



University School of Automation and Robotics
GURU GOBIND SINGH INDRAPIRASTHA UNIVERSITY
East Delhi Campus, Surajmal Vihar
Delhi - 110092



Engineering Chemistry-I (BS-109)

Thermochemistry

Dr. Shruti Khanna Ahuja

Assistant Professor

USAR, GGSIPU

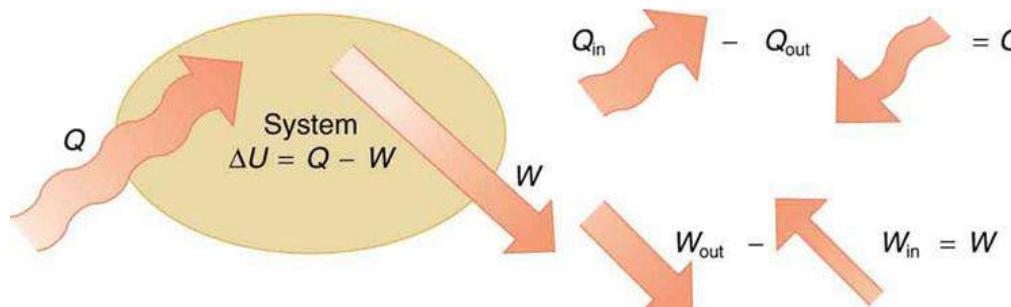


- **What is the difference between Thermodynamics and Thermochemistry?**

Thermodynamics is the branch of physical science that deals with the relations between heat and other forms of energy such as mechanical, electrical, or chemical energy.

Thermochemistry is the quantitative study of the relation between heat and chemical reactions. It primarily deals with the transfer of heat between a chemical system and its surroundings when a change of phase or a chemical reaction takes place within the system.

- Thermochemistry, in fact, implies the first law of thermodynamics to a chemical reaction. According to this law, “ Energy can neither be created nor can be destroyed, but can be converted from one state to the other” (Conservation of Energy)
- In other words, change in internal energy of a system equals the net heat transfer into the system minus the net work done by the system.
- In equation form, the first law of thermodynamics is $\Delta U = Q - W$, where ΔU is the change in internal energy, U of the system. Q is the net heat transferred into the system—that is, Q is the sum of all heat transfer into and out of the system. W is the net work done by the system—that is, W is the sum of all work done on or by the system.





- **Change of internal energy in a chemical reaction:**

In chemical systems, the most common type of work is pressure-volume (PV) work, in which the volume of a gas changes. Substituting this in for work in the above equation, we can define the change in internal energy for a chemical system:

$$\Delta U = Q - P\Delta V$$

Let's examine the internal energy change, ΔU , at constant volume. At constant volume, $\Delta V=0$, the equation for the change in internal energy reduces to the following:

$$\Delta U = Q_V \dots\dots\dots \text{Heat exchanged at constant } V$$

So, let U_R be the internal energy of reactants and U_P be that of products,

$$\Delta U = U_P - U_R = Q_V \dots\dots\dots \text{Heat of reaction at constant } V$$

- This internal energy is often very difficult to calculate in real life settings, though, because chemists tend to run their reactions in open flasks and beakers that allow gases to escape to the atmosphere. Therefore, volume is not held constant, and calculating ΔU becomes problematic. To correct this, the concept of *enthalpy* is considered, which is much more commonly used by chemists.



- **Change of enthalpy in a chemical reaction:**

Change in enthalpy of a given reaction can be expressed as follows:

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

When you run a chemical reaction in a laboratory, the reaction occurs at constant pressure, because the atmospheric pressure around us is relatively constant.

$$\Delta U = Q - W = Q - P\Delta V$$

Substituting to combine these two equations, we have:

$$\Delta H = Q - P\Delta V + P\Delta V = Q_p$$

Thus, at constant pressure, the change in enthalpy is simply equal to the heat released/absorbed by the reaction.

- In general, if HR is the enthalpy of reactants and HP is the enthalpy pf products, then

$$\Delta H = H_p - H_r = Q_p \dots\dots \text{Enthalpy of reaction}$$

- $\Delta H = \sum a_i H_p - \sum b_i H_r$, where a_i and b_i are stoichiometric coefficients of products and reactants, respectively

e.g. for a reaction, $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$

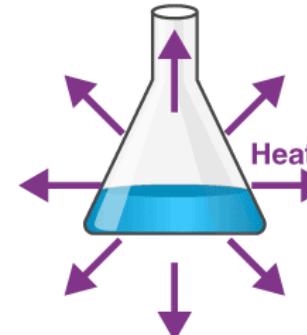
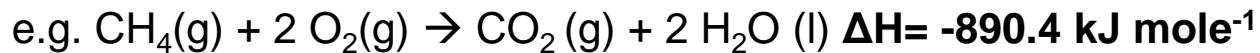
$$\Delta H = [2H_{(\text{Fe, s})} + 3H_{(\text{H}_2\text{O, l})}] - [H_{(\text{Fe}_2\text{O}_3, \text{s})} + 3H_{(\text{H}_2, \text{g})}]$$

- **Enthalpy of a reaction:** The amount of heat evolved or absorbed in a chemical reaction, when number of moles of the reactants by the chemical reaction have completely reacted

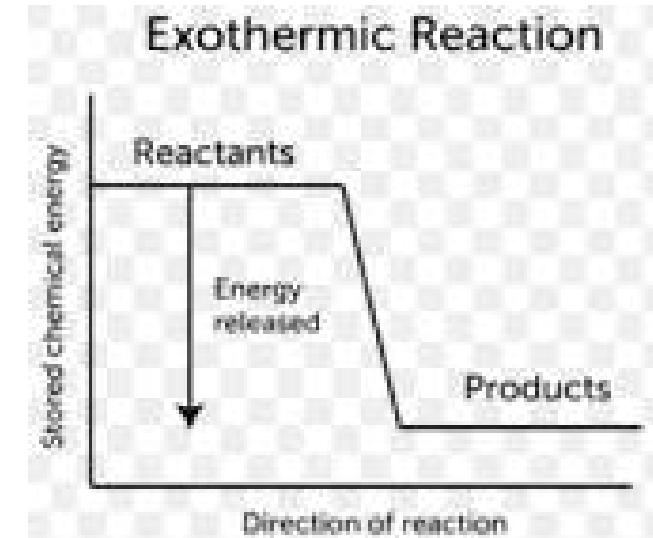


- Exothermic and Endothermic reactions:

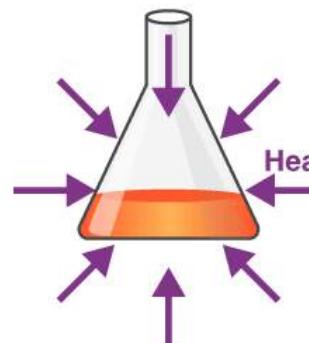
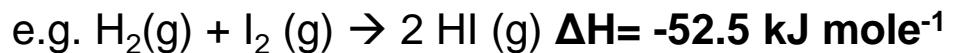
Exothermic reactions: A reaction that releases energy in the form of heat. Here, $\Sigma H_P < \Sigma H_R \Rightarrow \Delta H = \text{negative}$



