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BS-109 Engineering chemistry-I

Thermochemistry

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- It principally, deals with the transfer of heat between a chemical system and its surrounding when a change of phase or a chemical reaction takes place within the system.
- Depending upon the conditions under which reaction is carried out, quantity of heat transferred is related to energy change or enthalpy change due to change of states which occur in the system.
- In laboratory, mostly we perform reactions under condition of constant pressure, therefore heat transferred is equal to the change in enthalpy of system.
- Thermochemistry, in fact, implies the First law of thermodynamics to chemical reaction.
- 1st law states, energy can neither be created nor destroyed, although it can be transferred from one form to another. (conservation of energy).



* Change of Internal Energy in a chemical reaction:

Let us consider a chemical reaction taking place at constant temperature and at constant volume. In such a case, $W=0$ and hence from equation of first law (viz, $\Delta U = q + w$)

$$\Delta U = q_v \quad (q_v = \text{heat exchanged as constant } V)$$

So, let U_R is internal energy of reactants and U_p that of products, then

$$\Delta U = U_p - U_R = q_v = \text{heat of reaction at constant } V.$$



* Change of Enthalpy in a chemical reaction:

let q_p be heat exchanged in chemical reaction taking place at constant pressure.
so heat exchanged at constant pressure is termed as Enthalpy change. Thus.

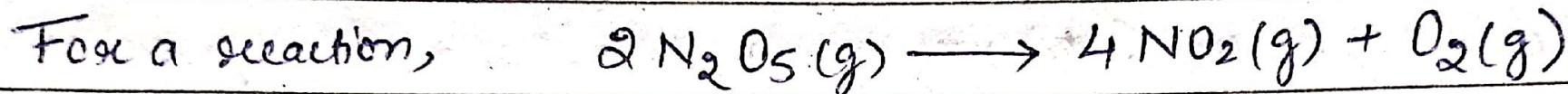
$$\Delta H = q_p$$

In general, if H_R is enthalpy of reactants and H_P that of products, then

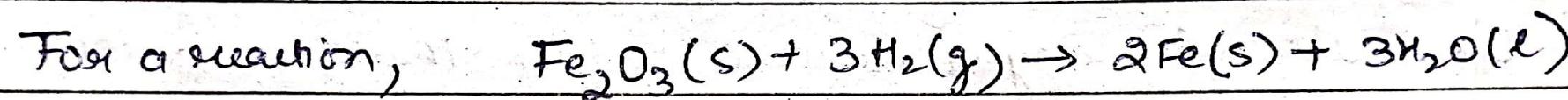
$$\Delta H = H_P - H_R = q_p = \text{Enthalpy of reaction.}$$

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

a_i & b_i are stoichiometric coefficients of products and reactants.



$$\Delta H = \left[(4H_{\text{NO}_2} + H_{\text{O}_2}) - 2H_{\text{N}_2\text{O}_5} \right]$$



$$\Delta H = \left[(2H_{\text{Fe}} + 3H_{\text{H}_2\text{O}}) - (H_{\text{Fe}_2\text{O}_3} + 3H_{\text{H}_2}) \right]$$



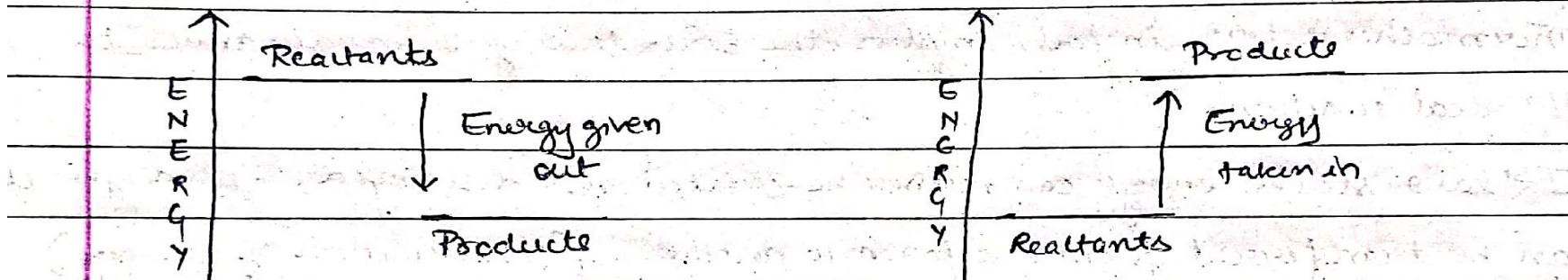
Exothermic and Endothermic reaction:

✓ Reactions that give out heat, i.e., when there is evolution of heat, are called exothermic reactions.

In such reactions, $H_p < H_R$, so that $\Delta H = -ve$

✓ Reactions that take in heat, i.e., which are accompanied by absorption of heat are called endothermic reactions.

In these reactions, $H_p > H_R$, so that $\Delta H = +ve$

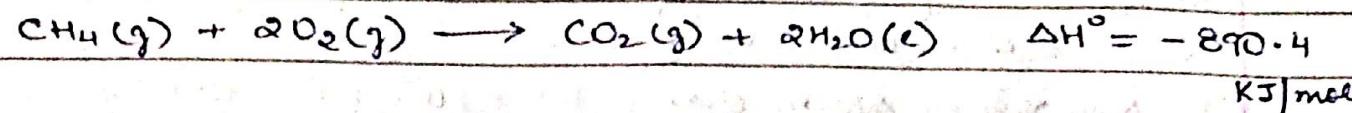


(a) Exothermic

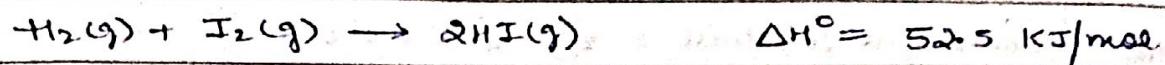
(b) Endothermic.



