + \frac{3}{2}O_2(g),$

$\Delta_r H^\ominus = +726\ kJ\,mol^{-1}$ (ΔH sign also reverse)

The second equation remains as such

$C(graphite) + O_2(g) \rightarrow CO_2(g)\quad \Delta_c H^\ominus = -393\ kJ\,mol^{-1}$

On multiplying eq three by 2 we get.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l);\ 2\Delta_f H^\ominus$

$= 2 \times -286\ kJ\,mol^{-1} = -572\ kJ\,mol^{-1}$

Que Enthalpies of formation of $CO(g)$, $CO_2(g)$ $N_2O(g)$ and $N_2O_4(g)$ are -110, 81 and 9.7 kJ mol⁻¹ respectively find the value of $\Delta_r H$ for rxn.

$$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$$

Soln. $\Delta_r H^\circ = \sum \Delta_f H^\circ_{products} - \sum \Delta_f H^\circ_{reactants}$

$= [\Delta_f H^\circ(N_2O) + 3\Delta_f H^\circ(N_2O_4) + 3\Delta_f H^\circ(CO$

$= [81 + 3\times(-393)] - 9.7 + [3\times -110]$ kJ

$= -777.7$ kJ $\simeq 778$ kJ.

Que The value of $\Delta_f H^\ominus$ for NH_3 is -91.8 kJ mol⁻¹ Calculate enthalpy change for the following rxn.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g).$$

Soln. Here $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3$

$\Delta_f H^\ominus = -91.8$ kJ mol⁻¹

∴ Enthalpy change for the formation of 2 moles of NH_3

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g).$

$\Delta_f H^\ominus = 2\times -91.8 = -183.6$ kJ mol⁻¹.

On adding these three equations we get

$$C(\text{graphite}) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$$

Enthalpy of formation of CH_3OH

$$= \Delta_f H = \Delta_s H^\ominus + \Delta_c H^\ominus + 2\Delta_f H^\ominus$$

$$\Delta_f H = +726 - 393 - 572 \text{ kJmol}^{-1}$$

$$= -293 \text{ kJmol}^{-1}$$

Enthalpy of atomization ($\Delta_a H^\ominus$)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

Eg $H_2(g) \rightarrow 2H(g)$; $\Delta_a H^\ominus = 435.0 \text{ kJmol}^{-1}$

* The enthalpy of atomization is also known as bond dissociation enthalpy.

Bond Enthalpy (Symbol $\Delta_{bond} H^\ominus$).

It is also known as bond energy which is the measure of bond strength in a chemical bond.

Otherhand It is defined as enthalpy change associated with chemical bond is known as bond Enthalpy,

Bond Enthalpy $\Delta_{bond}H^\ominus$

Bond Dissociation Enthalpy

Enthalpy change accompanying the breaking of one mole of covalent bond of gaseous covalent compound to give products in the gas phase, is called Bond dissociation enthalpy.

$H_2(g) \rightarrow 2H$

$\Delta_{H-H}H^\ominus = 435.0 \text{ kJ mol}^{-1}$

Mean bond Enthalpy

Found in case of Polyatomic molecules

↓

all the bonds btwn similar atoms are identical in bond length and energy but they differ in their strength is required to break each individual bond.

Enthalpy of atomisation for methane

$CH_4(g) \rightarrow CH_3(g) + H(g)$

$\Delta_{bond}H^\ominus = +427 \text{ kJ mol}^{-1}$

$CH_3(g) \rightarrow CH_2 + H(g)$

$\Delta_{bond}H^\ominus = +439 \text{ kJ mol}^{-1}$

$CH_2(g) \rightarrow CH(g) + H(g)$ — $+452 \text{ kJ mol}^{-1}$

$CH(g) \rightarrow C(g) + 4H(g)$

$\Delta_a H^\ominus = 1665 \text{ kJ mol}^{-1}$

$$\therefore CH_4 \quad \Delta_{C-H}H^{\ominus}$$

$$\Delta_{C-H}H^{\ominus} = \frac{1}{4}(\Delta_a H^{\ominus}) = \frac{1}{4}(1665)(kJ\,mol^{-1})$$

$$= 416\,kJ\,mol^{-1}.$$

Note :-

- The mean bond enthalpy vary slightly from compound to compounds.
- As bond multiplicity increases, bond enthalpy increases.

