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ENERGETICS OF CHEMICAL REACTIONS

The branch of science which deals with heat changes is called THERMODYNAMICS. The branch of chemistry which deals with the energy changes in or chemical reactions is called THERMOCHEMISTRY.

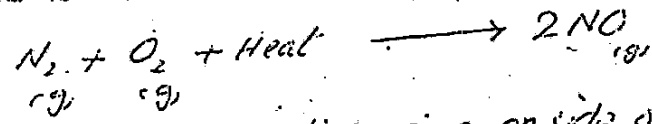
WHAT IS HEAT OF REACTION? CLASSIFY THE CHEMICAL REACTIONS ON THE BASIS OF HEAT OF REACTION?

The amount of heat absorbed or evolved in a chemical reaction when molar quantities of reactants and products are same as represented by balanced chemical reaction is called HEAT OF REACTION.

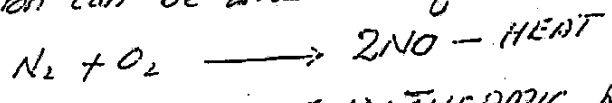
Different chemical substances have different energies. Thus when one chemical substance is converted into another substance, heat is either absorbed or evolved. On the basis of heat absorbed or evolved, the chemical reactions are divided into two categories.

- (i) ENDOTHERMIC REACTIONS.
- (ii) EXOTHERMIC REACTIONS.

ENDOTHERMIC REACTIONS: - These are chemical reactions in which heat is absorbed. For example consider following reaction

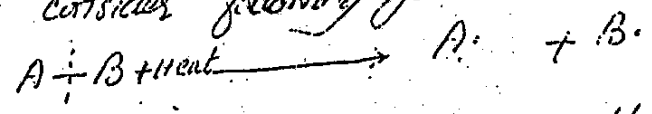


The heat written with positive sign on side of reactants indicates that heat is being absorbed during the reaction. (The same reaction can be written as follows)



HOW TO ACCOUNT FOR ENDOTHERMIC REACTIONS:

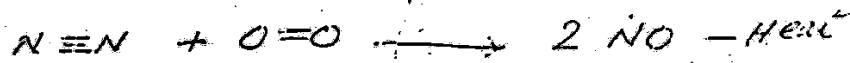
The chemical reactions in which bonds are broken but no bonds are formed are called mostly endothermic. For example consider following general reaction:



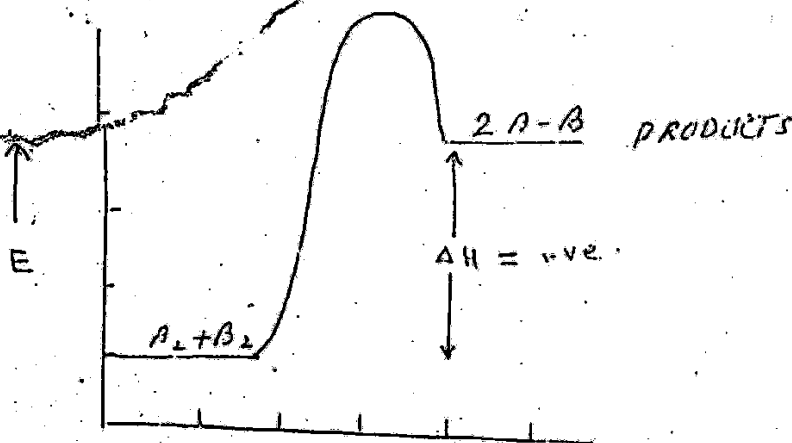
In some chemical reactions bonds are formed as well as broken. If more number of bonds are broken than number of bonds formed then reaction is endothermic. For example consider following reaction.



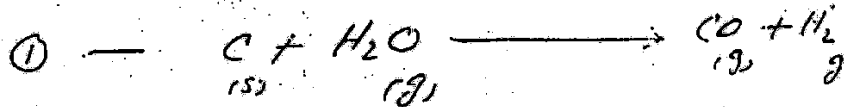
If number of bonds formed is equal to number of bonds broken then reaction will be endothermic if stronger bonds are broken and weaker bonds are formed.



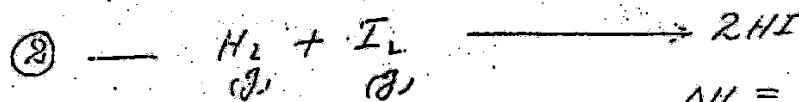
Still another simple way of expressing an endothermic reaction is that if energy of reactants is <sup>less</sup> than energy of products, then reaction is endothermic.



Some more examples of endothermic reactions are



$$\Delta H = +131.4 \text{ kJ}$$



$$\Delta H = 52.96 \text{ kJ}$$

The equation ① shows that,

1 mole of steam reacts with 1 mole of carbon to form 1 mole of CO and 1 mole of  $H_2$ . The heat absorbed is 131.4 kJ. Thus it is endothermic reaction.

## MEASUREMENT OF INTERNAL ENERGY

It is not possible to measure absolute value of internal energy of system.

But it is possible to determine change in internal energy " $\Delta E$ " of system.

## HOW TO CHANGE INTERNAL ENERGY OF SYSTEM

Heat and work are two ways of transferring energy to or from a system.

HEAT:- The quantity of energy that flows across the boundary of system ~~due to~~ during a change in its state. This flow of energy is due to difference in temperature between system and surrounding. Heat absorbed or evolved by system is represented by " $q$ ". Heat absorbed by system is " $+q$ " and evolved by system is " $-q$ ". Heat is not a property of system. It is not a state function.

WORK:- The product of force and distance is called work. Its unit is Joules. There are different kinds of work. The most common form of work is pressure volume work. It is usually written as  $W = -P\Delta V$ . The work done on the system is +ve and work done by the system is negative. Work is NOT a state function.

WHAT IS FIRST LAW OF THERMODYNAMICS. GIVE ITS MATHEMATICAL FORM. SHOW THAT  $q_v = \Delta E$  and  $q_p = \Delta H$   
 The law of conservation of energy is also called FIRST LAW OF THERMODYNAMICS. It can be stated as

"Energy can neither be created nor can be destroyed but it can be changed from one form to another." It can also be stated as "The total energy of system and surroundings is conserved."

Heat and work are forms of energy.

Energy can be transferred into and out of system in the form of heat and work. The energy change is equal to sum of heat and work given to the system. Thus total energy of system and surroundings remain constant.

$$\Delta E = q + w \quad \text{--- (1)}$$

$\Delta E$  = change in internal energy of system.

$q$  = Heat given to the system.

$w$  = Work done on the system.

Equation (1) is called mathematical form of first law of Thermodynamics. In this form of law following sign conventions are generally used.

SIGN CONVENTIONS:

Heat given to the system is positive =  $+q$

Heat given out by the system is negative =  $-q$

Work done on the system is positive =  $+w$

Work done by the system on surroundings =  $-w$

$\Delta E$  is positive when system gains energy =  $+\Delta E$

$\Delta E$  is negative when system loses energy =  $-\Delta E$

Work done on the system and heat given to the system increase internal energy of system so these are positive.

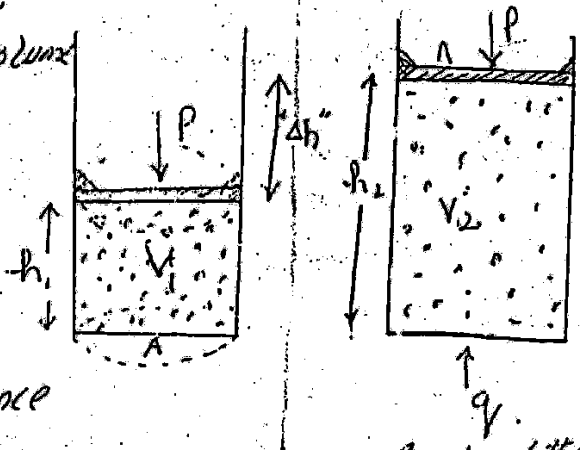
Work done by the system and heat lost by a system decrease its internal energy so these are given negative sign.

**CALCULATION OF WORK DONE:-**

In chemistry we are mostly concerned with pressure-volume work.

Work is defined as "product of force and distance covered by body"

$$W = \text{Force} \times \text{Distance}$$



Let us consider a gas enclosed in a cylinder fitted with a movable piston. The area of cross-section is "A". The pressure is "P". The initial height of cylinder is "h<sub>1</sub>". It is given heat "q" and piston moves up. Let its final height of piston is "h<sub>2</sub>".

distance covered by piston = "Δh" [P = F/A]

Force applied on the piston by the gas = F = P x A

Initial volume of gas = V<sub>1</sub> = A x h<sub>1</sub>  
 Final volume of gas = V<sub>2</sub> = A x h<sub>2</sub>  
 Change in volume = ΔV = V<sub>2</sub> - V<sub>1</sub>

$$\Delta V = Ah_2 - Ah_1$$

$$\Delta V = A(h_2 - h_1)$$

$$\Delta V = A \Delta h$$

$$\frac{\Delta V}{A} = \Delta h \quad \text{--- (2)}$$

The work done by the piston "W" = Force x distance

$$W = P \times A \times \Delta h$$

Putting value of Δh from eq. (2) we have

$$W = P \times A \times \frac{\Delta V}{A}$$

$$W = -P \Delta V \quad \text{--- (3)}$$

(The negative sign indicates that work is done on the surroundings)

SYSTEM AT CONSTANT VOLUME:-

If volume of system does not change (constant volume),  $\Delta V = 0$

The heat given at constant volume is " $q_v$ "

The first law could be written as

$$\Delta E = q_v + w$$

$$\Delta E = q_v - P\Delta V \quad (\text{Putting value of work from eq (3)})$$

Since at constant volume  $\Delta V = 0$

$$\Delta E = q_v - P \times 0$$

$$\boxed{\Delta E = q_v} \quad \text{--- (4)}$$

Equation (4) says that heat given at constant volume increases internal energy of system and not heat is used in pushing up the piston.