Example: (exothermic reaction)



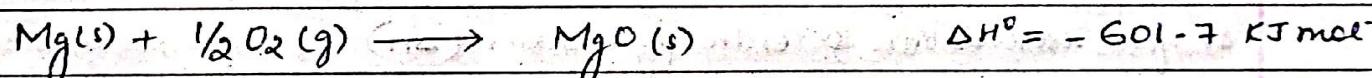
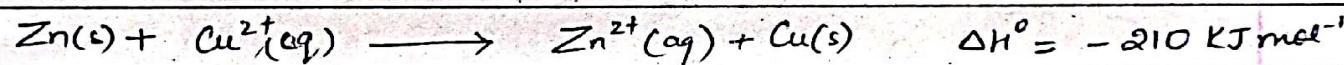
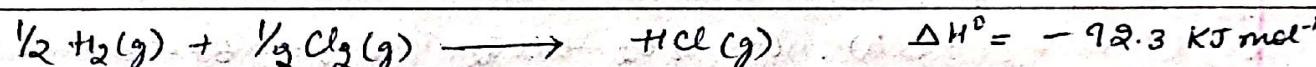
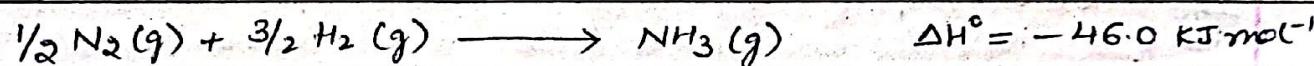
(endothermic reaction)



* Standard Enthalpy of reaction:

When all the chemical species in a chemical equation are present in the respective standard states, the enthalpy of reactions determined at 25°C and one atm pressure (101.325 KPa) is spelled as standard enthalpy of reaction.

Examples:





* HESS'S LAW OF CONSTANT HEAT SUMMATION:

During reactions, molar enthalpies of reactants and products are involved which have definite value & it is obvious that enthalpy change of chemical reaction would also have definite value, irrespective of the way the reaction is carried out.

Thus, during transformation of reactants to products by more than one sequence of chemical reaction, total enthalpy change must be same for every sequence. This rule is consequence of the first law of thermodynamics, is known as "HESS'S LAW", which is stated as follow:

"The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps."

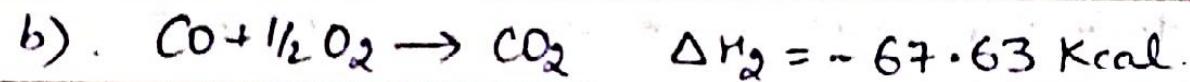
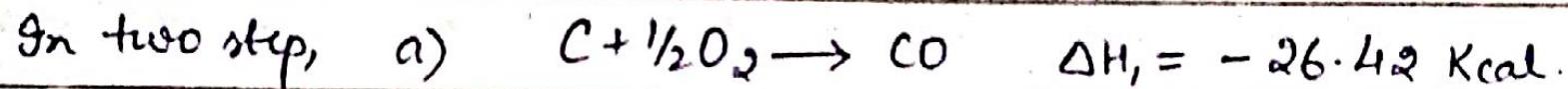
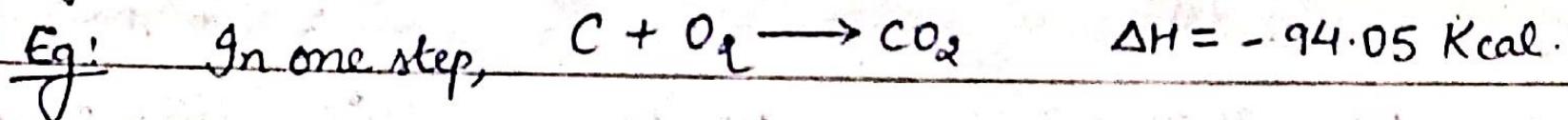


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Suppose in a process, the system changes state from A to B in one step and heat exchanged is 'q'.

Now suppose system changes state A to B in three steps involving a change from A to C, C to D and finally D to B. If q_1 , q_2 & q_3 are heat exchanged in first, second & third step, respectively, then as per Hess's law,

$$q_1 + q_2 + q_3 = q$$

So, in general, enthalpy of reaction depends only upon initial reactants and final products and not at all on intermediate products that may be formed.



so, summation $\Delta H_1 + \Delta H_2 = (-26.42) + (-67.63) = -94.05 \text{ Kcal}$

Applications of Hess's law:

1. for calculation of enthalpy changes (ΔH)
2. lattice energies calculation in Born-Haber cycle.



Variation of Enthalpy of a reaction with temperature (KIRCHHOFF'S RELATION)

The enthalpy of any process, whether physical or chemical, varies with temperature.