The standard enthalpy of rxn. $\Delta_r H^{\ominus}$ is related to bond enthalpies of the reactant and products in gas phase rxn

$$\Delta_r H^{\ominus} = \sum \text{bond Enthalpies}_{\text{reactant}} - \sum \text{bond Enthalpies}_{\text{products}}$$

Net Enthalpy change of a rxn :-

The net enthalpy change of a rxn is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules.

Enthalpy of Solution :-

It is the enthalpy change when one mole of its dissolves in a specified amount of Solvent.

- The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions are negligible.

$$\Delta_{sol}H^{\ominus} = \Delta_{lattice}H^{\ominus} + \Delta_{hyd}H^{\ominus}$$

$\Delta_{lattice}H^{\ominus}$ = change in lattice Enthalpy

$\Delta_{hyd}H^{\ominus}$ = change in hydration enthalpy of ions.

Note :- For Ionic compounds $\Delta_{sol}H^{\ominus}$ is +ve and dissociation process is Endothermic.

2) Solubility of salt & Temp.

Lattice Enthalpy & Dissolution of ~~[illegible]~~

Que Why solubility of fluorides is less as compared to chlorides ?

Ans Due high lattice enthalpy of flourine and their small size.

Lattice Enthalpy

It is defined as the Enthalpy change which occur when one mole of ionic compound dissociates into its ions in gaseous state.

Eg $Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g)$

$\Delta_{lattice} H^\ominus = +788 \, kJ mol^{-1}$

Method to Measure the lattice Enthalpy

Born Haber Cycle It is indirect method to measure the lattice Enthalpy of compound.
(It is proceed in no. of steps)

1) $Na(s) \longrightarrow Na(g)$

Sublimation of Metal
$\Delta_{sub} H^\ominus = 108.4 \, kJ mol^{-1}$

2) $Na(g) \longrightarrow Na^+(g) + e^-(g)$

Ionisation of sodium atom
$\Delta_i H^\ominus = 496 \, kJ mol^{-1}$

3) $\frac{1}{2} Cl_2(g) \longrightarrow Cl(g)$ Dissociation of chlorine.

$\frac{1}{2}\Delta_{bond}H^\ominus = 121$ kJmol⁻¹

4) $Cl(g) + e^{-1}(g) \rightarrow Cl^-(g)$.

$\Delta_{eg}H^\ominus = -346$ kJmol⁻¹ ~~121 kJmol⁻¹~~

electron gain enthalpy

5.) $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(g)$

~~$\Delta_{eg}H^\ominus = -348.6$ kJmol⁻¹~~

The sequence of steps is known as Born Haber cycle.

Note → . Sum of the Enthalpy changes round a cycle = 0.

Applying Hess's law

$\Delta_{lattice}H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$

$\Delta_{lattice}H^\ominus = +788$ KJ.