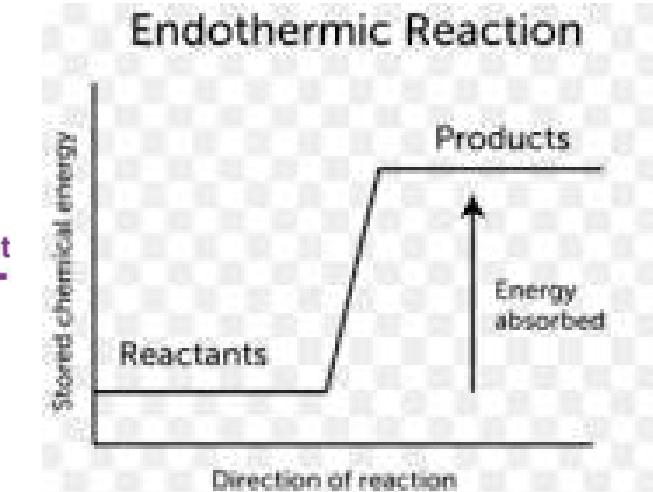
Exothermic Reaction



Endothermic reactions: A reaction wherein heat is absorbed by the system from the surroundings. Here, $\Sigma H_P > \Sigma H_R \Rightarrow \Delta H = \text{positive}$



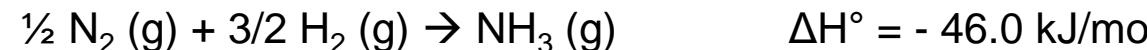
Endothermic Reaction





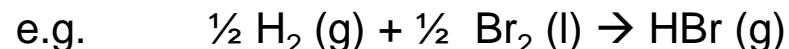
- **Standard enthalpy of reaction:**

When all the chemical species in a chemical equation are present in the respective standard states, the enthalpy of reaction determined at 25 °C and 1 atm pressure, then it is known as standard enthalpy of reaction (ΔH°).



- **Standard enthalpy of formation (ΔH_f°):** The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable states of aggregation.

$$\Delta H_f^\circ = \sum H_f^\circ \text{ Products} - \sum H_f^\circ \text{ Reactants}$$



$$\Delta H_f^\circ = [H_f^\circ_{(HBr, g)}] - [\frac{1}{2} H_f^\circ_{(H_2, g)} + \frac{1}{2} H_f^\circ_{(Br_2, l)}]$$

- The standard enthalpy of formation of every element in its stable state of aggregation at 1 bar pressure and at specified temperature (25 °C) is assigned a zero value.

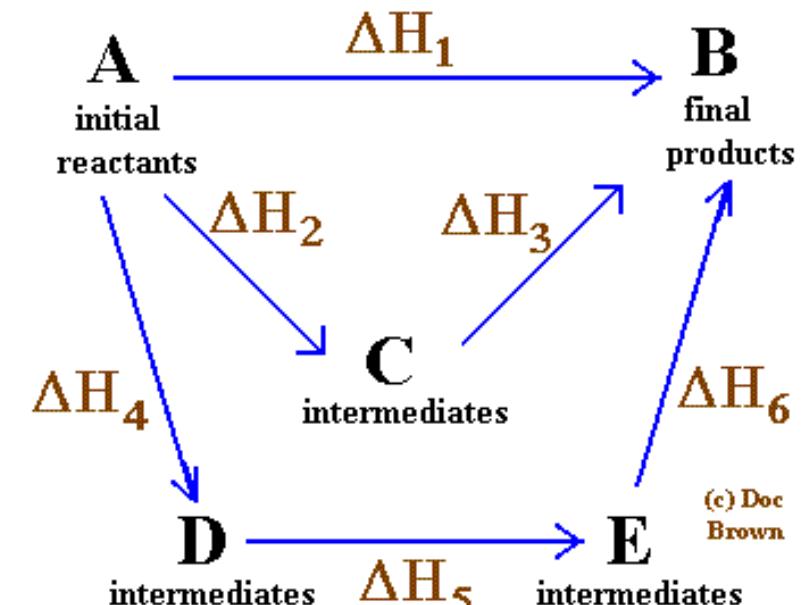
e.g.	$\Delta H_f^\circ (O_2, g) = 0$	$\Delta H_f^\circ (S, \text{ rhombic}) = 0$
	$\Delta H_f^\circ (C, \text{ graphite}) = 0$	$\Delta H_f^\circ (P, \text{ white}) = 0$
	$\Delta H_f^\circ (Br_2, l) = 0$	



- **Hess's Law of constant heat summation:** Named after Russian Chemist and Doctor Germain Hess. According to this law, “ The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps”
- All steps have to proceed at the same temperature and the equations for the individual steps must balance out.
- It is a consequence of the first law of thermodynamics and need not be considered a separate thermodynamic law; in thermochemistry, however, it retains its identity because of its importance as the basis for calculating heats of reactions.
- Hess's law can be written as $\Delta H^\circ = \sum \Delta H_n$, where ΔH° is the heat absorbed or evolved and $\sum \Delta H_n$ is the sum of the heat absorbed or evolved in the individual n steps of the reaction.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation.

Reactant A can form product B by following three different steps. C, D and E are intermediates in the other stepwise reactions. Hess' law states that the enthalpy of the reaction (ΔH_1) is the same irrespective of the path.

So, the enthalpy of direct single-step reaction and other paths giving intermediates C, D and E should be the same. $\Delta H_1 = \Delta H_2 + \Delta H_3 = \Delta H_4 + \Delta H_5 + \Delta H_6$.



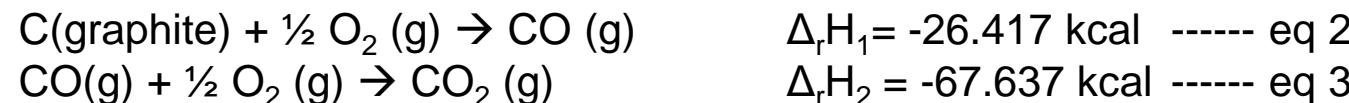


- **Applications of Hess's Law:**

1. **Determination of enthalpy of a reaction.** Sometimes, it is difficult to determine the enthalpy of a reaction experimentally, e.g. enthalpy change in the following reaction



can be estimated from the following two reactions:



on adding eqns 2 and 3, we get eq 1:

$$\begin{aligned}\Delta_r H &= \Delta_r H_1 + \Delta_r H_2 \\ \Delta_r H &= -26.417 + (-67.637) = -94.054 \text{ kcal}\end{aligned}$$

2. **Determination of lattice energy of a crystal (Born-Haber cycle).** Lattice energy is defined as the energy released when number of positive and negative ions combine to form one mole of the ionic compound.

- Larger the lattice energy, more stable is the ionic compound and more tightly the ions are held.



3. Enthalpy change in a physical change

Carbon and diamond are allotropes of carbon. But measuring the energy change in the conversion of graphite to diamond cannot be determined, as the process cannot be carried out. Still, the heat changes for this hypothetical physical change can be calculated using Hess law.

Graphite and diamond combine with oxygen with the heat of reaction as -393.4 kJ and – 395.4 kJ respectively.



Subtracting (2) from (1)



Enthalpy change in the allotrope transition of graphite to diamond is endothermic of 2 kJ.