The exact influence of temperature can be worked as follow:

So, enthalpy of a reaction



is given by

$$\begin{aligned}\Delta H &= \sum H_{\text{products}} - \sum H_{\text{reactants}} \\ &= (cH_C + dH_D) - (aH_A + bH_B) \quad \dots \dots (1)\end{aligned}$$

now, differentiating with respect to temperature, keeping pressure constant,

we have,

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

$$= c C_{P,C} + d C_{P,D} - a C_{P,A} - b C_{P,B} = \Delta C_P \quad \dots \dots (2)$$

$$\left(C_P = \left(\frac{\partial H}{\partial T} \right)_P \right)$$



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:

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

OR

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

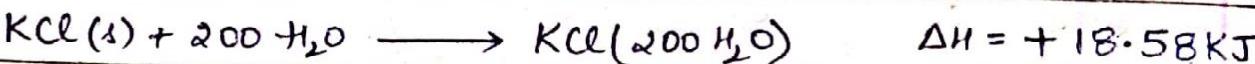
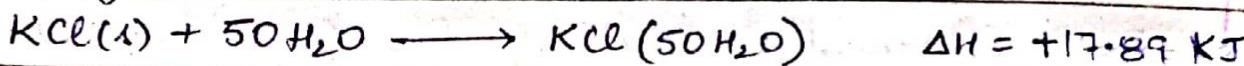


I) Heat of solution & Heat of dilution:

The heat change taking place when 1 mole of solute is dissolved in a sufficient amount of solvent is called the heat of solution.

(Integral heat of dilution)

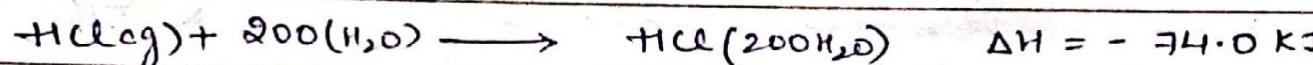
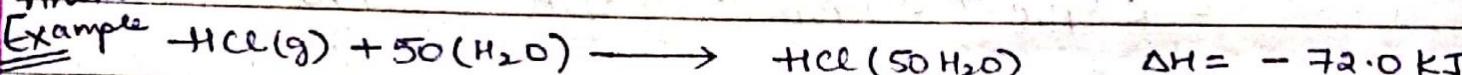
The heat of solution changes with concentration, i.e., one mole of KCl dissolved in 50 moles of water and in 200 moles of water will cause different heat changes.



If heat is absorbed from the solution (i.e. solution is cooler), $\Delta H = +ve$

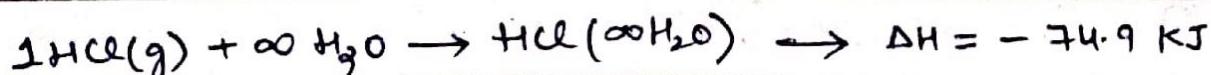
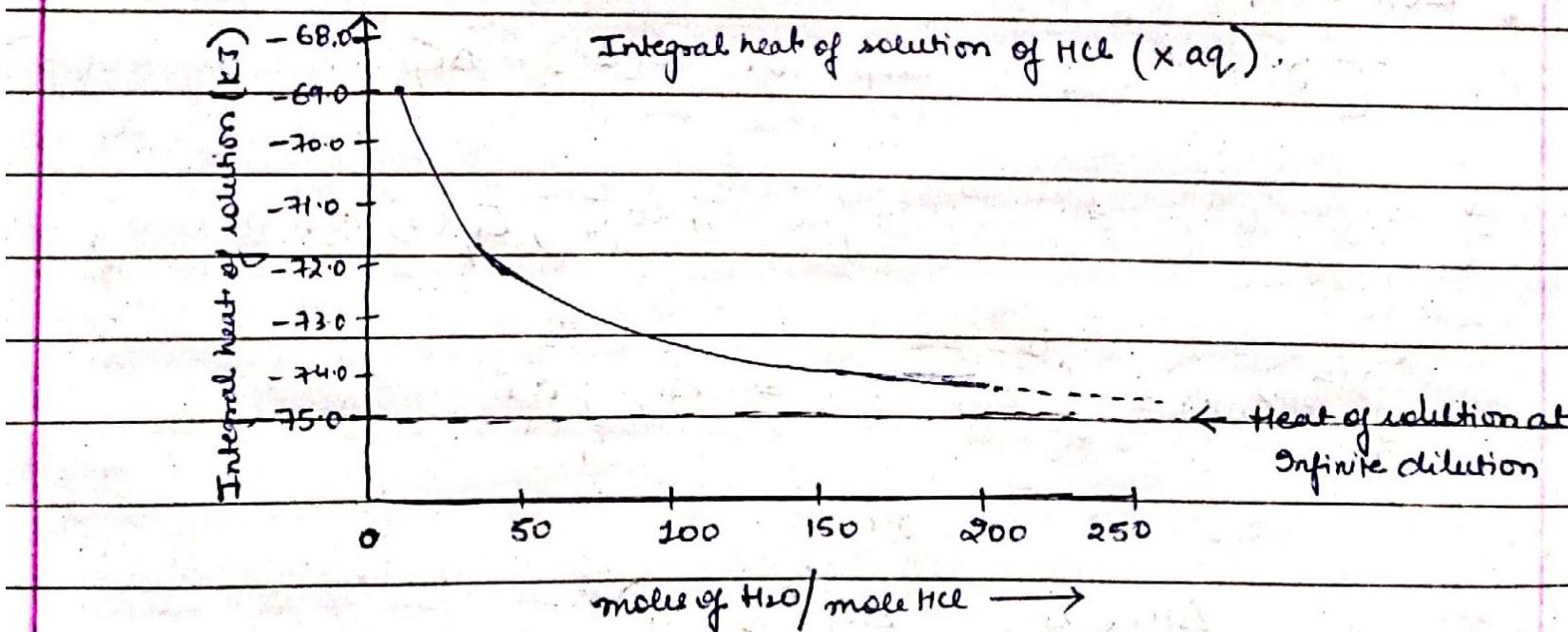
If heat is evolved and given to solution (i.e. solution is warmer), $\Delta H = -ve$

Another





The value of heat of solution obtained graphically by extrapolating ΔH to infinite dilution is the integral heat of solution at infinite dilution.
At infinite dilution, the heat change becomes constant.