for $NaCl_{(s)} \rightarrow Na^+(g) + Cl^-(g)$

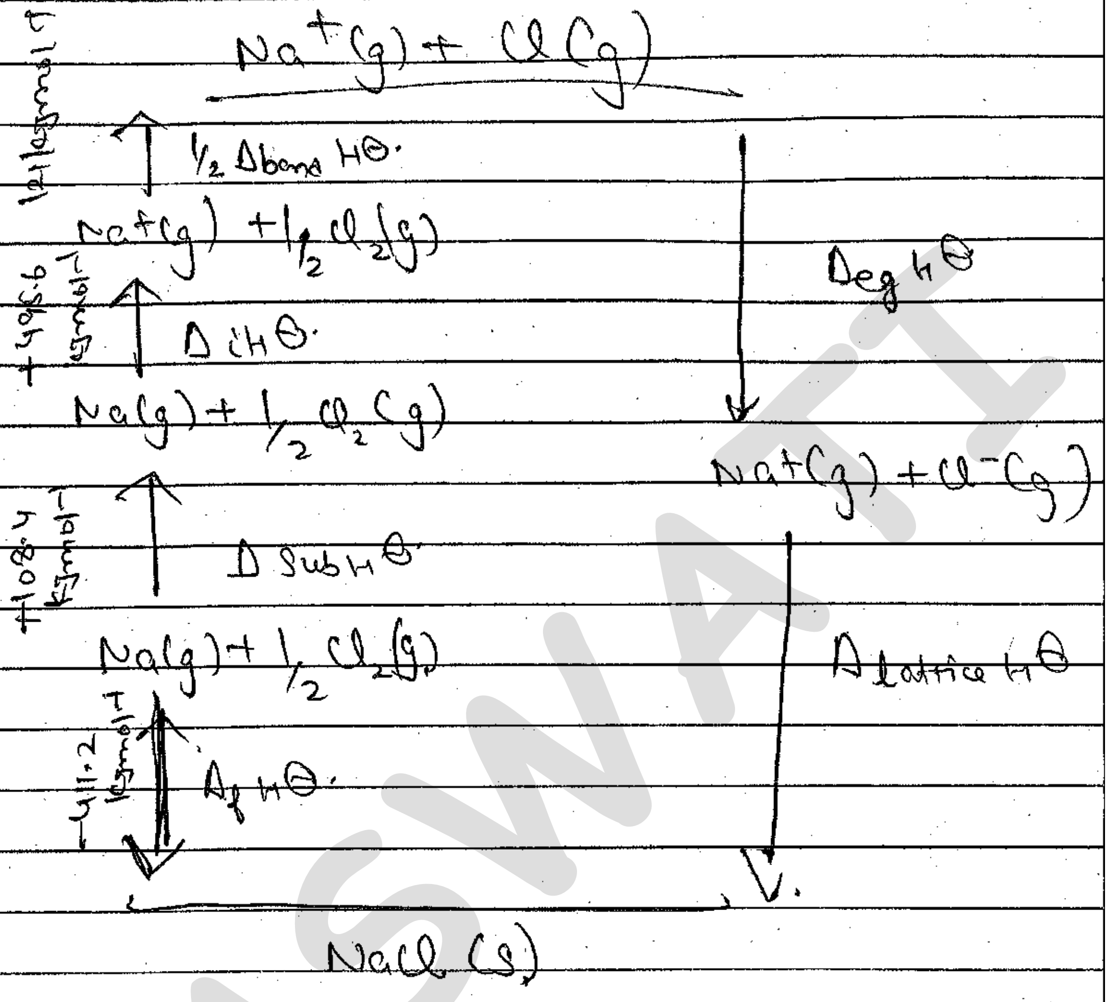
I.E < 2RT.

Note. L.E (lattice Enthalpy used to Calculate enthalpy of Solution).

$\Delta_{sol}H^\ominus = \Delta_{lattice}H^\ominus + \Delta_{hyd}H^\ominus$.

$\Delta_{soln.}H^\ominus = +7.88$ kJmol⁻¹ $- 784$ kJmol⁻¹

$= +4$ kJmol⁻¹.



Enthalpy Diagram for Lattice enthalpy of NaCl.

Reaction Enthalpy ⟹ $\frac{1}{2}$ of Bond Dissociation enthalpy.

$\frac{1}{2}\Delta_{bond}H^{\ominus} = 121\ kJmol^{-1}$.

Ionisation Energy | enthalpy It is the minimum amount of Energy which is required to remove the e^-s from ~~its~~ gaseous state of an atom.

Note 1 → I.E and

Second Law of thermodynamics

for all the Spontaneous processes totally entropy Change must positive.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundy} > 0.$$

Tells us about the direction of flow of heat.

- All natural process in universe are irreversible process & Spontaneous
- Due to Spontaneous process entropy of Universe increase Continously.

Spontaneity :- Means 'having the potential to proceed without the assistance of external agency'.