- **Variation of enthalpy of a reaction with temperature (Kirchhoff's Relation):** is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants.
- The heat change accompanying chemical or physical processes generally depends on the temperature at which the process takes place.
- Kirchhoff equation relates the heat of reaction with the definite heats of a structure before and after the reaction.
- Consider a reaction, $aA + bB \rightarrow cC + dD$, the enthalpy change for the above reaction will be:

$$\Delta H = \sum a_i H_P - \sum b_i H_R$$

$$\Delta H = [cH_C + dH_D] - [aH_A + bH_B] \quad \dots\dots(1)$$

On differentiating the above equation w.r.t. temperature at constant pressure, we get

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = c \left(\frac{\partial H_C}{\partial T} \right)_P + d \left(\frac{\partial H_D}{\partial T} \right)_P - a \left(\frac{\partial H_A}{\partial T} \right)_P - b \left(\frac{\partial H_B}{\partial T} \right)_P$$

The variation of enthalpy of a substance with temperature at a given pressure is given by:

$$(dH/dT)_P = C_P \quad \text{where } C_P \text{ is the heat capacity}$$

On substituting it in above eq:

$$\left[\frac{\partial(\Delta H)}{\partial T} \right]_P = c C_{P,C} + d C_{P,D} - a C_{P,A} - b C_{P,B} = \Delta C_P \quad \dots\dots(2)$$



where, $\Delta C_p = \left(\frac{\text{sum of heat capacities}}{\text{of products}} \right) - \left(\frac{\text{sum of heat capacities}}{\text{of reactants}} \right)$

So, Eq (2) is called KIRCHHOFF'S Equation. It states that variation of ΔH of a reaction with temperature at constant pressure is equal to ΔC_p of system. We can write it as.

$$[\frac{\partial(\Delta H)}{\partial T}]_p = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p dT \quad \dots \dots \quad (3)$$

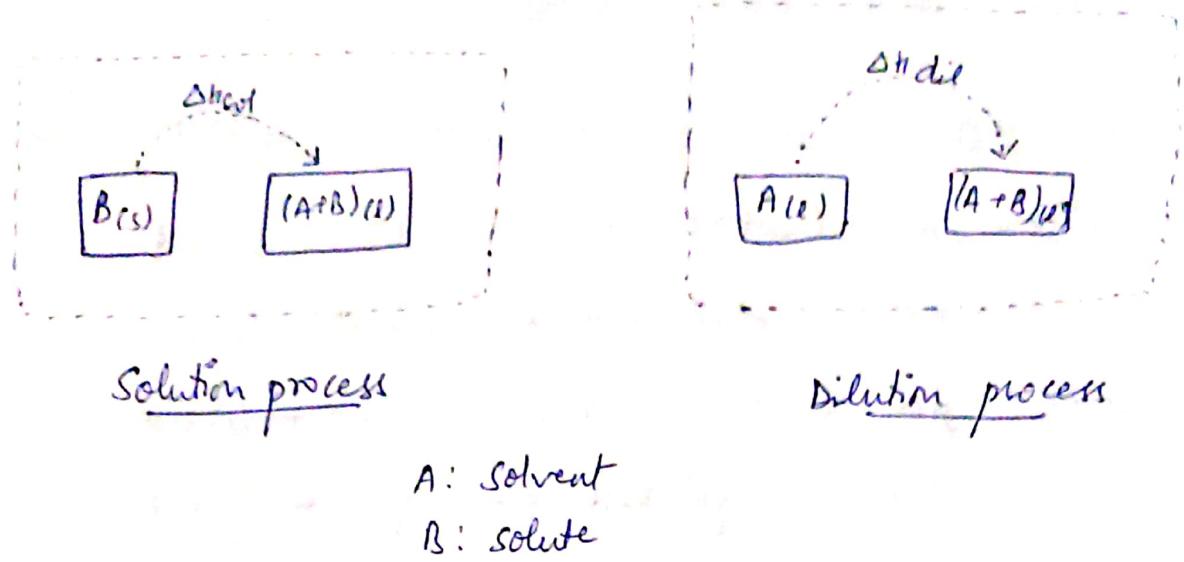
If taking temperature range from T_1 to T_2 , Eq (3) can be easily integrated, we get:

$$\int_{T_1}^{T_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p \int_{T_1}^{T_2} dT$$

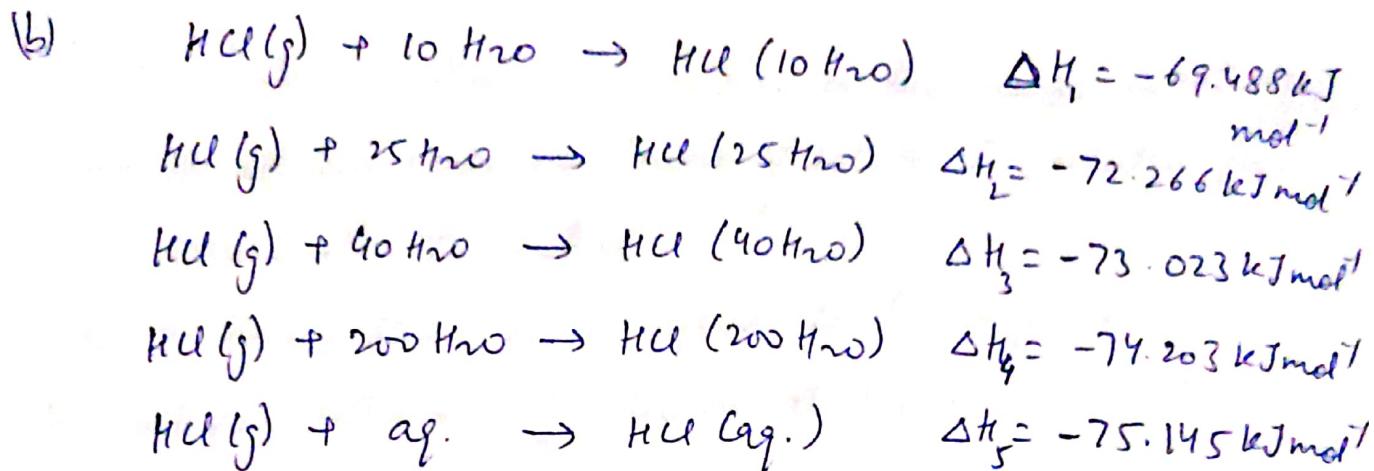
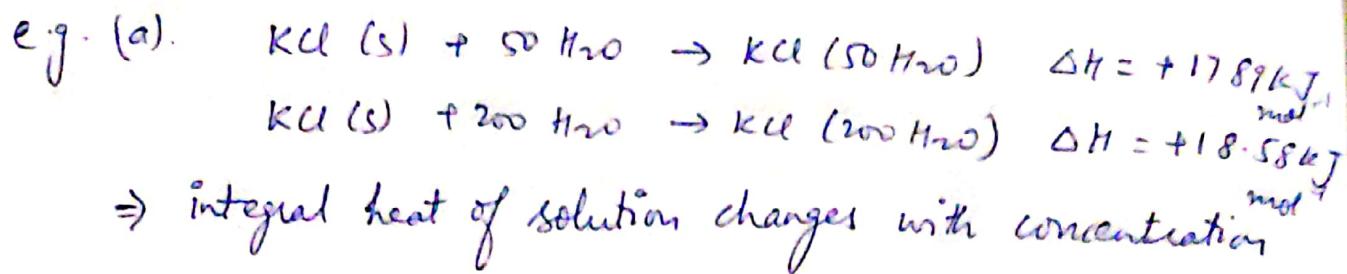
O.R