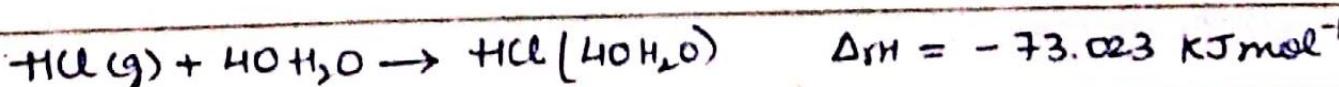
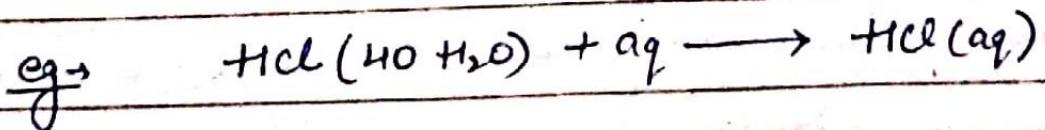




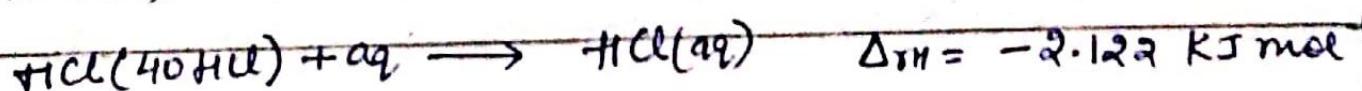
So, enthalpy of solution of a solute varies with concentration implies that there must be change in enthalpy when a solution is diluted by adding more solvent.

So, integral enthalpy of dilution is the change in enthalpy when a solution containing one mole of solute is diluted from one concentration to another.

So according to Hess's law, it is equal to difference between integral enthalpies of solution at two concentration.



on subtraction,



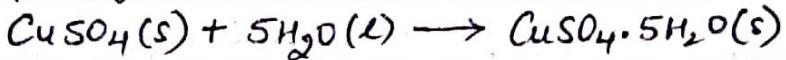


II) Heat of hydration :

For a given anhydrous or partially hydrated salt is the "enthalpy changed when one mole of it combines with requisite amount of water to form a new hydrated stable salt."

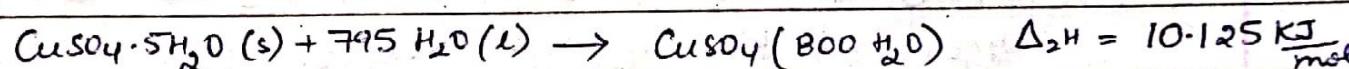
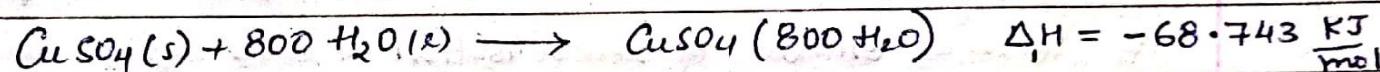
Example:

Hydration of anhydrous copper sulphate

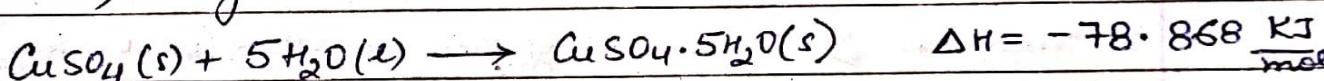


There is almost invariably a liberation of heat in such reactions, i.e. the value of ΔH is negative.

This value of enthalpy of hydration is readily been calculated from integral enthalpies of solution of hydrated and anhydrous salt. E.g.



by subtraction, we get





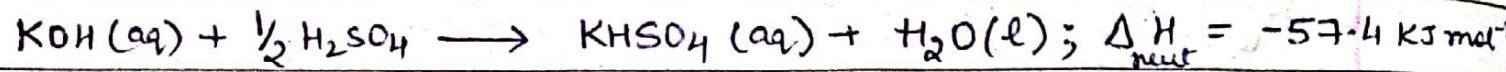
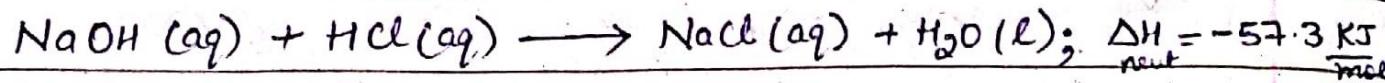
III) Heat of neutralization: ($\Delta_{\text{neut}} H$)