SYSTEM AT CONSTANT PRESSURE:- (ENTHALPY CALCULATIONS)

In laboratory as well as in industry most of reactions are carried out at constant pressure (atmospheric pressure). Thus a chemist is more interested in system at constant pressure. Heat given at constant pressure is written as " $q_p$ "

First law of Thermodynamics could be written

as 
$$\Delta E = q_p + w$$

$$\Delta E = q_p - P\Delta V \quad (\text{FROM EQ (3)})$$

$$\Delta E = E_2 - E_1 \quad \text{and} \quad \Delta V = V_2 - V_1$$

$$E_2 - E_1 = q_p - P(V_2 - V_1)$$

$$E_2 - E_1 = q_p - PV_2 + PV_1$$

$$E_2 + PV_2 - E_1 - PV_1 = q_p$$

$$(E_2 + PV_2) - (E_1 + PV_1) = q_p$$

$$H_2 - H_1 = q_p$$

$$\Delta H = q_p$$

$$\left[ \begin{array}{l} E_2 + PV_2 = H_2 \\ E_1 + PV_1 = H_1 \\ E + PV = H \end{array} \right]$$

" $\Delta H$ " is called enthalpy change. The sum of internal energy and pressure volume work is called Enthalpy of system. It indicates total heat contents of system.

WHAT IS ENTHALPY OF SYSTEM: The sum of internal energy and product of pressure and volume is called

ENTHALPY OF SYSTEM  $H = E + PV$

It is also called heat contents of system.

Enthalpy is a state function. It is measured in joules.

It is not possible to measure the enthalpy of a system in given state. However change in enthalpy can be measured for a change in state in system.

$$\Delta H = \Delta E + \Delta(PV)$$

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

At constant pressure  $\Delta P = 0$

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

In liquids and solids  $\Delta V \approx 0$

$$\Delta H = \Delta E$$

According to first law of thermodynamics

$$\Delta E = q + w$$

$$\Delta E = q_p - P\Delta V \quad (w = -P\Delta V \text{ work done by the system})$$

$$\Delta E = q_p \quad (\text{At const vol } \Delta V = 0)$$

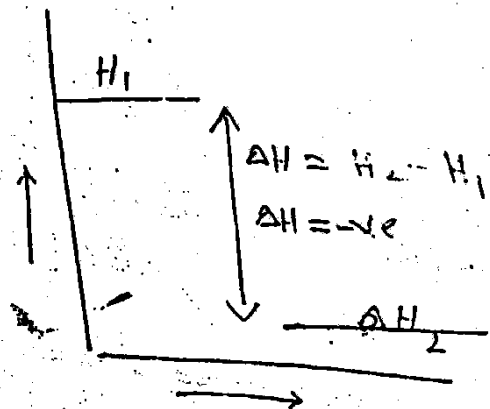
Thus enthalpy change is equal to heat of reaction at constant pressure. Since most of reactions are carried out at constant pressure so we are mostly concerned with heats of reactions  $\Delta H$  rather than  $\Delta E$ .

ENTHALPY OF REACTION

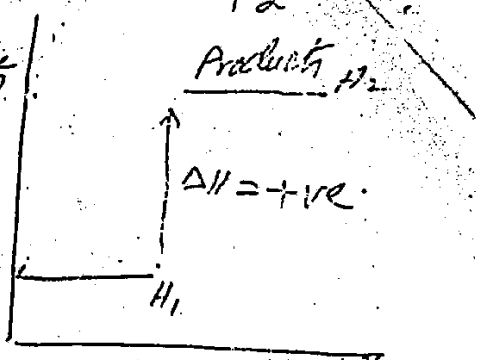
In an exothermic reaction the enthalpy of products is less than reactants. Thus enthalpy change is negative in these reactions.

$$\Delta H = \Delta H_2 - \Delta H_1$$

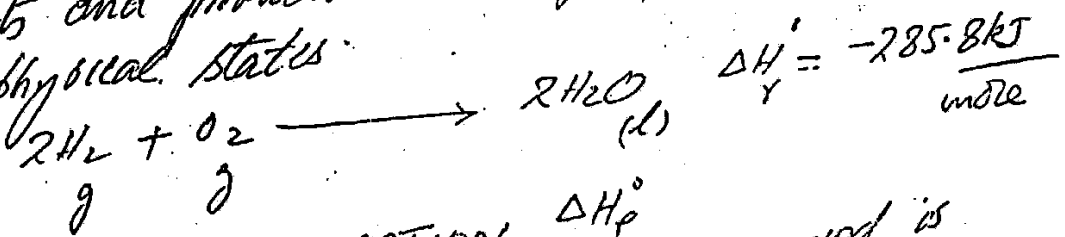
$$\Delta H = (-ve)$$



In ENDOTHERMIC REACTIONS enthalpy of products is greater than that of reactants. Thus enthalpy change is positive.

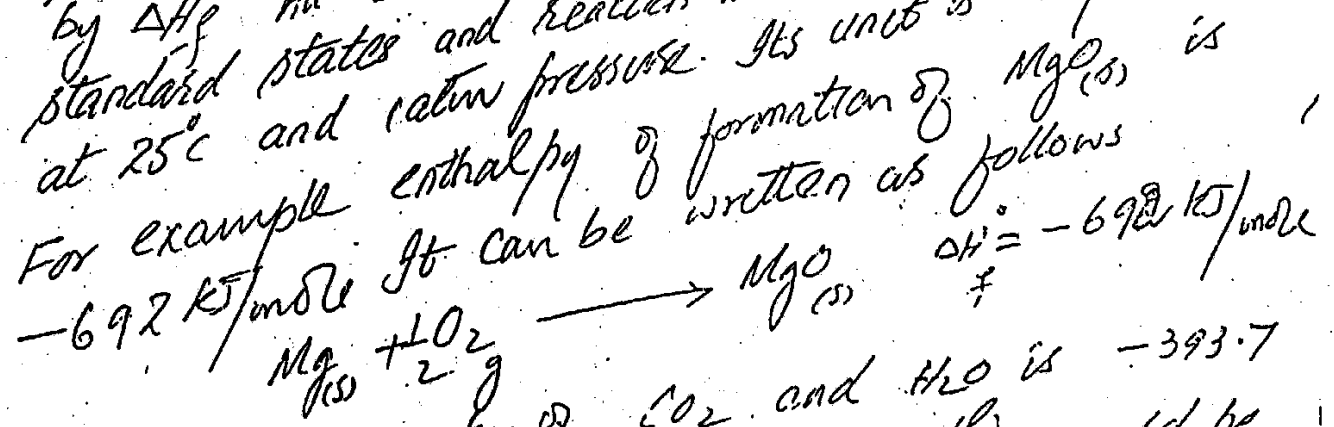


STANDARD ENTHALPY CHANGE: - The enthalpy change which takes place when number of moles of reactants present in balanced equation react to form number of moles of products under standard condition (at 25°C and 1 atm). All reactants and products must be present in their standard physical states.

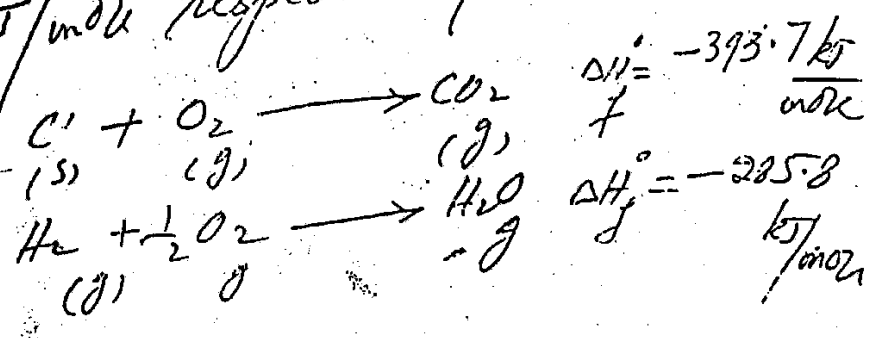


Def: ENTHALPY OF FORMATION  $\Delta H_f^\circ$

The change in enthalpy when 1 mole of compound is formed from elements in their standard states. It is denoted by  $\Delta H_f^\circ$ . All substances must be present in their standard states and reactants must be carried out at 25°C and 1 atm pressure. Its unit is kJ/mole.