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

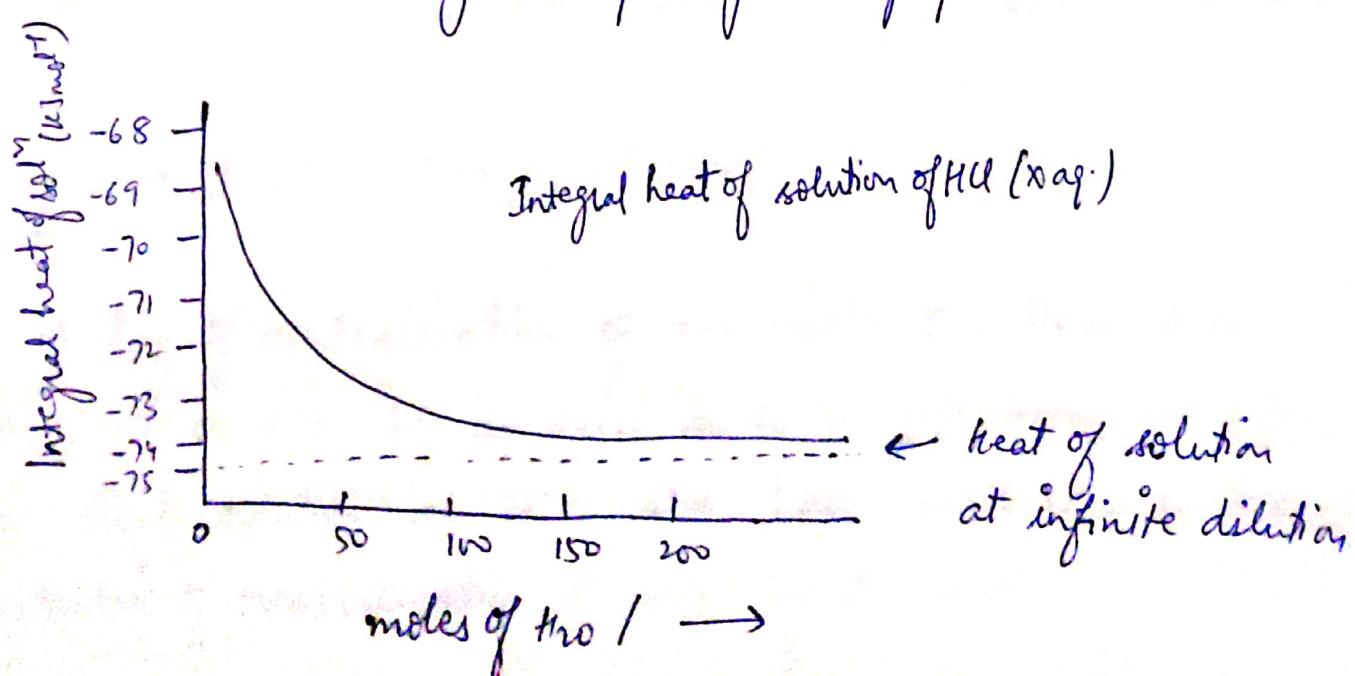
- Heat of solution and heat of dilution:



- The processes of solution (dissolution) and dilution are related.
- During a solution process, a solute is transferred from a pure solute phase (solid, liquid, or gas) to a solvent or solution phase.
- During a dilution process, solvent is transferred from a pure solvent phase to a solution phase.
- The dissolution of solute in a solvent is often accompanied by either evolution or absorption of heat. The amount of heat evolved or absorbed depends on the nature of solute and the solvent and also on the composition of the solution.
- "The enthalpy change when one mole of the solute is dissolved in a definite amount of solvent to produce a solution of desired concentration is known as integral enthalpy of solution at the given concentration"



Where, ΔH_5 represents the limit of enthalpy change when 1mol of $\text{HCl}(\text{g})$ is dissolved in a very large quantity of water. The resultant solution is known as an infinite diluted solution. The value of ΔH at infinite dilution can be obtained by extrapolating the graph.

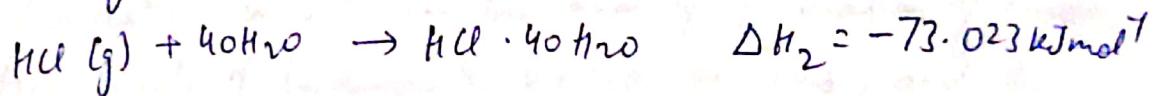
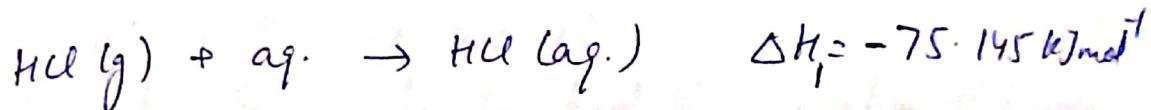
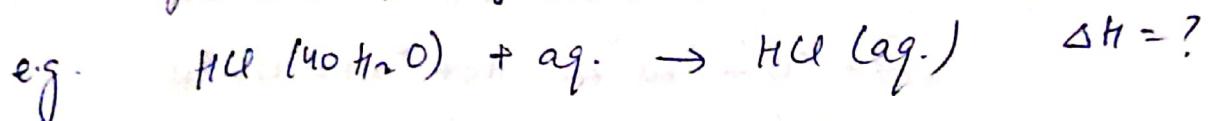


At infinite dilution, the heat change becomes constant

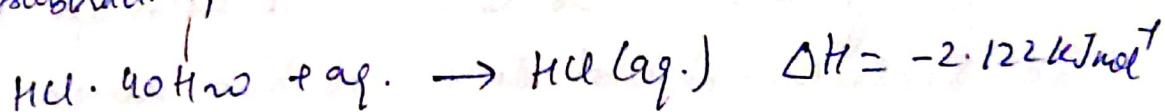
→ Now that, the enthalpy of solution of a solute varies with its concentration implies that there must be a change of enthalpy when a solution is diluted by adding more solvent.

"The integral enthalpy of dilution is the change in enthalpy when a solution containing 1 mole of solute is diluted from one concentration to another"

Acc. to Hess's law, it is equal to the difference between the integral enthalpies of solution at the two concentrations.

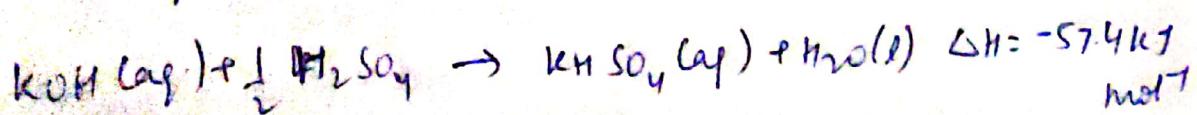
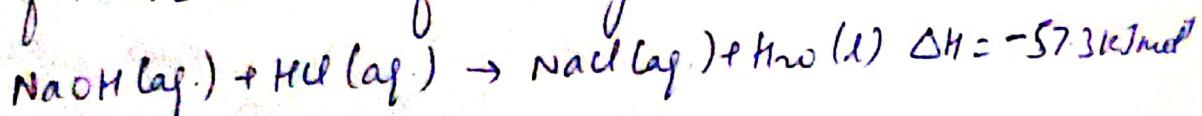


on subtraction,

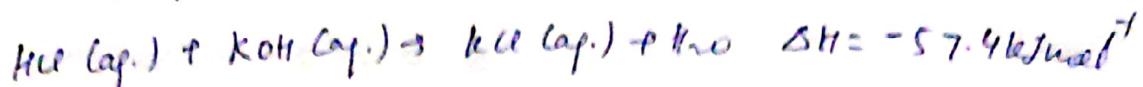


Heat of neutralization ($\Delta H_{\text{neutral.}}$):

→ Enthalpy of neutralization of one mole of a base such as NaOH or KOH by an acid such as HCl, HNO₃ and H₂SO₄ in dilute solution at 25°C and 1 atm pressure is called enthalpy of neutralization of base by the acid.