Note:→ Spontaneity never tell us about the rate of rxn.

Spontaneous process :→ It is an irreversible process and may only be reversed by some external agency.

Spontaneous criteria :→

⇒ ΔS system + ΔS surrounding = ΔS universe

⇒ ΔS universe for reversible process

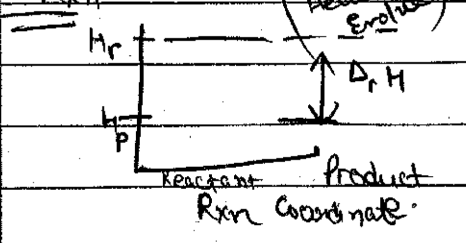
$\boxed{\Delta S_{universe} = 0}$

⇒ ΔS universe for irreversible process / Natural process

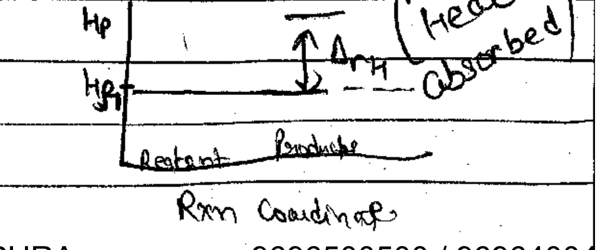
$\boxed{\Delta S_{universe} > 0.}$

- Exothermic process ⇒ Spontaneous.
- Endothermic process ⇒ Non Spontaneous.

Enthalpy Dia for Exothermic Rxn



Enthalpy Dia. for Endothermic Rxn



H_p = Total Enthalpy of products
H_r = Total Enthalpy of reactants.

$\Delta_r H$ = Net heat evolved in rxn for exothermic

$\Delta_r H$ → Net heat absorbed from surrounding in the rxn.

Types of Spontaneous process / Rxns

Spontaneous process	Non-Spontaneous processes
Process which occur in a particular direction itself	Process which occur in particular direction in presence of external agency.
flow of heat from hotter body to colder body.	flow of heat from colder body to hotter body.
Eg Dissolution of sugar in water.	It's a kind of process in which initial is required. Eg $2H_{2(g)} + O_{2(g)} \xrightarrow[\text{Spark}]{\text{Electric}} 2H_2O$ Rxn initiate by Electric Spark.

Limitations of the criterion of Decn in Energy.

(i) In case of Endothermic rxn ΔH is +ve i.e. enthalpy of the System increase but there are several endothermic Rxn that are Spontaneous.

Eg $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$,

$\Delta_f H^\ominus = +33.2\ kJ\,mol^{-1}$

(2) if ΔH = -ve Rxn is rarely proceed for completion even though ΔH remains -ve throughout.

3.) Several rxn proceed when ΔH = 0.

$CH_3COOH(l) + C_2H_5OH \rightarrow CH_3COOC_2H_5(l)$
ethyl acetate
$+ H_2O(l)$

(4) Some Rxns occur in forward and reverse direction. so it is obvious that although dec. in enthalpy may be criteria for spontaneity but it is not true for all the processes.

Entropy :→ (S)

→ Measure degree of randomness of the system.

→ Extensive property and state function.

$\Delta S = \frac{q_{irreversible}}{T}$

Factors affecting Entropy.

$\Delta n_g > 0 \leftarrow \Delta S > 0$

$\Delta n_g < 0 \leftarrow \Delta S < 0$

$\Delta n_g = 0 \Leftarrow \Delta S = 0$

Entropy Order →

Solids < Liquid < Gas.

$\Delta S \propto \frac{T}{P}$

Mixture ! → S+S ↓ then S ↑ Entropy
L+L
g+g

S - Solid
L - Liquid
G - gas

Entropy for different process.