Enthalpy of neutralization of one mole of a base such as NaOH and KOH

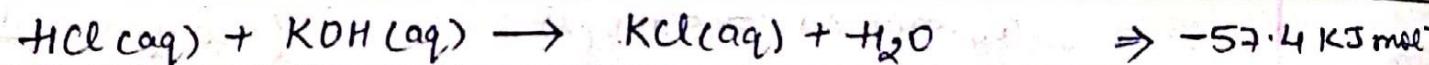
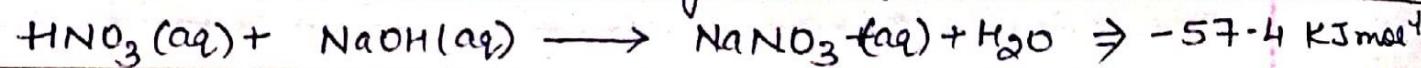
by an acid such as HCl, H_2SO_4 and HNO_3 in dilute solution at $25^\circ C$

and 1 atm pressure is called standard enthalpy of neutralisation of base

by the acid. Thus,



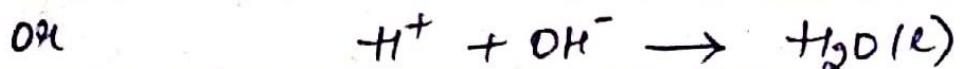
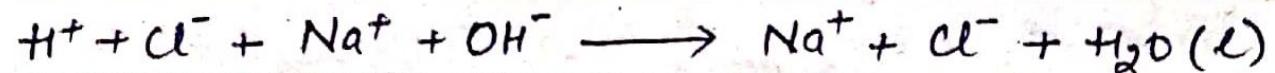
Similarly, the enthalpy change accompanying the neutralisation of 1 mol of an acid by a base in dilute solutions at $25^\circ C$ and 1 atm pressure is known as standard enthalpy of neutralisation of acid by the base.





It can be said that, amount of heat liberated (exothermic) when 1 mol of an acid is neutralised by 1 mol of base in large excess of water.

When acid and base are both strong, they can be assumed completely dissociated,

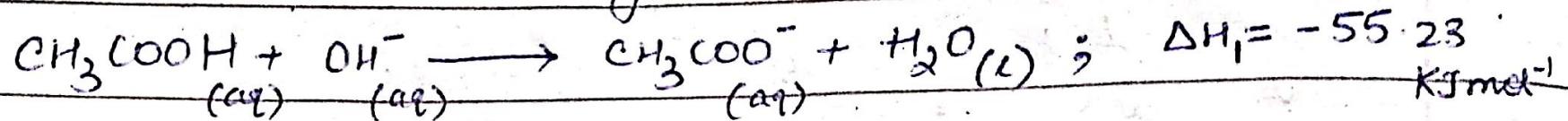


Therefore, the heat of neutralisation is really the heat of formation of 1 mol of water from 1 mole of hydrogen and hydroxide ions, and this is always equivalent to 13.7 Kcal or 57.32 KJ of heat.

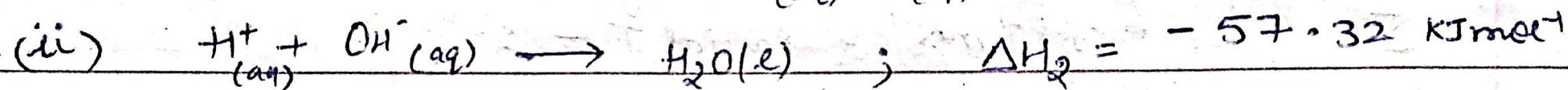
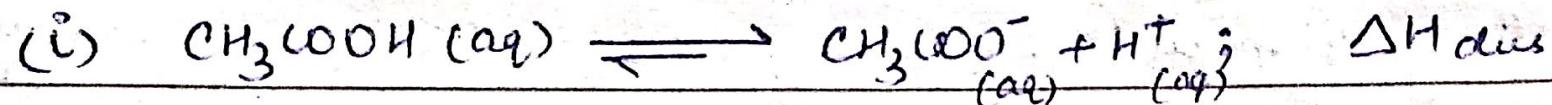
But when a weak acid or a weak base is neutralised, the heat of neutralisation deviates considerably from 13.7 Kcal. because it involves dissociation of weak acid or weak base as well.



For example, weak acid and strong base.



this equation can be considered in two steps:



as per Hess's law,

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

$$\Delta H_{\text{diss}} = \Delta H_1 - \Delta H_2 = (-55.23 + 57.32) \text{ kJ mol}^{-1}$$

$$= 2.09 \text{ kJ mol}^{-1}$$



IV) Heat of combustion: ($\Delta H_{\text{comb}}^{\circ}$)

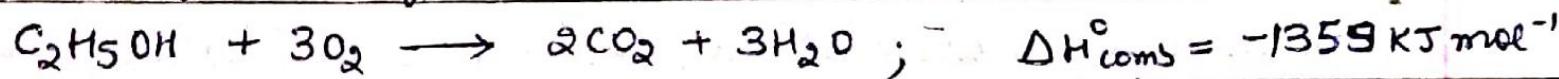
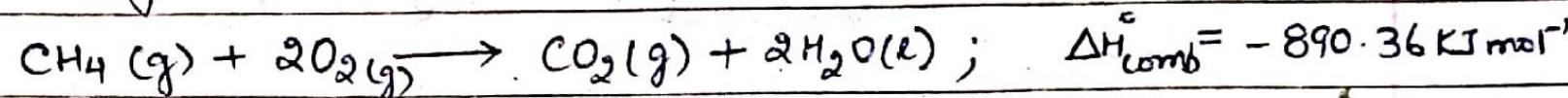
Standard enthalpy of combustion is enthalpy change (ΔH) accompanying complete combustion of one mole of the substance at 25°C and 1 atm pressure.

OR

enthalpy change when one mole of this compound combines with the requisite amount of oxygen to give products in their stable form.

example

1. Combustion of methane



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



FLAME TEMPERATURE :-

Combustion of gaseous fuel in air takes place so suddenly that heat produced during combustion does not get any opportunity to be dissipated to the surrounding. The combustion process is, therefore, practically equivalent to an adiabatic process.