Enthalpy of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  is  $-393.7$  and  $-285.8 \text{ kJ/mole}$  respectively. It could be written as follows



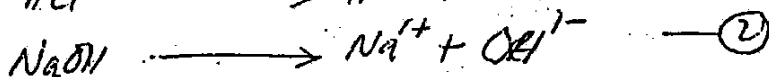


ENTHALPY OF ATOMIZATION  $\Delta H_{\text{atom}}$

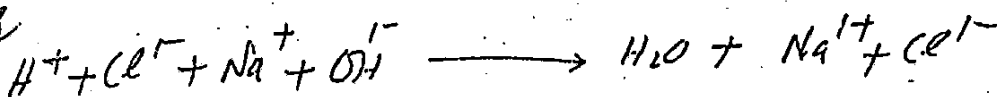
It is defined as the enthalpy change which takes place when 1 mole of gaseous atoms are formed from elements under standard conditions. For example enthalpy of atomization of hydrogen is given below  $\frac{1}{2} \text{H}_2 \longrightarrow \text{H(g)}$   $\Delta H_{\text{atom}}^\circ = 218 \text{ kJ/mole}$

ENTHALPY OF NEUTRALIZATION

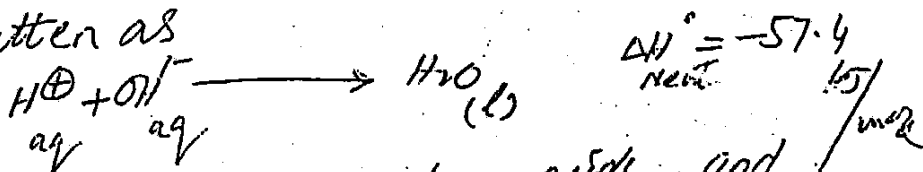
It is defined as amount of heat evolved when 1 mole of  $\text{H}^+$  ions from an acid react with 1 mole of  $\text{OH}^-$  ions from a base to form 1 mole of water. For example enthalpy of neutralization of NaOH by HCl is  $-57.4 \text{ kJ/mole}$ . When strong acid and strong base are added in water they ionize completely.



When solution of acid is mixed with solution of a base the net reaction is combination of  $\text{H}^+$  and  $\text{OH}^-$  to form water



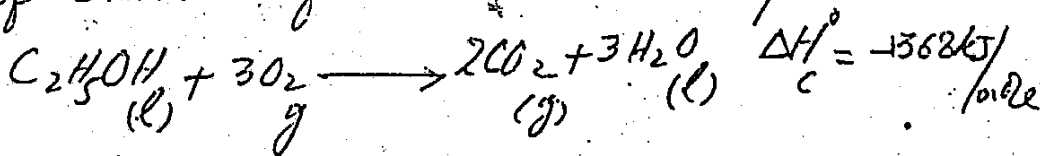
It can be written as



Enthalpy of neutralization of all strong acids and all strong bases is approximately the same ( $-57.4 \text{ kJ/mole}$ )

ENTHALPY OF COMBUSTION  $\Delta H_c$

It is defined as "Enthalpy change which takes place when 1 mole of compound is completely burnt in excess of  $\text{O}_2$  under standard conditions. For example standard enthalpy of combustion of ethanol is  $-1368 \text{ kJ/mole}$



## ENTHALPY OF SOLUTION / " $\Delta H_{sol}^\circ$ "

The amount of heat absorbed or evolved when 1 mole of compound (substance) is dissolved in a suitable solvent that further dilution results no detectable heat change is called heat of solution.

For example enthalpy of solution  $\Delta H_{sol}^\circ$  of  $\text{NH}_4\text{Cl}$  is  $+15.1 \text{ kJ/mole}$  while  $\Delta H_{sol}^\circ$  of sodium carbonate is  $-25.0 \text{ kJ/mole}$ .

Thus when  $\text{NH}_4\text{Cl}$  is dissolved in water it is endothermic process and water cools down. The solubility of  $\text{Na}_2\text{CO}_3$  is exothermic process and temp. of solvent rises during solution formation.

Q.No: WRITE METHODS OF MEASUREMENT OF ENTHALPIES OF REACTIONS.

Ans: The accurate values of  $\Delta H$  can be determined by using calorimeters.

### GLASS CALORIMETER

For most purposes glass calorimeters can be used to determine  $\Delta H_r$ . It is an insulated container with a thermometer and a stirrer.

Reactants are mixed in stoichiometric amounts. When reaction proceeds the heat energy will absorb or evolve. Thus temperature of system decreases or increases. The temperature of system is recorded before and after the chemical reaction. By using temp. change  $\Delta T$ , mass of reactants, and specific heat capacity of reaction mixture we can calculate "q" heat absorbed or evolved during reaction.

$$q = m \times s \times \Delta T \quad (\text{see example no 2})$$

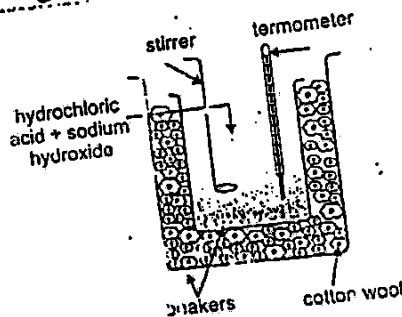
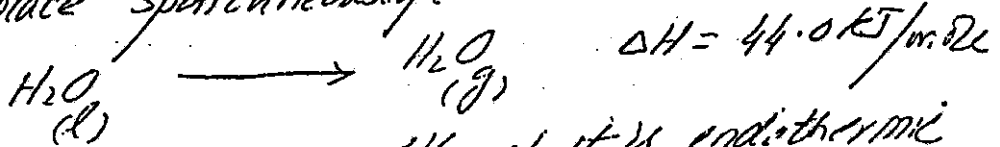


Fig (7.1) Glass Calorimeter

## EXAMPLES

- 1) Pumping of water uphill.
- 2) Transfer of heat from cold interior part of refrigerator to hot surroundings.
- 3) Reaction of  $N_2$  and  $O_2$  in presence of electric spark  
$$N_2 + O_2 \rightleftharpoons 2NO \quad \Delta H = +ve.$$

In most of the cases exothermic reactions are spontaneous. However there are some endothermic reactions which may take place spontaneously.



$NH_4Cl$  dissolves in water although it is endothermic process  
$$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq) \quad \Delta H = 15.1 \text{ kJ}$$

To predict whether a reaction will occur spontaneously or not, free energy of system must be taken into consideration.

DEFINE AND EXPLAIN FOLLOWING TERMS.

**SYSTEM:** - Any real or imaginary portion of universe which is under study or consideration is called system. For example if we are heating water in a beaker, that water is system.

**SURROUNDING:** - Anything around the system is called surrounding. For example we mix Zinc and  $CuSO_4$  in a flask. Thus Zinc and  $CuSO_4$  are systems while flask, air, lab etc are surrounding.

**BOUNDARY:** - The real or imaginary surface, separating the system from surrounding is called boundary surface. Surrounding = Universe - System.

**STATE OF SYSTEM:** - It means, conditions of system. The description of system in terms of  $P, T, \text{volume}$  is called state of system. The state of system before thermochemical change is called Initial State.  $P_1, V_1, T_1$ . The state after thermochemical change is called final state  $P_2, V_2, T_2$  etc.

By comparing initial and final state we can describe change taking place in system.  $\Delta T = T_2 - T_1$

STATE FUNCTION: It is a macroscopic property of a system which has some definite values of initial and final states and it is independent of the path adopted to bring about change. By convention, capital letters are used as symbols for state function. P, T, V, internal energy "E", Enthalpy "H" all are state functions.

Let us suppose " $V_1$ " is initial vol of a gas. A change is brought about and its final volume becomes  $V_2$ . The change in vol.  $\Delta V = V_2 - V_1$ . Now this change can be brought about either by decreasing "P" or increasing Temp. Since vol. is <sup>or</sup> ~~is~~ a state function  $\Delta V$  will be independent of the way of gas has been changed. It depends upon initial and final volumes of the gas.

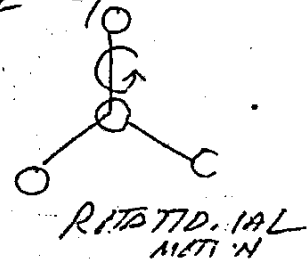
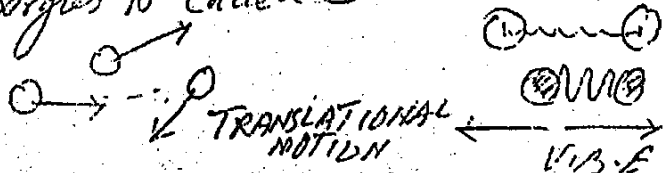
### DEFINE AND EXPLAIN INTERNAL ENERGY OF SYSTEM.

The total of all possible kinds of energies of the system is called INTERNAL ENERGY OF SYSTEM.

A system containing some quantity of matter has definite amount of energy present in it. This energy is the sum of kinetic as well as P.E. of particles contained in it.

KINETIC ENERGY is due to translational, rotational and vibrational motion of particles contained in system. ~~Internal~~ POTENTIAL energy is due to attractive forces present in system. These attractive forces include all types of bonds and Vander Waals forces present between particles.

The total of all possible kinds of energies is called INTERNAL ENERGY OF SYSTEM.