Isothermal

$\Delta S = nR \ln V_2/V_1$

$nR \ln P_1/P_2$

Isobaric

$nC_p \ln T_2/T_1$

Isochoric

$nC_v \ln \frac{T_2}{T_1}$

#. Entropy change in Phase transition

1) Fusion $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$

$$\Delta S = \frac{\Delta H_{fusion}}{T_f}$$

2) Vaporisation $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

$$\Delta S = \frac{\Delta H_{vap}}{T_{vap}}$$

3) Sublimation is $X_s \rightleftharpoons X_g$

$$\Delta S = \frac{\Delta H_{sub}}{T_{sub}}$$

Entropy change in Chemical rxn.

$$\Delta S = \sum S_{products} - \sum S_{Reactants}$$

Third law of Thermodynamics

- Determine absolute entropy of substance.
- At absolute temp. (Zero kelvin) the entropy of perfectly crystalline is Zero.

⇒ 3rd law of thermodynamics states that
Acc. to this law The Entropy of a perfectly a crystalline substance approaches to zero as the absolute zero of temp is approached.

$$\lim_{T \to 0} \Rightarrow S = 0.$$

Note Residual Entropy :- The entropy possessed by a substance at absolute zero.

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

$$dS = \frac{C_p dT}{T}$$

$$\int dS = \int C_p dT$$

$$C_p \ln T$$

$$S_T = 2.303\, C_p \log T$$
$$\text{or } 2.303\, C_v \log T.$$

Note → (1) In case of atoms or molecules belonging to different elements, the one with higher mass have greater entropy for inert gases

$$S_{He} < S_{Ne} < S_{Ar} < S_{Kr} < S_{Xe} < S_{Rn}$$

||ly for Halogen

$$S_{F_2} < S_{Cl_2} < S_{Br_2} < S_{I_2}$$

② The Molecules with more atoms of given type or with greater nos of chemical bonds or greater capacity to take up energy means greater entropy (due to thermal disorder)

$S_{acetylene} < S_{ethylene} < S_{ethane}$

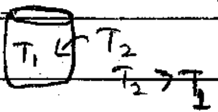
Entropy change of universe.

$$(dS)_{uni} = (dS_{sys}) + (dS)_{surrounding}$$

ΔS Universe

Reversible process

Irreversible process



Cyclic process

$ds_{(sys)} = 0$

$d(s)_{surr} = 0$

$ds_{(uni)} = 0$

Non cyclic Process.

$ds_{system} = \frac{+q_{rev}}{T_1}$

$ds_{surr} = \frac{-q_{rev}}{T_2}$

$ds_{uni} = \frac{+q_{rev}}{T_1} - \frac{q_{rev}}{T_2}$

$$\boxed{ds_{uni} = +ve}$$

ON next Page

Entropy change of irreversible process

Cyclic process

$ds_{sys} = 0$

$ds_{surr} > \frac{q_{irr}}{T}$

$ds_{uni} = +ve$

Non-cyclic process.

$T_2 > T_1$

$ds_{sys} > \frac{q_{irr}}{T_1}$

$ds_{surr} > \frac{q_{irr}}{T_2}$

$$\boxed{ds_{uni} = +ve}$$

#. Gibbs free Energy (ΔG)

Gibbs free Energy = Enthalpy Change − temp × Entropy change

- G is an extensive property and a State function.

$$\boxed{G = H - TS}$$

Change in Gibbs Energy for System.

$$\boxed{\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{system} - S_{sys}\Delta T}$$

At Constant temp. $T=0$

$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}.$

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

⇒ ΔG relates to Spontaneity

$\Delta S_{total} = \Delta S_{System} + \Delta S_{surr.}$

a) $(\Delta G)_{sys} =$ −ve Sponteneous

b) $(\Delta G)_{sys} =$ +ve Non Sponteneous.

(c) $(\Delta G)_{sys} = 0$ at Equilibrium.

Condition for Spontaneous process. ($\Delta G = -ve$).