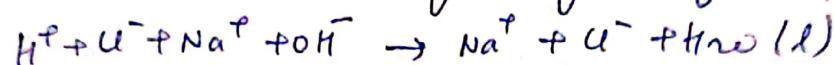


Similarly, the enthalpy change accompanying the neutralisation of 1 mole of an acid by a base in dilute solutions at 25°C and 1 atm pressure is known as standard enthalpy of neutralisation of acid by the base.



⇒ Amount of heat evolved (exothermic) when 1 mole of an acid is neutralised by 1 mole of base in large excess of water.

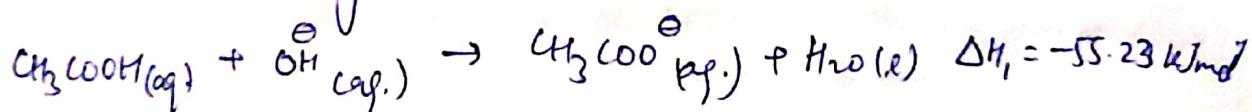
→ When acid and base are both strong, they undergo complete dissociation,



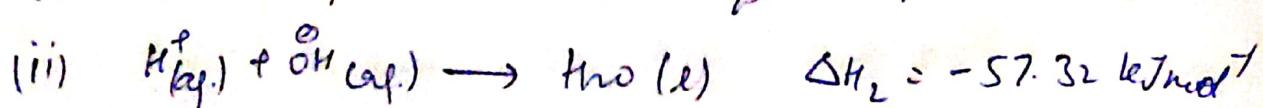
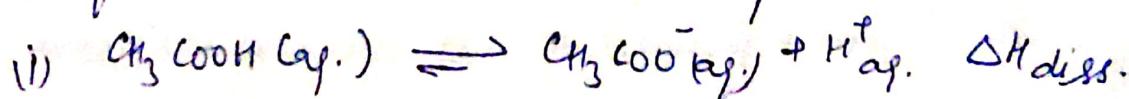
i. heat of neutralisation is actually the heat of formation of 1 mole of water from 1 mole of hydrogen & hydroxide ions, and this is always equivalent to 13.7 kcal or 57.32 kJ of heat.

→ However, when a weak acid or a weak base is neutralised, the $\Delta H_{\text{neu.}}$ changes as there is no complete dissociation of ions.

e.g. weak acid and strong base :



this equation can be considered in 2 steps:



Acc to Hess's law,

$$\Delta H_1 = \Delta H_{\text{diss.}} + \Delta H_2$$

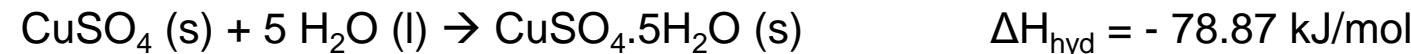
$$\begin{aligned}\Delta H_{\text{diss.}} &= \Delta H_1 - \Delta H_2 \\ &= -55.23 - (-57.32) \\ &= 2.09 \text{ kJ/mol}^{-1}\end{aligned}$$



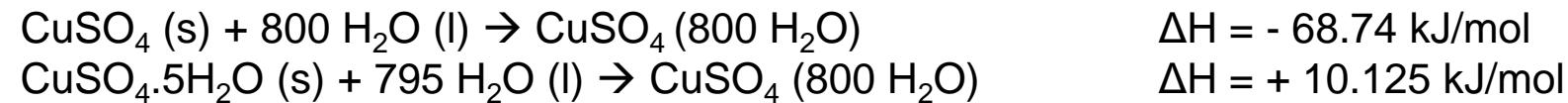
- **Heat of hydration:**

The enthalpy change when a given anhydrous or partially hydrated salt combines with the requisite amount of water to form a new hydrated stable salt.

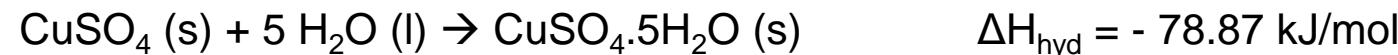
e.g. hydration of anhydrous cupric sulphate :



- In order to dissolve an ionic solid, water molecules must break up the interactions between all of the ions in the solid. To do this, they orient themselves such that they effectively reduce the localized charge on the ions. This is called hydration.
- Hydration of ions is a thermodynamically favorable process, and as such can **release heat i.e. $\Delta H = \text{negative}$**
- Enthalpy of hydration can be readily calculated from the integral enthalpies of solution of the hydrated and anhydrous salts.

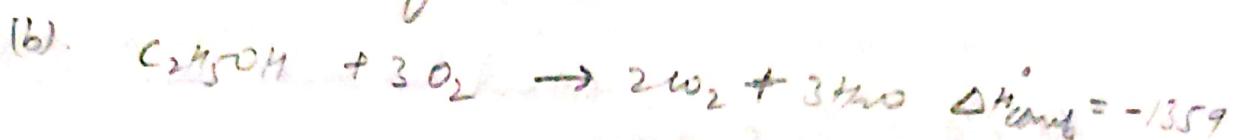
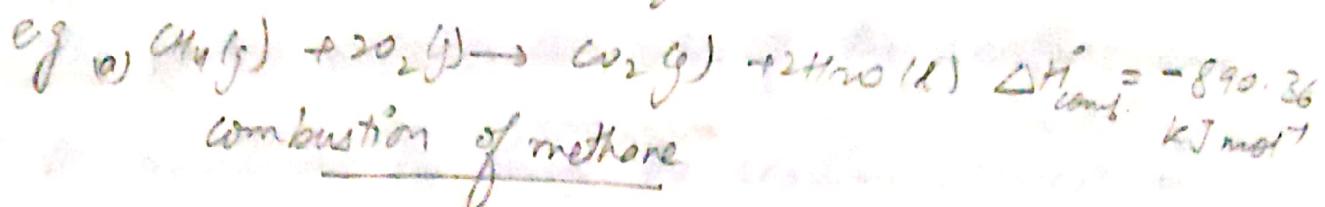


subtracting the two, we get



- Heat of Combustion (ΔH_{comb}):

It is the enthalpy change when 1 mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.



Heat of combustion is experimentally determined in a "bomb calorimeter", which is a pressure vessel internally enamelled with platinum.

- Flame temperature:

→ Adiabatic flame temperature is a temperature which the system attains if the changes in the system are carried out under adiabatic condition. It is the maximum temperature of the combustion gas that can be reached during combustion.

→ For an isobaric (const pressure) adiabatic process, the flame temperature can be calculated using the Krichhoff eq

$$\frac{d(\Delta H)}{dT} = \Delta Q \quad \text{or} \quad d(\Delta H) = \Delta Q dT$$

on integration,

Assumption:
over neglecting
change, $\Delta P = \text{const} \Rightarrow \Delta H = \Delta Q$

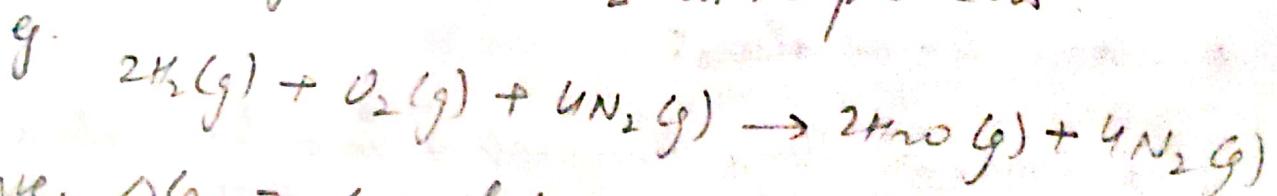
$$\int d(\Delta H) = \Delta Q \int_{T_i}^{T_f} dT$$

$$\Delta H = \Delta Q (T_f - T_i)$$

T_i : initial temp
 T_f : final temp
(flame temp)

→ Comment on ΔG_f : The flame temp° would obviously depend on the composition and heat capacities of the resultant gases. In the flames produced by combustion of fuels in air, unreacted nitrogen, present in the atmosphere, is also heated up along with the gaseous products to the flame temperature.