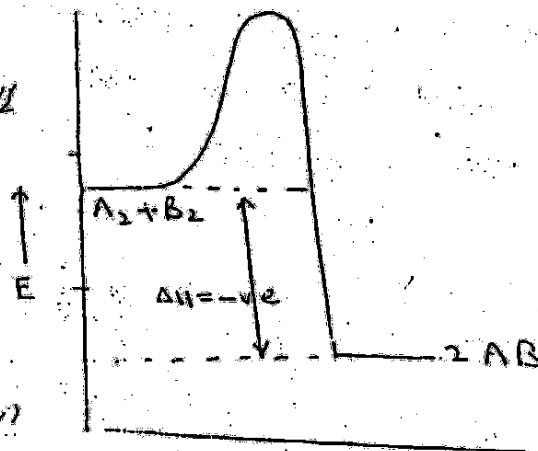


## EXOTHERMIC REACTIONS:-

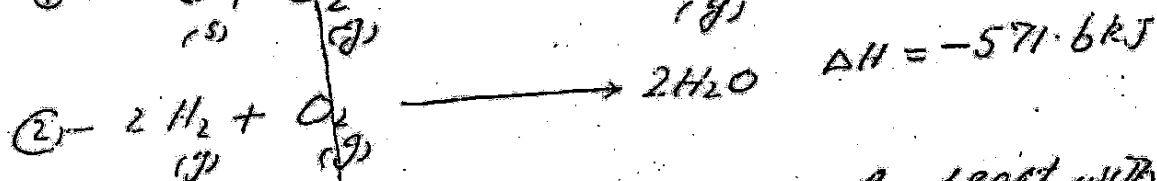
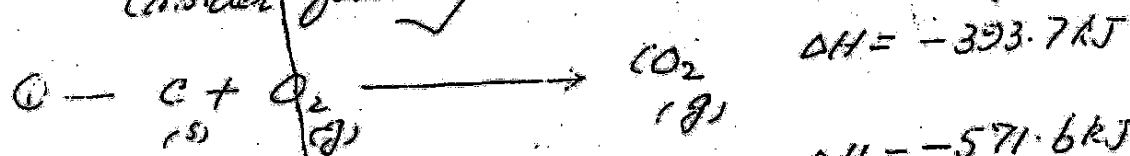
The chemical reaction in which heat is evolved are called exothermic reactions. If reactants are of high energy than products then reaction is exothermic.

If in a reaction more number of bonds are formed than number of bonds broken, then reaction is exothermic.

OR, If stronger bonds are being formed & and weaker bonds being broken reaction is Exothermic.



Consider following reactions



The equation ① shows that 1 mole of  $\text{C}_{(s)}$  react with 1 mole of oxygen gas to form 1 mole of  $\text{CO}_2$  with the liberation of  $-393.7 \text{ kJ/mole}$  heat. Thus reaction is exothermic.

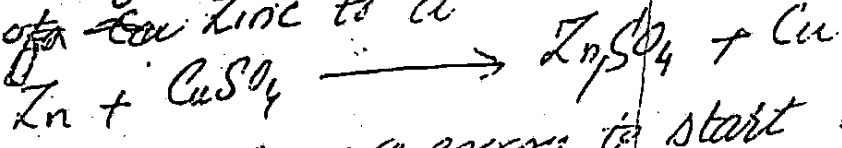
# SPONTANEOUS AND NON SPONTANEOUS REACTIONS.

DEFINITION: The reaction which takes place on its own without any outside assistance and moves from a non-equilibrium state to an equilibrium state is called spontaneous or natural process. It is unidirectional, irreversible and real process.

## EXAMPLES

- 1) Water flows from higher level to lower level without any external aid. This flow cannot be reversed without any external aid.
- 2) Neutralization of strong acid and strong base is a spontaneous acid base reaction.  
$$\text{HCl}_{aq} + \text{NaOH}_{aq} \longrightarrow \text{NaCl}_{aq} + \text{H}_2\text{O}_{(l)}$$

3) Reaction of Zinc with  $\text{CuSO}_4$  is a spontaneous reaction. Blue colour of  $\text{CuSO}_4$  solution is discharged on addition of zinc to it.



Reactions which require energy to start with but once started they go on by itself.

For example burning of coal does not start in air at its own. But once ignited by spark it will go on by itself. It is also spontaneous reaction.

## NON-SPONTANEOUS REACTION

A reaction which does not take place at its own and does not occur in nature is called non spontaneous reaction.

Some nonspontaneous reactions can be made to take place by supplying energy from external source.

Reversible process is a limiting case between spontaneous and non spontaneous processes.

# BOMB CALORIMETER

A bomb calorimeter is usually used to determine enthalpy of combustion of food, fuel and other compound in an accurate manner.

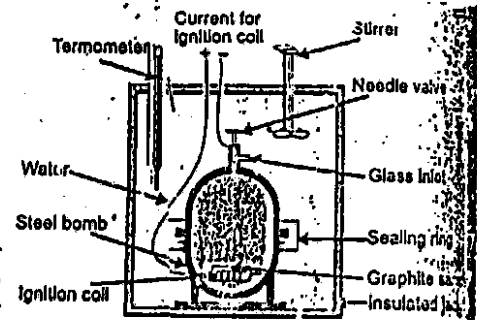


Fig. 7.7) Bomb calorimeter

It consist of a strong cylindrical steel vessel, It is lined with enamel to prevent corrosion.

A known mass of test substance (about 1g) is placed in platinum crucible inside the bomb. The lid is tightly closed then oxygen is provided inside until pressure inside is about 20 atm. Screw valve is closed. The bomb calorimeter is dipped in known mass of water. It is allowed to attain a steady temp. The initial temp is measured.

The test substance is ignited electrically by passing electric current through ignition coil. The temp. of water, is determined after every 30 sec. The maximum temp. attained is determined. By using  $\Delta t$ , mass of whole system and specific heat of (system) calorimeter, water, stirrer) it is possible to determine heat of combustion

$$q = m \times s \times \Delta t$$

'm' is number of moles of substance burnt  
 $\Delta t$  is rise in temp.  
 s specific heat of whole system (see example 3)

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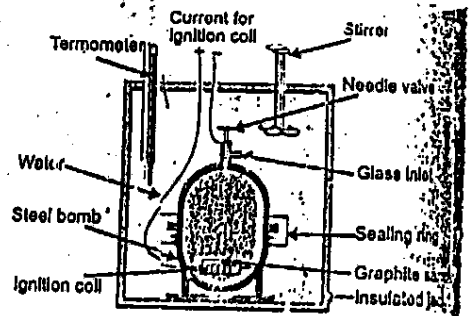


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 s specific heat of whole system. (see example 3)



DEFINE AND EXPLAIN HESS'S LAW OF CONSTANT HEAT SUMMATION? GIVE EXAMPLES. 16

DEFN: IF A CHEMICAL CHANGE TAKES DIFFERENT ROUTES THE OVERALL ENERGY CHANGE IS THE SAME REGARDLESS OF THE ROUTE BY WHICH CHEMICAL CHANGE OCCURS PROVIDED INITIAL AND FINAL CONDITIONS ARE THE SAME. IT IS CALLED HESS'S LAW OF CONSTANT HEAT SUMMATION.

Mathematically  $\sum \Delta H_{\text{cycle}} = \text{ZERO}$ .

OR  $\Delta H_1 = \Delta H_2 + \Delta H_3$

EXAMPLE No 1: ENTHALPY OF CONVERSION OF GRAPHITE TO "CO".

The heat of formation of CO cannot be determined directly from graphite due to formation of some CO<sub>2</sub>. However if enthalpy of combustion of graphite to form CO<sub>2</sub> and enthalpy of formation of CO<sub>2</sub> from "CO" is known, we can calculate enthalpy of formation of "CO" as follows

1) Oxidation of graphite to CO<sub>2</sub>  $\Delta H_1 = -393.7 \frac{\text{kJ}}{\text{mole}}$

① —  $\text{C}_{\text{graphite}} + \text{O}_2 \longrightarrow \text{CO}_2$  (g)

2) Combustion of "CO" to "CO<sub>2</sub>" is written as  $\Delta H_2 = -283 \frac{\text{kJ}}{\text{mole}}$

② —  $\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2$  (g)

3) We want to determine  $\Delta H_3 = ?$

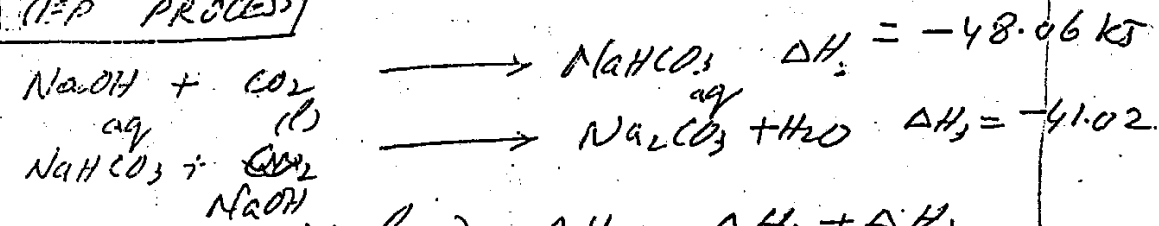
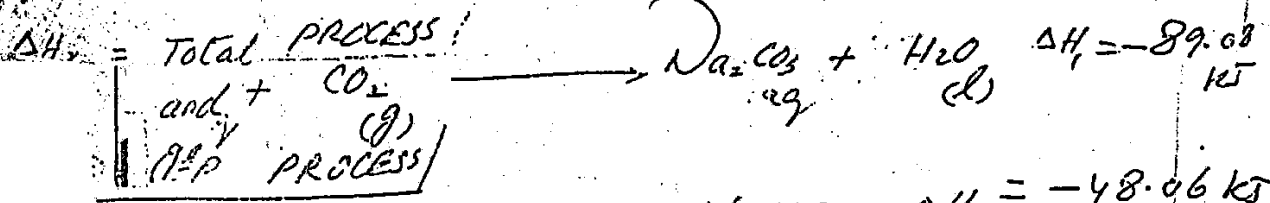
③ —  $\text{C}_{\text{(s)}} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_{\text{(g)}}$

Subtracting eq ② from eq ① we get

$\Delta H_3 = \Delta H_1 - \Delta H_2$   
 $= -393.7 - (-283)$   
 $\Delta H_3 = -110.7 \text{ kJ/mole}$

FORMATION OF Na<sub>2</sub>CO<sub>3</sub> (SODIUM CARBONATE)

The formation of sodium carbonate may be studied in a single step or in two steps via sodium hydrogencarbonate formation.