The entire amount of heat produced thus goes to heat the gases produced during combustion as also unreacted N_2 . The maximum temperature attained by the flame-zone (containing resultant gases) due to the heat liberated by the combustion of fuel under adiabatic conditions at constant pressure is known as "flame temperature".

So for an isobaric (constant pressure) adiabatic process, the flame temperature can be calculated using the Kirchhoff equation, viz.

$$\frac{d(\Delta H)}{dT} = \Delta C_p \quad \text{or} \quad d(\Delta H) = \Delta C_p dT \quad \dots \text{(1)}$$

On integration of eq (1)

$$\int d(\Delta H) = \Delta C_p + \int_{T_e}^{T_f} dt \quad \text{or} \quad \Delta H = \Delta C_p(T_f - T_e) \quad \text{--- (2)}$$



Here we assumed that over the given temperature range, ΔC_p remains constant. Hence, knowing, ΔH , ΔC_p & T_i we can calculate T_f (flame temp)

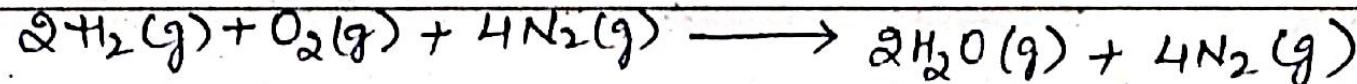
Comment on ΔC_p :

flame temperature would obviously depend upon the composition and heat capacities of only the resultant gases. In the flames produced by combination of fuels in air, there is present in gaseous products unburnt N_2 which is also heated up along with the gaseous products to the flame temperature.



Since air contains about 20% by volume of O_2 and 80% by volume of N_2 ,
the combustion reaction involving 1 mole of O_2 is associated with 4 moles of
unreacted N_2 in the products.

the combustion of H_2 gas in air can be schematically represented as



Hence, ΔC_p is considered as equal to sum of the C_p s of products
plus the C_p of $4N_2$ per mole of O_2 used during combustion. Therefore,

$$\Delta C_p = \sum C_{p, \text{products}} + 4 C_{p, N_2}$$

So, eq(1) becomes

$$d(\Delta H) = (\sum C_{p, \text{products}} + 4 C_{p, N_2}) dT$$



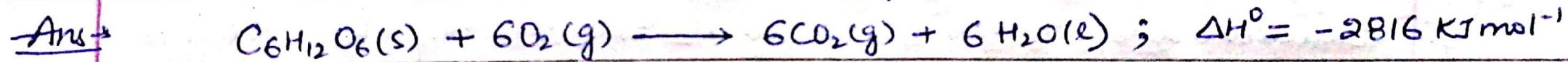
1. Comment by a student, "In an endothermic reaction, if heat is taken in during the reaction, the temperature should go up, not down." Clear the doubt.

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

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

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

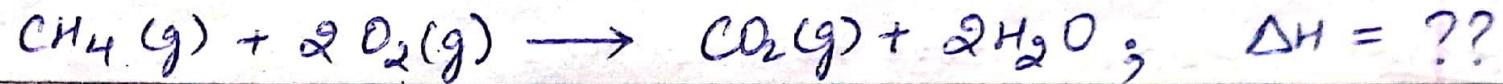
$$\Delta H_f^\circ (C_6H_{12}O_6) = -1260.4 \text{ KJ mol}^{-1}$$



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

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

Ans The combustion of methane is represented as:



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

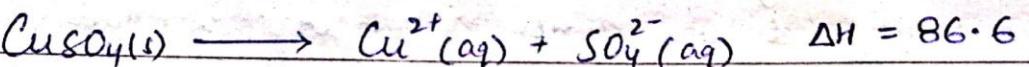


4. The heat evolved on dissolving $\text{CuSO}_4(s)$ in water is 86.6 kJ mol^{-1} .

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.



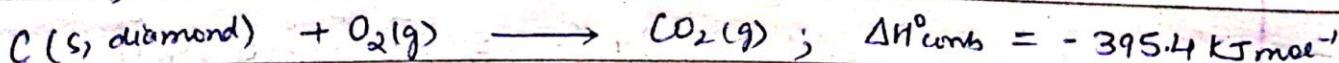
So,

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

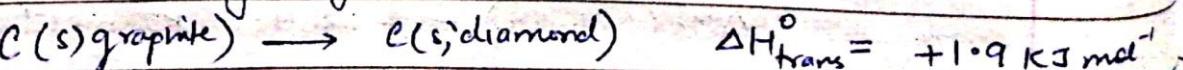
$$86.6 = 64.4 + \Delta H_f^\circ(\text{SO}_4^{2-}) - (-770.0)$$

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

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.