→ Since air contains about 20% O₂ and 80% N₂ by volume, the combustion involving 1 mole of O₂ is associated with 4 moles of unreacted N₂ in the products.



Hence, $\Delta G_f = \text{sum of } G_f \text{ of products} + G_f \text{ of 4 moles}$
 $\text{of unreacted } N_2$
per mole of O₂

$$\Rightarrow \Delta G_f = \sum G_{f\text{products}} + 4G_{f,N_2}$$



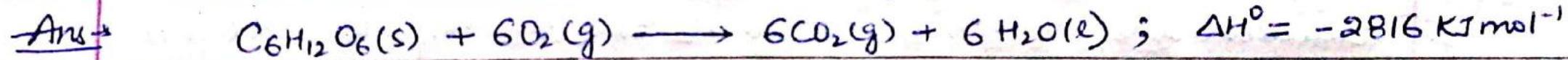
1. Comment by a student, "In an endothermic reaction, if heat is taken in during the reaction, the temperature should go up, not down." Clear the doubt.

Ans If reaction being endothermic, the energy taken in is being consumed to break the bonds in reactants so that it does not have chance to appear as heat and raise the temperature.



9. Enthalpy of combustion of glucose $C_6H_{12}O_6(s)$ is $-2816 \text{ KJ mol}^{-1}$ at 25°C .

Calculate $\Delta H_f^\circ (C_6H_{12}O_6)$. The ΔH_f° value for $CO_2(g)$ and $H_2O(l)$ are -393.5 and $-285.9 \text{ KJ mol}^{-1}$, respectively.



Since, $\Delta H = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$, we find that

$$-2816 \text{ KJ mol}^{-1} = [6(-393.5) + 6(-285.9)] - [\Delta H_f^\circ (C_6H_{12}O_6) + \Delta H_f^\circ (O_2) \times 6]$$

$$-2816 \text{ KJ mol}^{-1} = [(-2361) + (-1715.4)] - [\Delta H_f^\circ (C_6H_{12}O_6)] \text{ as, } \Delta H_f^\circ (O_2) = 0$$

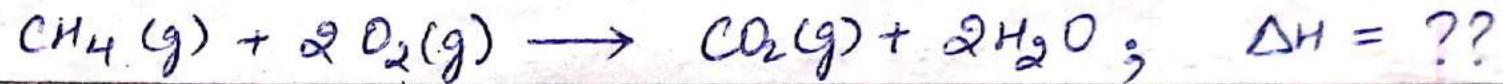
$$\Delta H_f^\circ (C_6H_{12}O_6) = -1260.4 \text{ KJ mol}^{-1}$$



3. Calculate enthalpy of combustion of methane at 25°C and 1 atm pressure.

Where $\Delta H_f^\circ(\text{CH}_4\text{(g)}) = -74.8 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{CO}_2\text{(g)}) = -393.5 \text{ kJ mol}^{-1}$ and
 $\Delta H_f^\circ(\text{O}_2\text{(g)}) = 0 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{H}_2\text{O(l)}) = -285.9 \text{ kJ mol}^{-1}$

Ans The combustion of methane is represented as:



$$\begin{aligned}\Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2) + 2\Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{CH}_4) - 2\Delta H_f^\circ(\text{O}_2) \\ &= (-393.5) + 2(-285.9) - (-74.8) - 2(0) \\ &= -890.5 \text{ kJ mol}^{-1}\end{aligned}$$

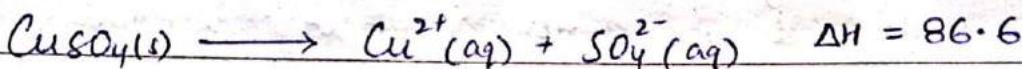


4. The heat evolved on dissolving $\text{CuSO}_4(s)$ in water is 86.6 kJ mol^{-1} .

If $\Delta H_f^\circ(\text{Cu}^{2+})$ is 64.4 kJ mol^{-1} , what is $\Delta H_f^\circ(\text{SO}_4^{2-})$?

$$\Delta H_f^\circ(\text{CuSO}_4(s)) = -770.0 \text{ kJ mol}^{-1}$$

Ans. Reaction can be written as.



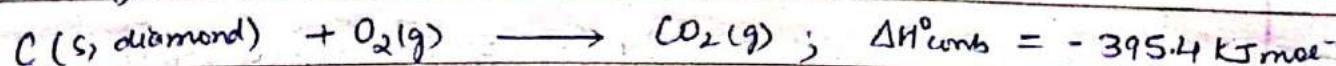
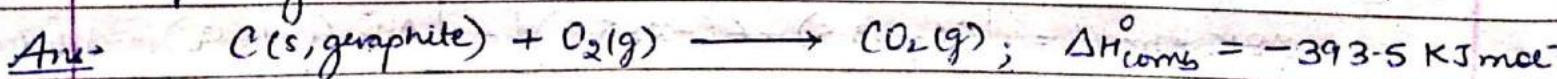
So,

$$\Delta H = \Delta H_f^\circ(\text{Cu}^{2+}) + \Delta H_f^\circ(\text{SO}_4^{2-}) - \Delta H_f^\circ(\text{CuSO}_4(s))$$

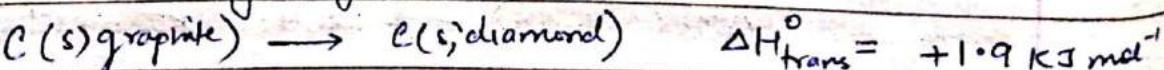
$$86.6 = 64.4 + \Delta H_f^\circ(\text{SO}_4^{2-}) - (-770.0)$$

$$\Delta H_f^\circ(\text{SO}_4^{2-}) = -747.8 \text{ kJ mol}^{-1}$$

5. Calculate the enthalpy change for the transition graphite \rightleftharpoons diamond from the $\Delta H_{\text{comb}}^\circ$ values of $-393.5 \text{ kJ mol}^{-1}$ and $-395.4 \text{ kJ mol}^{-1}$ for graphite and diamond, respectively.

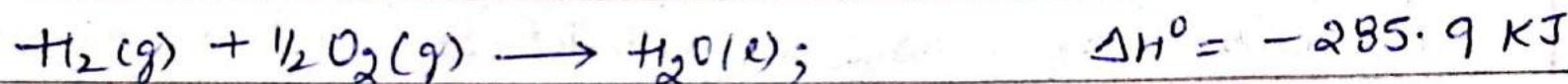
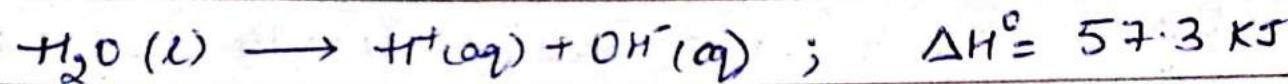


Subtraction of second reaction from first,

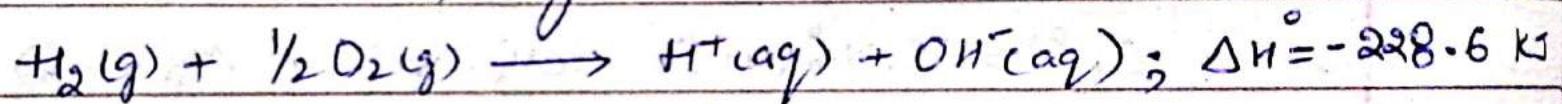




6. Calculate the enthalpy of formation of OH^- ions at 25°C from following thermo-chemical data:



Ans Adding above two reactions, we get -



$$\therefore \Delta H^\circ = \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{OH}^-) - \Delta H_f^\circ(\text{H}_2\text{g}) - \Delta H_f^\circ(\text{O}_2\text{g})$$

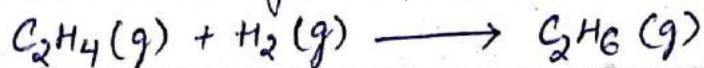
$$-288.6 = 0 + \Delta H_f^\circ(\text{OH}^-) - (0) - (0/2)$$

by convention $\Delta H_f^\circ(\text{H}^+) = 0$.