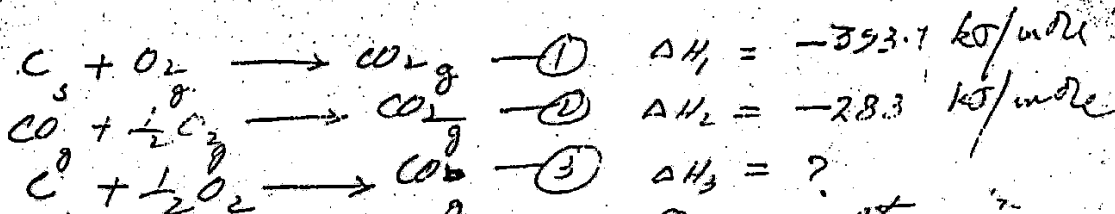
According to Hess's Law  $\Delta H_1 = \Delta H_2 + \Delta H_3$   
 $-89.08 = -48.06 + (-41.02)$   
 $-89.08 = -89.08$

Thus heats of reactions can be added algebraically.

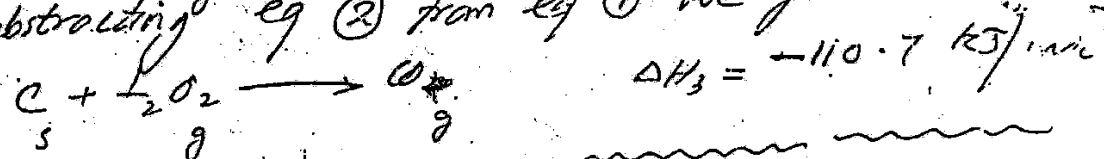
HESS'S LAW IS USED TO CALCULATE HEATS OF THOSE REACTIONS WHICH CANNOT BE NORMALLY CARRIED OUT IN LABORATORY EXPLAIN.

Ans: There are many compounds for which  $\Delta H$  cannot be measured directly by calorimetric methods. It may be due to any one of the following reasons

- (1) Some compounds like  $CCl_4$  cannot be prepared directly by using graphite and chlorine. Similarly  $CCl_4$  does not decompose easily into constituent elements.
  - (2) Enthalpies of formation of  $Br_2O_3$  and  $Si_2O_3$  cannot be determined directly because when these elements are burnt in oxygen a protective layer of oxide covers surface of unreacted element.
  - (3) Heat of formation of  $CO$  cannot be measured directly due to formation of  $CO_2$  along with it.
- In these cases enthalpies of these reactions can be determined by using Hess's law. For example if we know the enthalpy of combustion of graphite to  $CO_2$  and enthalpy of combustion of  $CO$  to  $CO_2$ , we can calculate enthalpy of formation of  $CO$ .



Subtracting eq (2) from eq (1) we get

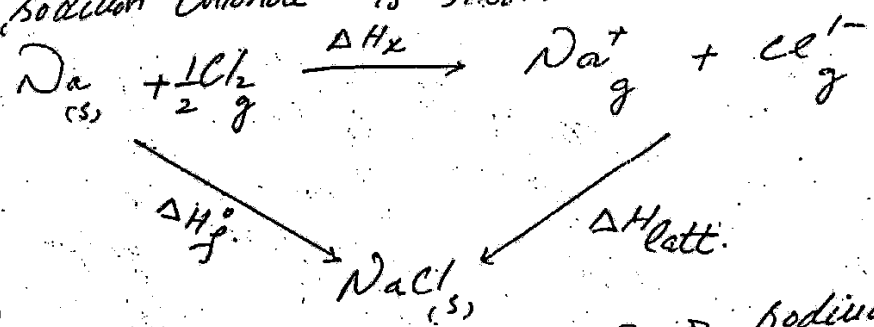


Q:- WHAT IS LATTICE ENERGY?  
 HOW DOES BORN HABER CYCLE HELP TO CALCULATE LATTICE ENERGIES.

Ans:- The lattice energy of an ionic crystal is defined as the enthalpy of formation of 1 mole of ionic compound from gaseous ions under standard conditions. The lattice energy of NaCl(s) can be represented as follows:

$$\text{Na}_g + \text{Cl}_g \longrightarrow \text{NaCl}_{(s)} \quad \Delta H_{\text{lattice}} = -776 \text{ kJ/mole}$$

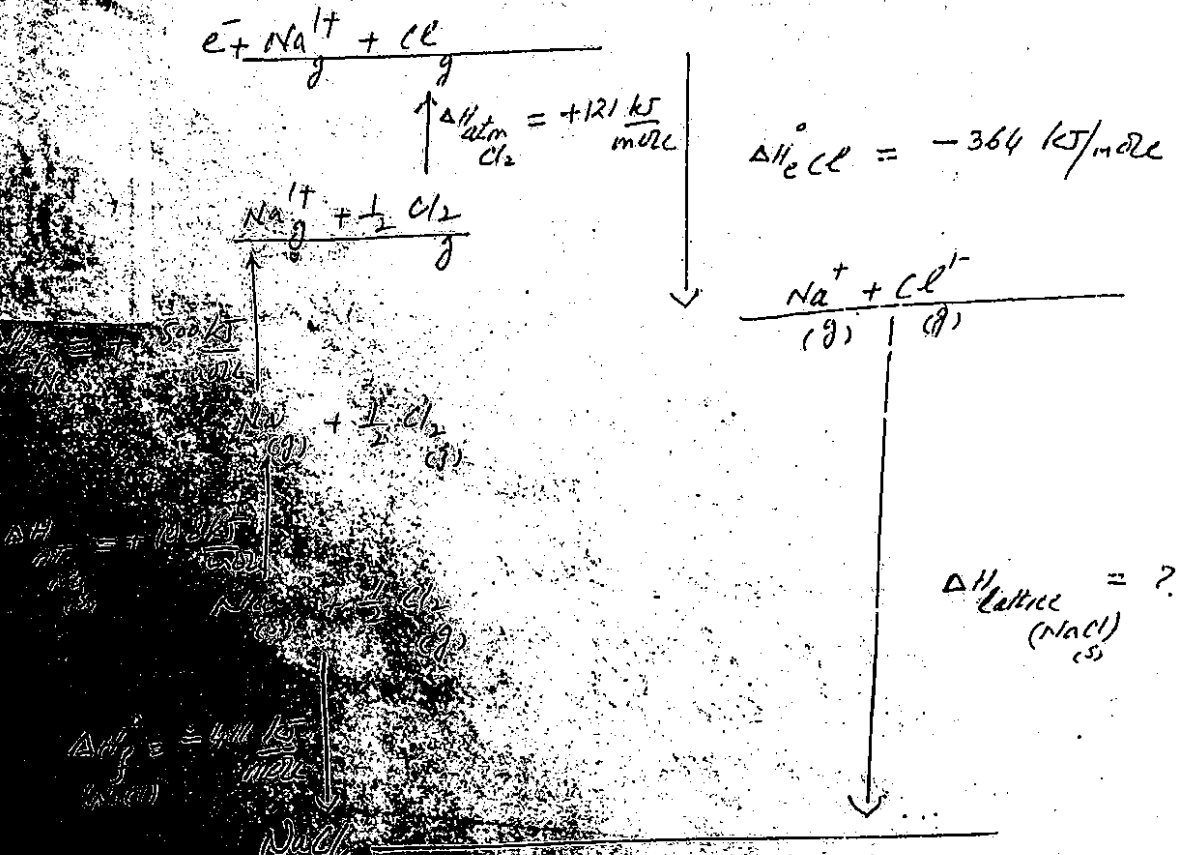
Lattice energies give some idea of force of attraction between  $\text{Na}^+$  and  $\text{Cl}^-$  ions, in crystalline sodium chloride. They are also helpful in discussing structure, bonding and properties of ionic compounds. Lattice energies cannot be determined directly but values can be obtained indirectly by means of an energy cycle. An energy triangle of sodium chloride is shown below.



$\Delta H_f^\circ$  = Heat of formation of 1 mole of sodium chloride. It can be measured by using calorimeter.