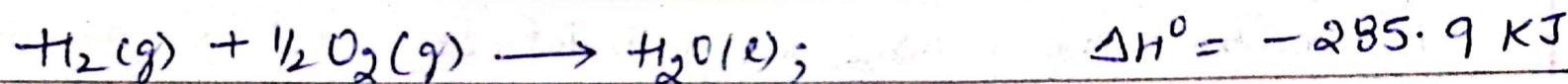
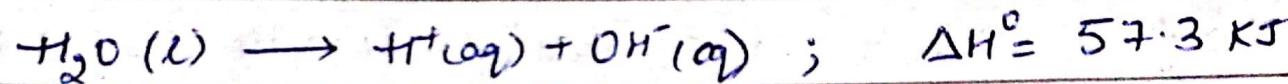


Subtraction of second reaction from first,

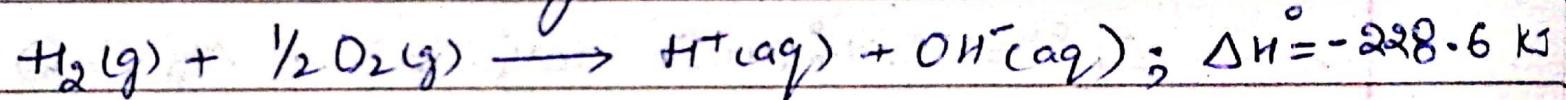




6. Calculate the enthalpy of formation of OH^- ions at 25°C from following thermo-chemical data:



Ans Adding above two reactions, we get -



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

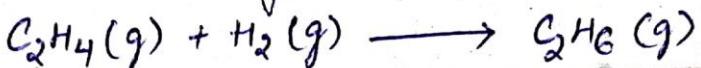
$$-228.6 = 0 + \Delta H_f^\circ(\text{OH}^-) - (0) - (0/2)$$

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

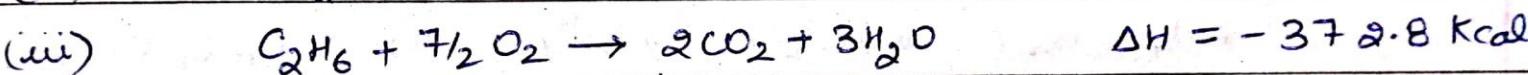
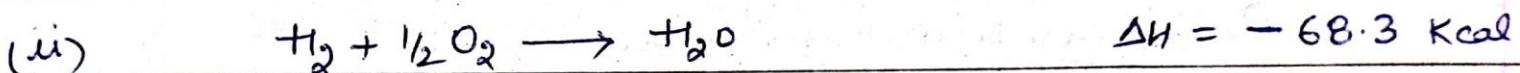
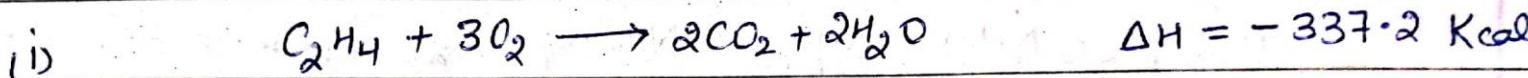
$$\therefore \Delta H_f^\circ(\text{OH}^-) = -228.6 \text{ kJ.}$$



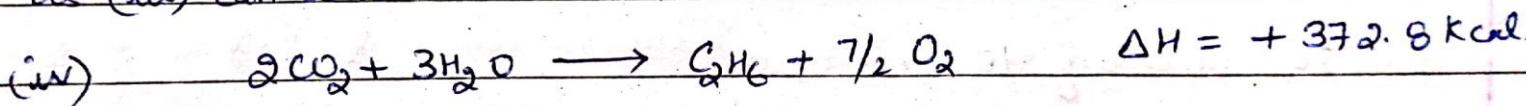
7 Heat of combustion of ethylene, hydrogen, and ethane are 337.2, 68.3, 372.8 Kcal mol⁻¹ at a definite temperature. Calculate heat of reaction of



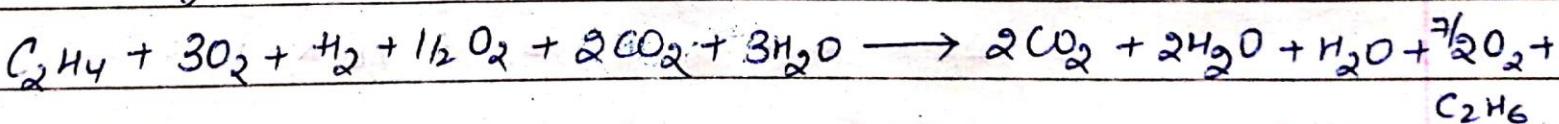
Ans. Given



as (iii) can be written as



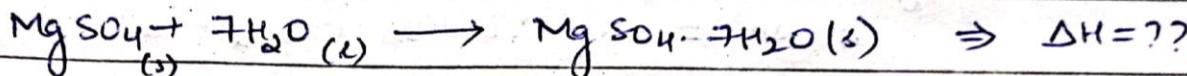
on adding (i), (ii) and (iv) we have,



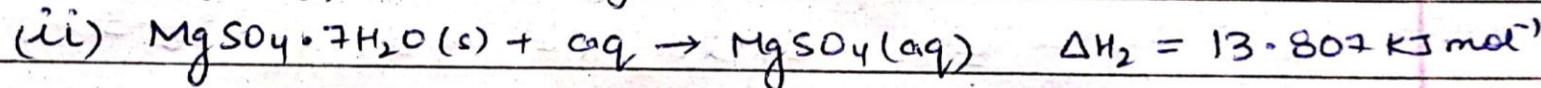
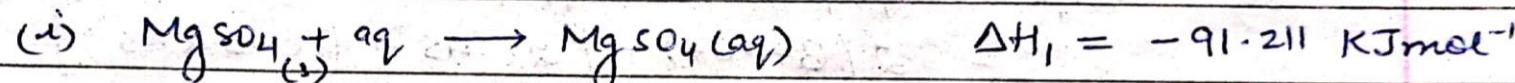
$$\begin{aligned} C_2H_4 + H_2 &\longrightarrow C_2H_6, \text{ so, } \Delta H = -337.2 - 68.3 + 372.8 \\ &= -32.7 \text{ Kcal mol}^{-1} \end{aligned}$$