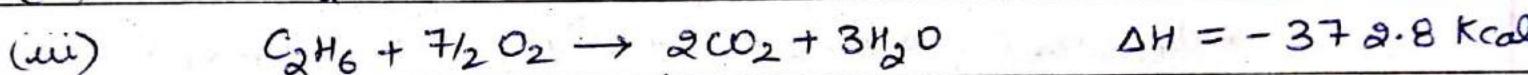
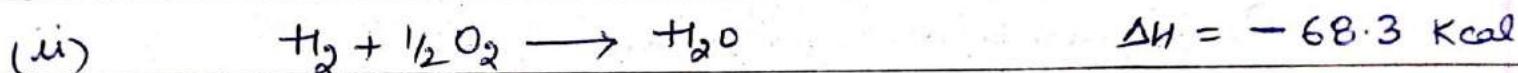
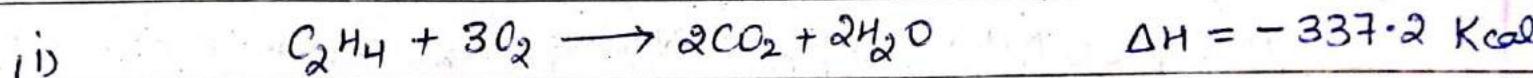
$$\therefore \Delta H_f^\circ(\text{OH}^-) = -288.6 \text{ kJ.}$$



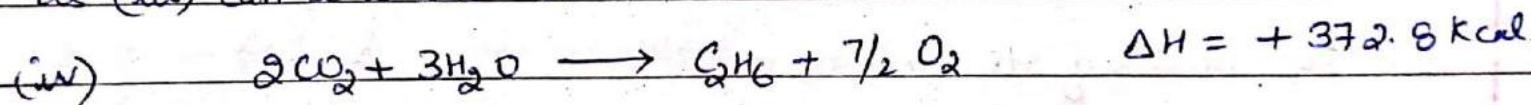
7 Heat of combustion of ethylene, hydrogen, and ethane are 337.2, 68.3, 372.8 Kcal mol⁻¹ at a definite temperature. Calculate heat of reaction of



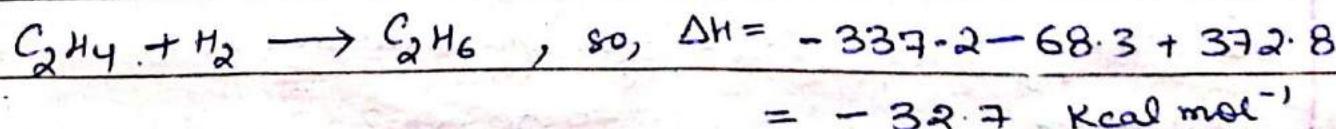
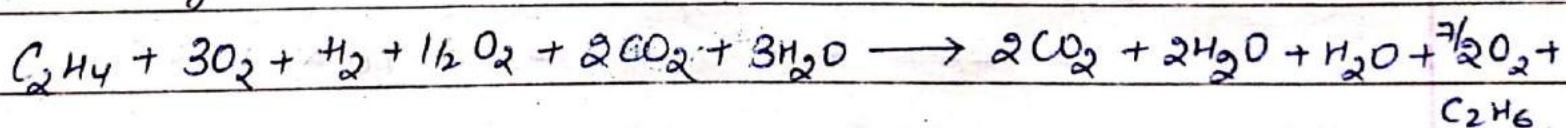
Ans Given



as (iii) can be written as

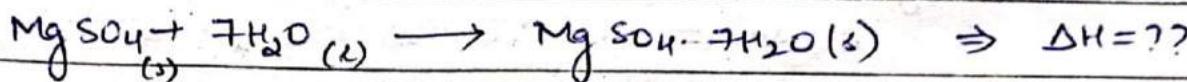


on adding (i), (ii) and (iv) we have,

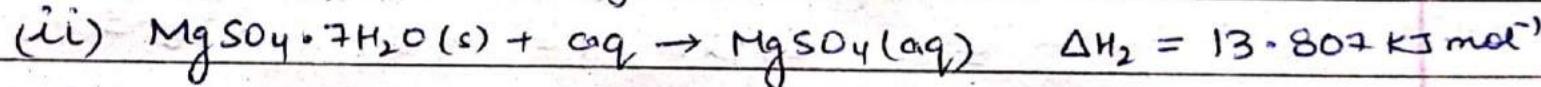
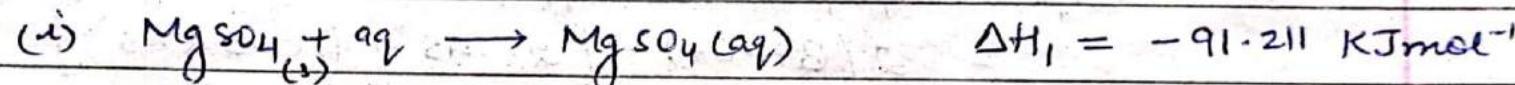




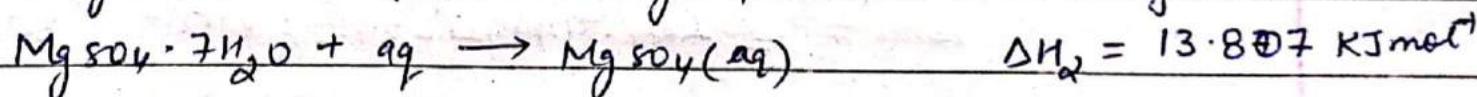
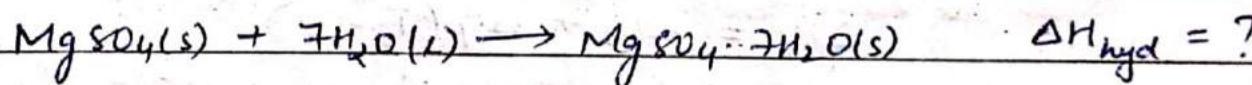
8. At 25°C , 1 mole of MgSO_4 was dissolved in water. The heat evolved was found to be -91.211 kJ . 1 mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.807 kJ . Find enthalpy of hydration.