$\Delta H_{\text{lattice}}$  = Lattice energy

$\Delta H_{\text{Born-Haber}}$  = Total energy change involved in changing sodium and chlorine from their normal physical states to gaseous ions. It can be calculated by a complete energy cycle called BORN HABER CYCLE.



It is clear from Born Haber cycle that:

$$\Delta H_{\text{Born-Haber}} = \Delta H_{\text{atom}}^{Na} + \Delta H_{\text{atom}}^{Cl_2} + \Delta H_{\text{ion}}^{Na} + \Delta H_{\text{e}}^{Cl} + \Delta H_{\text{lattice}}^{NaCl}$$

1st stage is atomization of solid sodium to gaseous atoms.  $\Delta H_{\text{atom}}^{Na} = +108 \frac{kJ}{mole}$

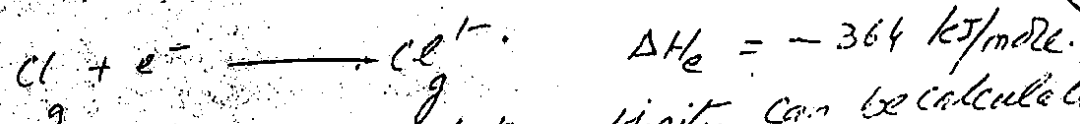
2nd stage is removal of  $e^-$  from gaseous ions to form  $Na^+$ . The enthalpy change is called ionization potential.



3rd stage is atomization of chlorine.  $\Delta H_{\text{atom}}^{Cl_2} = 121 \frac{kJ}{mole}$



4th stage is addition of  $e^-$  to chlorine atoms to form  $Cl^-$  ion. The heat released in this process is called electron affinity.  $\Delta H_{\text{e}}$



Heat of atomization and electron affinity can be calculated spectroscopically.

The heat of formation is  $\Delta H_f^\circ = \Delta H_x^\circ + \Delta H_{\text{lattice}}^\circ$

$$\Delta H_f^\circ - \Delta H_x^\circ = \Delta H_{\text{lattice}}^\circ$$

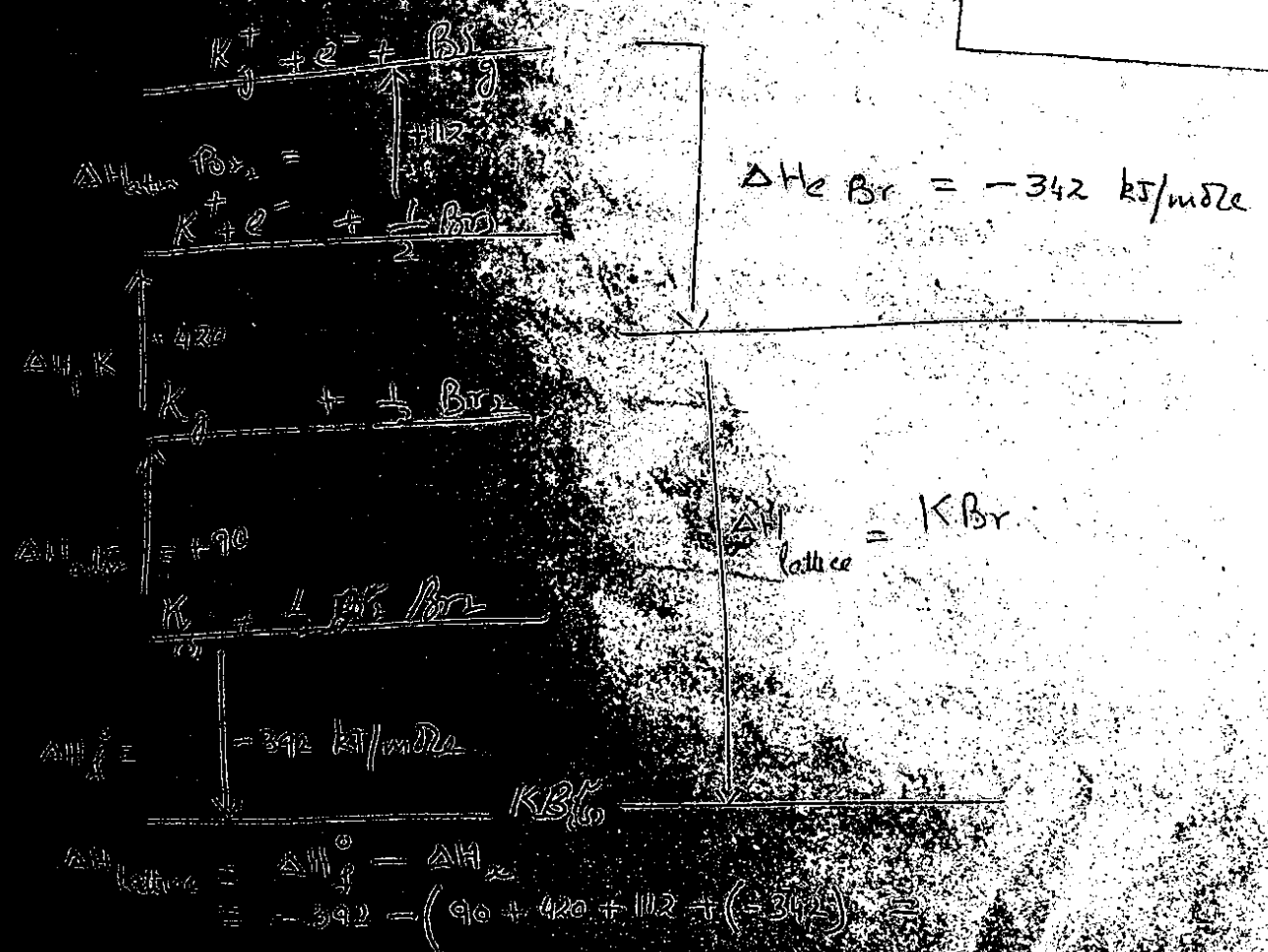
$$\Delta H_{\text{lattice}}^\circ = -411 - (\Delta H_{\text{atom}}^{\text{Na}} + \Delta H_{\text{I}}^{\text{Na}} + \Delta H_{\text{atom}}^{\text{Cl}} + \Delta H_e^{\text{Cl}})$$

$$= -411 - (108 + 500 + 121 + (-364))$$

$$= -776 \text{ kJ/mole}$$

The BORN-HABER CYCLE is a special application of Hess's Law to binary ionic compounds such as  $\text{MX}^{\oplus}\text{X}^{\ominus}$ . It is possible to calculate lattice energies with the help of BORN-HABER CYCLE.

BORN-HABER CYCLE FOR KBr IS SHOWN BELOW.



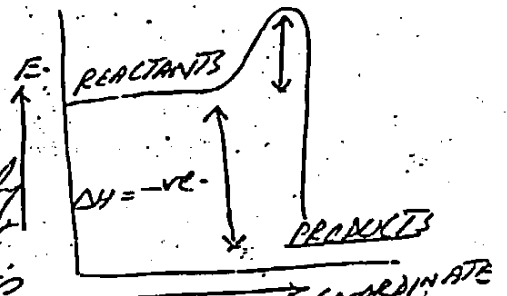
IF STRONGER BONDS ARE BROKEN AND WEAKER BONDS ARE FORMED REACTION IS EXOTHERMIC? (ENDOTHERMIC)

ANS:- The amount of energy required to break more of bonds is called bond energy. When stronger bonds are broken larger amount of energy is required. When weaker bond is formed lesser amount of energy is released. Thus when stronger bond is broken and weaker bond is formed, net reaction is endothermic. On the other hand when weaker bond is broken and stronger bond is formed more amount of energy is released. Hence reaction will be exothermic.

EXOTHERMIC REACTIONS ARE MOSTLY SPONTANEOUS?

Everything in universe has tendency to move from high energy state to low energy state.

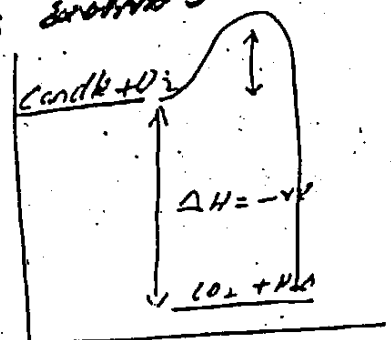
In exothermic reactions reactants have high energy as compared to products. Thus reactants spontaneously change into products. However to start an exothermic reaction some energy is required. It is called energy of Activation.



But once an exothermic reaction is started it will go on by itself. Thus exothermic reactions are mostly spontaneous.

EXPLAIN THAT BURNING OF CANDLE IS EXOTHERMIC SPONTANEOUS PROCESS:-

Burning of candle is exothermic process. And exothermic reactions are spontaneous. The reactants have high energy and products have low energy. Reactants have natural tendency to move from high energy state to low energy state. However burning of candle never starts by itself. Some energy is required to start this reaction. This is called energy of Activation. Once this reaction is started it will go on by itself. Hence it is spontaneous reaction.



WHAT IS EFFECT OF TEMP. ON SOLUBILITY OF  $Cl_2$ ?

Ans. The solubility of sodium chloride is an endothermic process.  
( $\Delta H_{\text{sol}} > 0$ ) Thus solubility of sodium chloride is favoured on heating. According to Le-Chatelier's principle increase in temp. favours endothermic reaction and decrease in temp. favours exothermic reaction.