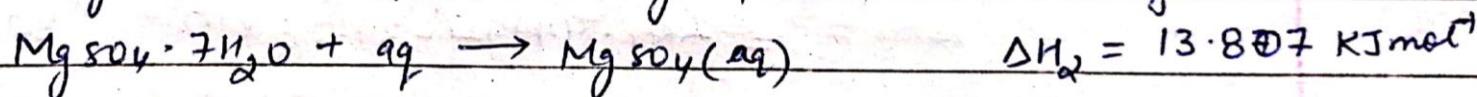
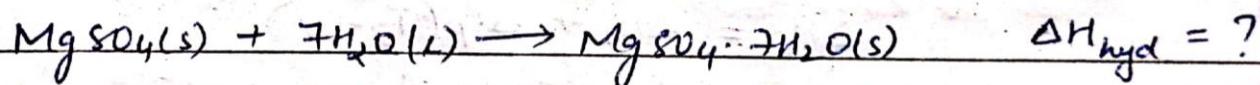
8. At 25°C , 1 mole of MgSO_4 was dissolved in water. The heat evolved was found to be -91.211 kJ . 1 mole of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ on dissolution gives a solution of the same composition accompanied by an absorption of 13.807 kJ . Find enthalpy of hydration.



Ans Given that:



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



as per Hess's law \rightarrow

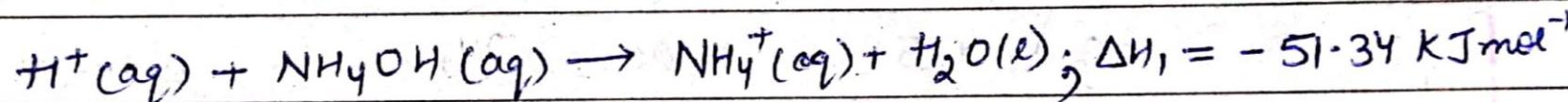
$$\Delta H_1 = \Delta H_{\text{hydr}} + \Delta H_2$$

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

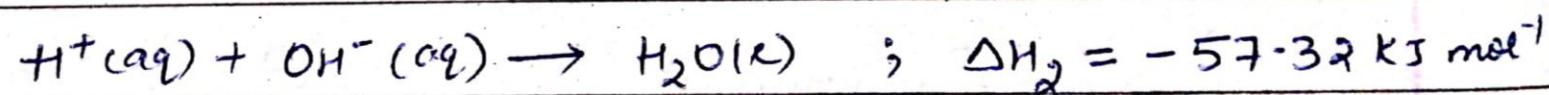
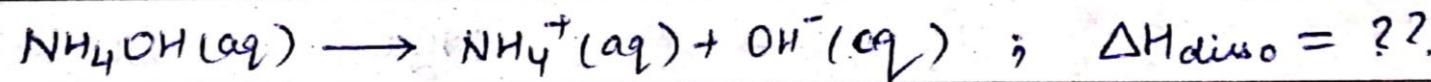


9. Enthalpy of neutralization of HCl by NaOH is $-57.32 \text{ kJ mol}^{-1}$ and by NH_4OH is $-51.34 \text{ kJ mol}^{-1}$. Calculate enthalpy of dissociation of NH_4OH .

Aus. Given that:



This reaction can be considered in two steps:



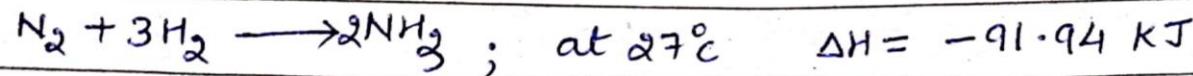
so, according to Hess law,

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

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



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,

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

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

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

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

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

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

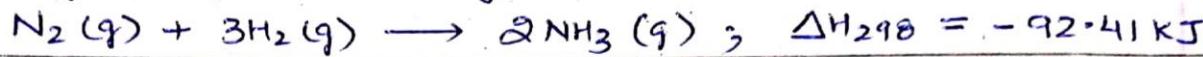
$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$$

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

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



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:

$$C_p(N_2) = 27.26 + 5.83 \times 10^{-3}T - 4.18 \times 10^{-9}T^2$$

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

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

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

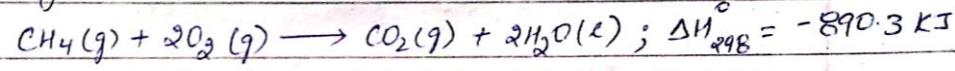
$$\Delta H_{398} - \Delta H_{298} = \left[-\frac{62.60}{2} + \frac{63.14 \times 10^{-3}}{3} T^2 - \frac{123.20 \times 10^{-7}}{3} T^3 \right]_{298}^{398}$$

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

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 thermodynamical data:

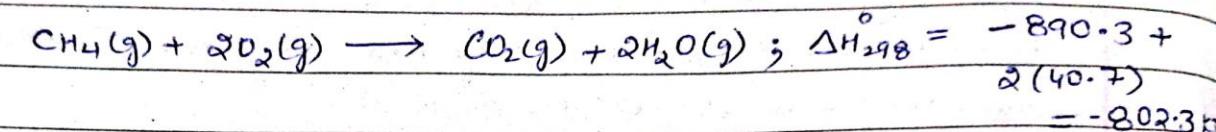


Calculate flame temperature. Assume gaseous product behave ideally.

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



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,

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

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

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

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