(a) $\left.\begin{array}{l}\Delta H = -ve \\ \Delta H = +ve\end{array}\right]$ $\Delta H = -ve$ for any value of ΔH and ΔS

b) $\left.\begin{array}{l}\Delta H = +ve \\ \Delta S = +ve\end{array}\right]$ $T\Delta S > \Delta H \geq \Delta H = -ve$

c) $\left.\begin{array}{l}\Delta H = -ve \\ \Delta S = -ve\end{array}\right]$ $\Delta H > T\Delta S = \Delta H = -ve.$

Conditions of temp. for Spontaneous process

$T_{spon.} > \frac{\Delta H}{\Delta S}$

$T_{equilibrium} = \frac{\Delta H}{\Delta S}$

$T_{equilibrium} < T_{spon.} \rightarrow$ Spontaneous.

$T_{eq} = T \rightarrow$ at Equilibrium

$T_{equi} > T \Rightarrow$ non-spontaneous.

ΔG of Chemical Rxns/s.

$n_1 A + n_B B \rightarrow n_3 C$

$(\Delta G)_{Rxn} = (\Delta G)_{Product} - (\Delta G)_{Reactant}$

$\Delta G^\circ - 0$ for Natural form of Elements.

Standard free Energy Change

$\Delta_r G^\circ = $ [Sum of standard free Energy of formation of Products] − [Sum of standard free energy of reactant].

$\Sigma\, \Delta_f G^\circ_{product} - \Sigma \Delta_f G^\circ_{(reactant)}$

Standard free Energy of formation

Free Energy change when 1 mole of compound is made from its Elements in their Standard States is called Standard free Energy of formation of compound.

\# Relationship between Standard Gibbs free Energy and Equilibrium Constant.

$\Delta G = \Delta G^\circ + RT \ln Q$

$\therefore$ at equilibrium $\Delta G = 0$
$Q = K$

$\Delta G = -RT \ln K$

$\Delta G^\circ = -RT \ln K = -2.303\, RT \log K$

Numericals

1- At 60°C dinitrogen tetroxide is fifty per cent dissociated. Calculate the Standard free Energy change at this temp. and 1 atm.

$N_2O_2(g) \rightleftharpoons 2NO_2(g)$.

if N_2O_4 is 50% dissociated

$x_{N_2O_4} = \frac{1-0.5}{1+0.5} \Rightarrow x_{NO_2} \frac{2\times 0.5}{1+0.5}$

$P_{N_2O_4} = \frac{0.5}{1.5}\times 1\,atm$ $\quad P_{NO_2} = \frac{1}{1.5}\times 1\,atm$.

The equilibrium constant Kp

$K_p \quad \frac{(P_{NO_2})^2}{P_{N_2O_4}} = \frac{1.5}{(1.5)^2(0.5)} = 1.33\,atm$ ①.

Since $\Delta_r G^\ominus = -RT\ln K_p$

$\Delta_r G^\ominus = (-8.314\,J\,K^{-1}\,mol^{-1}) \times (333)K \times 2.303 \times 0.1239$

$= -763.8\,k$.

Que For the rxn at 298 K $2A + B \rightarrow C$
$\Delta H = 400\,kJ\,mol^{-1}$ and $\Delta S = 0.2\,kJ\,K^{-1}\,mol^{-1}$.
At what temp. will the rxn become spontaneous considering ΔH and ΔS to be constant over the tempo range?

Note

for a rxn to be spontaneous $\Delta G \leq 0$ so Calculate the temp. at which $\Delta G = 0$ by using the rxn.

Gibbs free Energy $\Delta G = \Delta H - T\Delta S$.

$$0 = 400\ kJ mol^{-1} - T \times 0.2\ kJ K^{-1} mol^{-1}$$

$$Temp, T = \frac{400\ kJ mol^{-1}}{0.2\ kJ K^{-1} mol^{-1}} = 2000\ K.$$

∴ above 2000 K rxn will become spontaneous.

Relationship b/wn Gibbs free Energy and EMF of a cell

$$\boxed{\Delta G = -nFE_{cell}}$$

where E_{cell} = Emf of the cell.

n = no. of moles of e⁻s.

F = faraday's constant 96500 C.

If rxn & products are in their standard state

$$\Delta G^{\circ} = -nFE^{\circ}$$

E° = Standard cell potential.