CHANGE IN VOLUME CHANGES EQUILIBRIUM POSITION BUT NOT EQUILIBRIUM CONSTANT VALUE.

If number of moles of reactants and products are not equal equilibrium constant expression depends upon  $K_c$ . For example consider decomposition of  $PCl_5$

The expression depends upon  $K_c$ .  $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

$$K_c = \frac{x^2}{(a-x)V}$$

When volume is increased to  $V'$  then the reaction shifts forward.

$$K_c > \frac{x^2}{(a-x)V'}$$

producing more and more products until the ratio of conc. of products and reactants once again becomes equal to  $K_c$ . The value  $K_c$  will remain constant as it depends upon relative stabilities of reactants and products.

CHANGE IN TEMP. CHANGES BOTH EQUILIBRIUM POSITION AND EQUILIBRIUM CONSTANT VALUE.

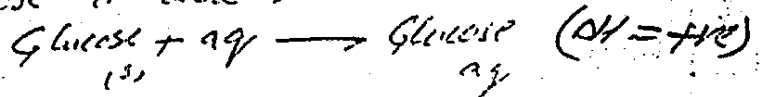
According to Le-Chatelier's principle increase in temp. favours endothermic reaction and decrease in temp. favours exothermic reaction. Thus by changing temp. either the forward or backward reaction is increased.

The temp. also affects relative stabilities of reactants and products therefore it also affects relative conc. and hence value of  $K_c$ .

SOLUBILITY OF GLUCOSE INCREASES WITH TEMP.

The solubility of glucose in water is an endothermic process. Endothermic processes are favoured on heating.

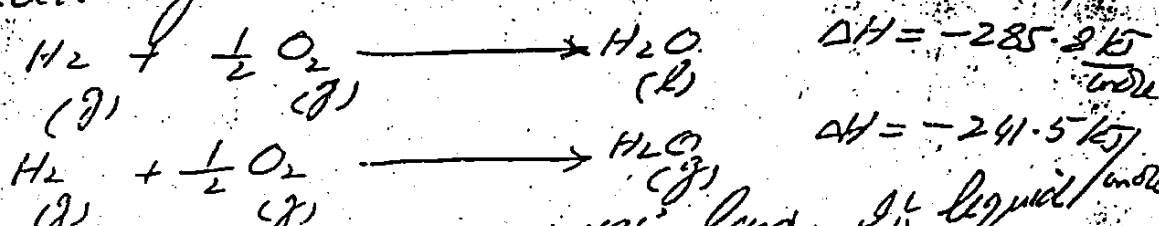
Hence solubility of glucose in water increases with temp.



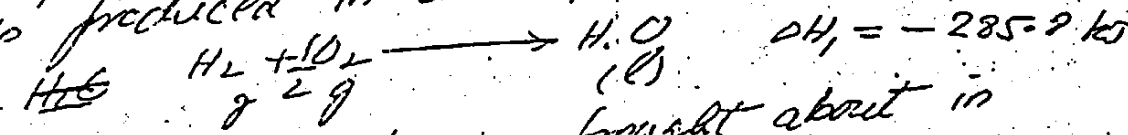
IT IS NECESSARY TO MENTION PHYSICAL STATES OF REACTANTS AND PRODUCTS IN THERMOCHEMICAL REACTIONS. EXPLAIN USING HESS'S LAW?

Each physical state has specific energy. Thus whenever a chemical reaction takes place, the amount of heat depends upon physical state of reactants and products.

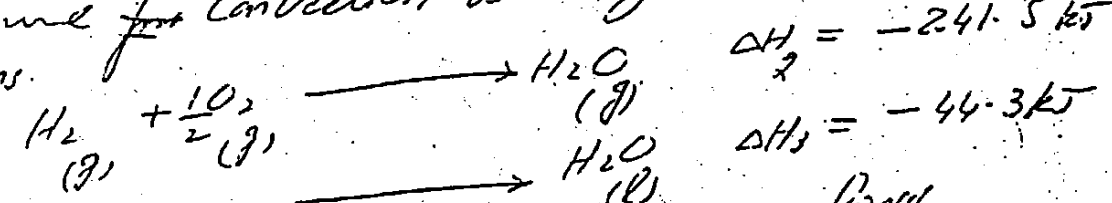
For example consider formation of water from  $H_2$  and  $O_2$ . When water is produced in liquid state the energy released is  $-285.8 \text{ kJ/mole}$ . But when it is produced in gaseous state heat released is  $-241.5 \text{ kJ/mole}$ .



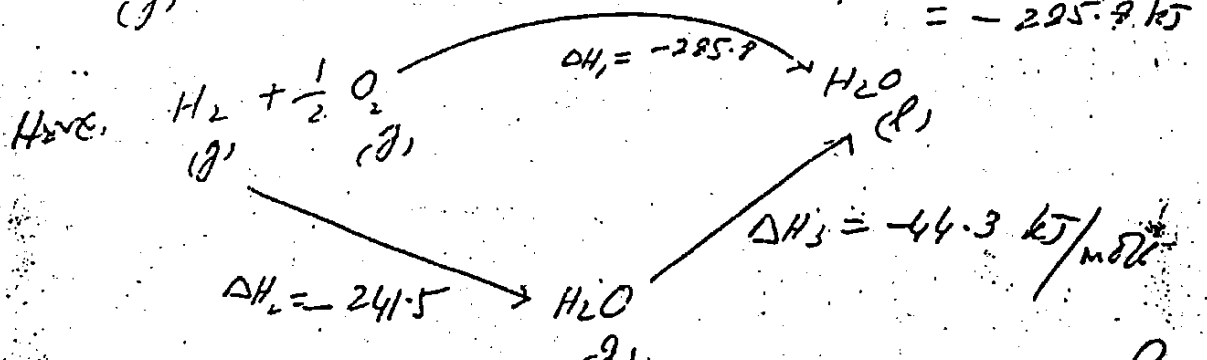
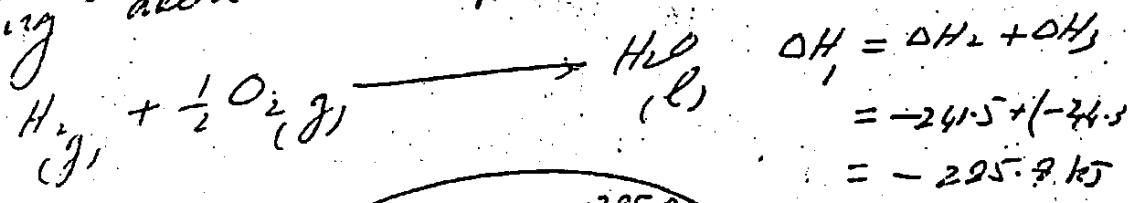
Let us explain it using Hesses' Law. If liquid water is produced in one step then  $\Delta H_1 = -285.8$



Now same for conversion is brought about in two steps.



By adding above two equations we have



Therefore it is always essential to mention physical states of reactants and products in a thermochemical reaction. The heat of reaction depends upon energy physical states of reactants and products.



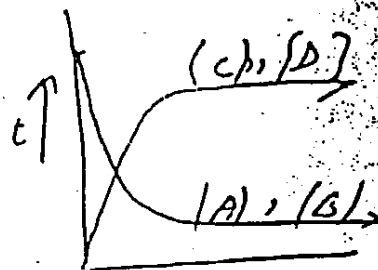
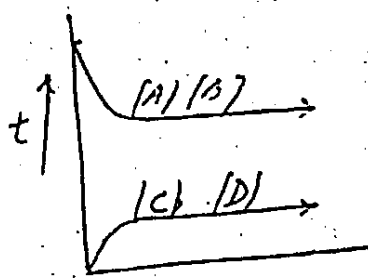
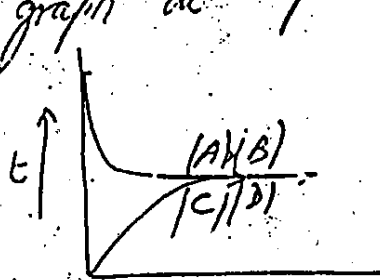
SHORT QUESTIONS:-

RATE OF REACTION DECREASES WITH TIME. EXPLAIN WHY?

Ans: According to law of Mass Action, rate of reaction is directly proportional to molar conc. of reactants. As reaction proceeds molar conc. of reactants decreases because they are converted into products. Thus rate of forward reaction decreases with fallage of time.

CONC. OF REACTANTS & PRODUCTS BECOMES CONSTANT BUT NOT ALWAYS EQUAL AT EQUILIBRIUM STATE?

The conc. of reactants and products at equilibrium state depend upon their relative stabilities. If reactants and products are equally stable their conc will be equal at equilibrium state. However in most of cases reactants and products are not equally stable. Hence their conc. is not equal. Since at eq. state rate of forward reaction and rate of backward reaction become equal therefore conc. of reactants and products becomes constant. It is clear from following graph at eq. state. For reaction  $A+B \rightleftharpoons C+D$

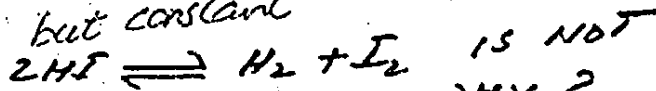


Conc. equal and const.

Conc. unequal but constant

Conc. unequal but const.