Ans Given that:



So, eq (i) can be considered in two steps.



as per Hess law \rightarrow

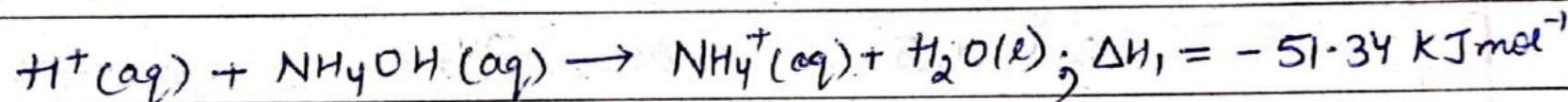
$$\Delta H_1 = \Delta H_{\text{hydr}} + \Delta H_2$$

$$\text{so, } \Delta H_{\text{hydr}} = \Delta H_1 - \Delta H_2 = -91.211 - 13.807 = -105.018 \text{ kJ mol}^{-1}$$

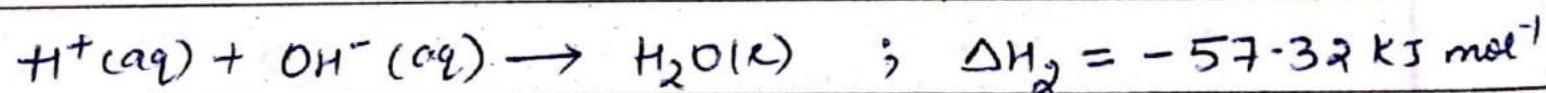
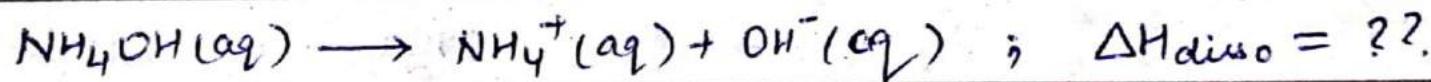


9. Enthalpy of neutralization of HCl by NaOH is $-57.32 \text{ kJ mol}^{-1}$ and by NH_4OH is $-51.34 \text{ kJ mol}^{-1}$. Calculate enthalpy of dissociation of NH_4OH .

Aus. Given that:



This reaction can be considered in two steps:



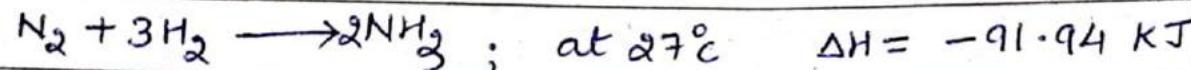
so, according to Hess law,

$$\Delta H_1 = \Delta H_{\text{diss}} + \Delta H_2$$

$$\begin{aligned}\Delta H_{\text{diss}} &= \Delta H_1 - \Delta H_2 = (-51.34 + 57.32) \text{ kJ mol}^{-1} \\ &= 5.98 \text{ kJ mol}^{-1}.\end{aligned}$$



10. The enthalpy of reaction (ΔH) for the formation of ammonia according to the reaction



What will be the enthalpy of reaction (ΔH) at $50^\circ C$? The molar heat capacity at constant pressure at $27^\circ C$ for N_2 , H_2 & NH_3 are 28.45 , 28.32 & 37.07 joules, respectively.

Ans: According to Kirchhoff equation,

$$\text{d}(\Delta H) = \Delta C_p \text{ d}T \text{ or } \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta H_1 = -91.94 \text{ KJ} ; \quad T_1 = 300K ; \quad T_2 = 323K ;$$

$$\text{so, } \Delta C_p = C_p, \text{products} - C_p, \text{reactants}$$

$$= 2(37.07) - [28.45 + (28.32 \times 3)]$$

$$= -39.28 \text{ JK}^{-1} = -39.28 \times 10^{-3} \text{ KJ K}^{-1}$$

assuming C_p do not change with temperature, ΔH_2 at $50^\circ C$, will be

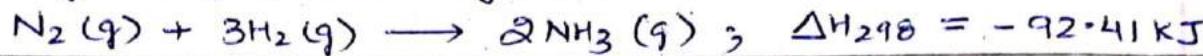
$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$$

$$= (-91.94) + (-39.28 \times 10^{-3})(323 - 300)$$

$$= -92.85 \text{ KJ}$$



11. Calculate the enthalpy change at 125°C for the reaction



Molar heat capacities (in $\text{JK}^{-1}\text{mol}^{-1}$) for various gases involved in the reaction vary with temperature as follow:

$$C_p(N_2) = 27.26 + 5.23 \times 10^{-3}T - 4.18 \times 10^{-9}T^2$$

$$C_p(H_2) = 29.02 + 8.35 \times 10^{-4}T + 20.80 \times 10^{-7}T^2$$

$$C_p(NH_3) = 25.86 + 32.94 \times 10^{-2}T - 30.42 \times 10^{-7}T^2$$

Ans.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\Delta C_p = 2C_p(NH_3) - C_p(N_2) - 3C_p(H_2)$$

$$\Delta C_p = -62.60 + 63.14 \times 10^{-3}T - 123.20 \times 10^{-7}T^2$$

Hence, $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} [-62.60 + 63.14 \times 10^{-3}T - 123.20 \times 10^{-7}T^2] dT$

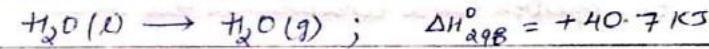
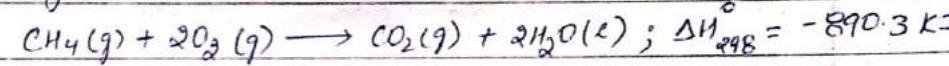
$$\Delta H_{398} - \Delta H_{298} = \left[-62.60 + \frac{63.14 \times 10^{-3}}{2} T^2 - \frac{123.20 \times 10^{-7}}{3} T^3 \right]_{298}^{398}$$

$$\Delta H_{398} = -96.50 \text{ kJ}$$

12.

In a bunsen burner, CH_4 gas is premixed with sufficient air to allow complete combustion and at flame temperature water is converted to steam.

Using the following thermochemical data:

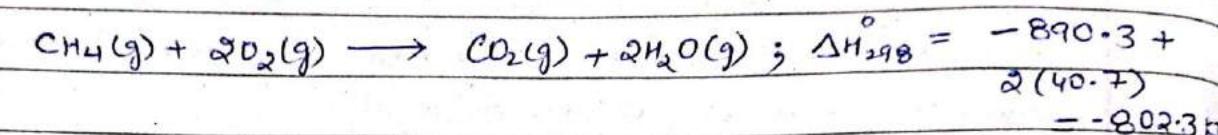


Calculate flame temperature. Assume gaseous product behave ideally.

$$\sum C_p = 41.8 \text{ J K}^{-1} \text{ mol}^{-1} \text{ & initial } T = 25^\circ\text{C}$$



Ans. from given equation, we have, at flame temperature (when water is in gaseous state)



$$\Delta C_p \text{ of gaseous products } (\text{CO}_2, \text{H}_2\text{O} \text{ & N}_2) = 41.8 \text{ J K}^{-1} \text{ mol}^{-1}$$

when,

1CO_2 reacted, 4N_2 remain unreacted, hence total moles of gaseous products will be $= 1 + 2 + (4 \times 2) = 11$

so, now, flame temperature (T_f) is attained when 802.3 kJ of heat is liberated above is used to heat 11 moles of gases.

By Kirchhoff equation,

$$\Delta H = \Delta C_p (T_f - T_i)$$

$$\Delta H_{\text{heating}} \rightarrow 802.3 \times 10^3 \text{ J} = (11 \times 41.8) \text{ J K}^{-1} \times (T_f - T_i)$$

$$\text{adibatic, } \Delta H = 0 \quad T_f - T_i = \frac{802.3 \times 10^3 \text{ J}}{459.6 \text{ J K}^{-1}} = 1746 \text{ K}$$

$$\text{so, } T_f = 1746 + T_i = 1746 + 298 = \boxed{2043 \text{ K}}$$