GASEOUS REACTION



EFFECTED BY PRESSURE CHANGES. WHY?

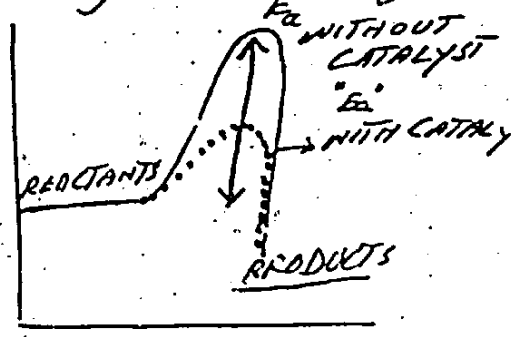
According to Le-Chatelier's principle increase in pressure shifts equilibrium in a direction of decrease in vol. or decrease in number of moles. Since in above reaction no. of moles are equal on both sides hence there is no effect of volume or pressure changes. In

ICE CAN BE MELTED BY APPLICATION OF PRESSURE WITHOUT SUPPLYING HEAT. WHY?

Ice and water are in equilibrium at  $0^\circ\text{C}$ .  $\text{ICE} \rightleftharpoons \text{H}_2\text{O}$   
 According to Lechatelier's principle increase in pressure shifts equilibrium in a direction of decrease in volume. Volume of water is less than ice. Thus when pressure is applied ice changes into water. The heat required for melting ice (heat of fusion) is absorbed from ice-water mixture. Hence temperature of equilibrium mixture decreases by applying pressure.

CATALYST DOES NOT CHANGE CONC. OF REACTANTS AND PRODUCTS? BUT DECREASES TIME TO REACH EQ. STATE

Catalyst speeds up the rate of reaction by decreasing energy of activation. The relative energies and stabilities of reactants and products remain the same by using catalyst. Hence conc. of reactants and products remains the same with or without catalyst. The rate of forward and backward reaction is increased. Hence catalyst decreases the time required to reach equilibrium state.



BUFFER SOLUTION HAS CONSTANT pH BUT ALL BUFFER SOLUTIONS DO NOT HAVE EQUAL pH.

pH of buffer solution depends upon  $pK_a$  of acid or  $pK_b$  of base and relative conc. of salt and acid or salt and base. It is given by Henderson equation.

Since all acids do not have equal  $pK_a$  and all bases do not have equal  $pK_b$ . Further pH and pOH can also be changed by changing relative conc. of salt and acid or salt and base. Thus buffer solutions have constant pH but all buffer solutions do not have equal pH.

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Q1) Q. - CALCULATE pH OF BUFFER SOLUTION CONTAINING 6.0g ACETIC ACID AND 8.2g SODIUM ACETATE ( $pK_a = 4.75$ )

SOLUTION:- pH OF BUFFER SOLUTION IS GIVEN BY HENDERSON EQ.

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

MOLES OF ACID =  $\frac{6.0}{60}$   
= 0.1 MOLES.

$$pH = 4.75 + \log \frac{0.1}{0.1}$$

MOLES OF SALT =  $\frac{8.2}{82}$   
= 0.1 MOLE

$pH = 4.75$  ANS.

(NOTE:- IF  $pK_a$  OF ACID IS GIVEN THEN FIRST FIND ITS  $pK_a = -\log K_a$ )

$pK_a = -\log 1.8 \times 10^{-5}$   
( $pK_a = 4.75$ )

Q2:- WHAT ARE OPTIMUM CONDITIONS FOR MAXIMUM YIELD OF  $NH_3$  BY HABER PROCESS.

ANS:- Chemical eq. of Haber process is  $N_2 + 3H_2 \rightleftharpoons 2NH_3 + \text{HEAT}$   
From chemical equation Le-Chatelier's principle predicts that for max. yield of  $NH_3$  following conditions are favourable  $\Delta H = -92.46$  KJ

(i) Reactants are continuously added to the reaction mixture ( $N_2, H_2$ ) and product  $NH_3$  must be removed from mixture.  $NH_3$  is removed by cooling in refrigeration coil until  $NH_3$  condenses.  $H_2$  and  $N_2$  remain in gaseous form.

(ii) Pressure must be kept high as there is decrease in number of moles in forward direction so at high P. reaction proceeds more and more in forward direction. In actual practice  $P = 200 - 300$  atm. Pressure is used.

(iii) Since reaction is exothermic. therefore according to Le-Chatelier's principle Temp. must be kept low. Actual Temp used is  $400^\circ C$ . Below this Temp. rate of reaction is decreased appreciably. Therefore Temp. is kept at moderate level to keep process economical.

(iv) Catalyst used is pieces of Iron Crystal embedded in fused mixture of  $MgO, Al_2O_3$  and  $SiO_2$ . Catalyst does not increase % yield but decreases time required to reach eq. state.

NOTE:- SAME QUESTION CAN BE ASKED FOR  $SO_3$  SYNTHESIS

Other words pressure will have some effect on both sides. Mathematically it could be shown as follows.

Let us consider "a" moles of HI in "V" litre flask. Let at eq. state 2x moles of HI decompose to produce "x" moles of H<sub>2</sub> and "x" moles of I<sub>2</sub>.

$$2HI \rightleftharpoons H_2 + I_2$$

Initial conc.	a mole	0	0
At eq. state	a - 2x	x	x

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-2x}{V}\right)^2}$$

$$K_c = \frac{x^2/V^2}{(a-2x)^2/V^2}$$

$$K_c = \frac{x^2}{(a-2x)^2}$$

Final expression is independent of volume changes. WHAT IS EFFECT OF PRESSURE ON EQUILIBRIUM POSITION OF FOLLOWING REACTION.

PCl<sub>5</sub> ⇌ PCl<sub>3</sub> + Cl<sub>2</sub>  
 According to Lechatlier's principle increase in pressure shifts equilibrium in a direction of decrease in volume or decrease in number of moles. In above reaction there is decrease in number of moles in backward direction thus it will shift in backward direction by increasing pressure. In other words dissociation is favoured at low pressure and high volume. It can be shown as follows.  
 By increasing pressure volume is decreased and expression becomes

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

a	0	0
a - x	x	x

$$\frac{a-x}{V} \rightleftharpoons \frac{x}{V} \quad \frac{x}{V}$$

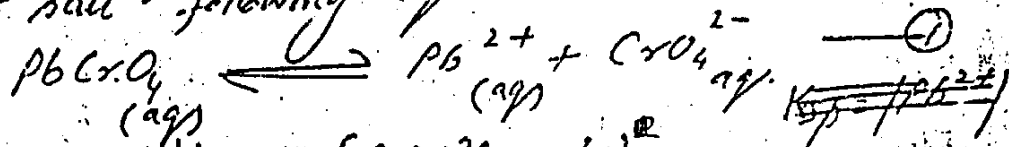
$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{(a-x)/V}$$

$$K_c = \frac{x^2}{(a-x)V}$$

Hence reaction shifts backward on increasing pressure.

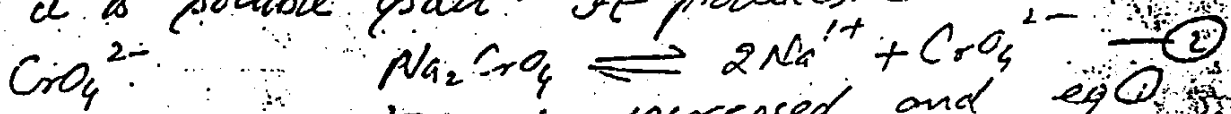
Q. No. \_\_\_\_\_ COMMON ION  
WHAT IS EFFECT OF SOLUBILITY ON SOLUBILITY?

ANS:- The common ions decrease probability of salt. Let us consider a sparingly soluble ionic salt. In a saturated solution of salt following equilibrium is established.



$$K_{sp} = [Pb^{2+}][CrO_4^{2-}]$$

Now if a strongly electrolyte  $Na_2CrO_4$  is added it is soluble salt. It produces common ions



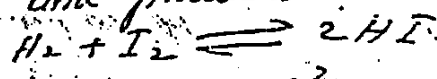
The conc of  $CrO_4^{2-}$  ions is increased and eq (1) shifts backward. Thus  $PbCrO_4$  is precipitated. While  $K_{sp}$  value remains constant. By addition of  $Na_2CrO_4$

it becomes  $K_{sp} < [Pb^{2+}][CrO_4^{2-}]$

Reaction shifts backward and solubility of  $PbCrO_4$  is decreased

WHAT ARE UNITS OF  $K_c$

Q. No. \_\_\_\_\_  
 The units of " $K_c$ " depends upon nature of reaction  
 If number of moles of reactants and products are equal  
 $K_c$  has no units

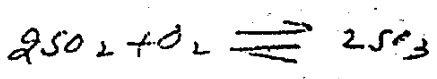


$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{(conc)^2}{(conc)(conc)} = \frac{1}{1}$$

If number of moles are not equal  $K_c$  has some units

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$



$$K_c = \frac{[conc]^2}{(conc)(conc)^2}$$

Thus in this case  $K_c$  has units of  $conc^{-1}$  or  $\frac{dm^3}{mole}$

$$K_c = \frac{1}{conc}$$

$$K_c = conc^{-1}$$

$$K_c = \left(\frac{mole}{dm^3}\right)^{-1}$$