THERMOCHEMISTRY

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

SPECIFIC HEAT (S)

Amount of energy required to raise the temp by 1° C of 1 gm of a substance.
Unit $\rightarrow$ Energy/gm$^\circ$C

HEAT CAPACITY

The amount of heat required to raise the temperature by 1°C or 1K of a given amount of a substance.

$\qquad$ C = m × s

$\qquad$ Unit $\rightarrow$ Energy/$^\circ$C

Total heat given to increase the temperature by Δt.

$\qquad$ q = msΔt

MOLAR HEAT CAPACITY

The amount of heat required to raise the temp by 1° of 1 mole of a substance.

CLASSIFICATION OF MOLAR HEAT CAPACITY

(A) Molar heat capacity at constant pressure (C_p)
(B) Molar heat capacity at constant volume (C_v)

Relation between C_p and C_v

$C_p - C_v = R$ $\qquad$ (Mayor's formula)

$\dfrac{C_p}{C_v} = \gamma$ $\qquad$ (Poison' Ratio)

RULES FOR THERMOCHEMICAL EQUATION

(1) It is necessary to mention physical state of all reactants and products.

(2) A $\rightarrow$ B

$\qquad$ $\Delta H = H_B - H_A$

$\qquad$ if $\Delta H > 0$ $\qquad$ (Endothermic reaction)

$\quad$ $\Delta H < 0 \Rightarrow$ (Exothermic reaction)

$\quad$ If A $\rightarrow$ B + x kJ/mole

$\qquad\qquad \Rightarrow \quad \Delta H = -x$ kJ/mole

$\quad$ If A + x kJ/mole $\rightarrow$ B

$\quad$ or A $\rightarrow$ B – x kJ/mole

$\qquad\qquad \Rightarrow \quad \Delta H = x$ kJ/mole

(3) After reversing a thermochemical eq^n then sign of enthalpy also get changed.

e.g. $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$

$\qquad\qquad\qquad$ $\Delta H = x$ kJ

$\quad$ $C_{(g)} + D_{(g)} \rightarrow A_{(g)} + B_{(g)}$
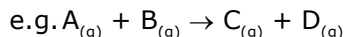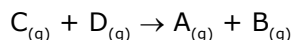
$\qquad\qquad\qquad$ $\Delta H = - x$ kJ

(4) When two reactions are added their enthalpies are also get added with their sigh.

$\quad$ e.g.

$\quad$ $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$ $\qquad$ $\Delta H = x_1$ kJ

$\quad$ $C_{(g)} + E_{(g)} \rightarrow F_{(g)}$ $\qquad$ $\Delta H = - x_2$ kJ

_____

$\quad$ $A_{(g)} + B_{(g)} + E_{(g)} \quad \rightarrow \qquad D_{(g)} + F_{(g)}$

$\qquad\qquad$ $\Delta H = x_1 - x_2$

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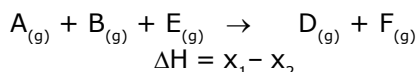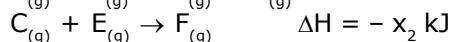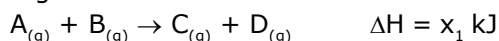
(5) If a thermochemical equation is multiplied by a number then enthalpy is multiplied by the same number.

e.g.

$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$ $\Delta H = x_1$ kJ
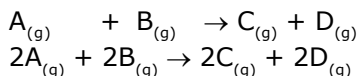
$2A_{(g)} + 2B_{(g)} \rightarrow 2C_{(g)} + 2D_{(g)}$ $\Delta H = 2x_1$ kJ

INTENSIVE PROPERTY

The property which does not depend upon the mass of substance is called intensive property.

e.g.   density, refractive index, specific heat, etc.

EXTENSIVE PROPERTY

Mass dependent properties are called extensive properties

e.g.

$\Delta H, \Delta S, \Delta G$

*   Two extensive property can be added or additive.
*   Ratio of two extensive properties is Intensive.
*   Intensive properties can not be added directly.

e.g.   We can not add the density of two liquids to get the density of the final mixture of the two.

$d = \dfrac{m}{v}$

$\Rightarrow m = dv$

$\Rightarrow d_{mix} \times (h_1 + h_2)A = d_1 h_1 A + d_2 h_2 A$

$\Rightarrow d_{mix} = \dfrac{d_1 h_1 A + d_2 h_2 A}{(h_1 + h_2)A}$ $\Rightarrow d_{mix} = \dfrac{d_1 h_1 + d_2 h_2}{h_1 + h_2}$

ENTHALPY

$$H = U + PV$$
$$\downarrow$$
Internal energy
$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

(i) Δt constant Pressure

   $V\Delta P = 0$ (as $\Delta P = 0$)

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

(ii)   At Constant Volume:

   $P\Delta V = 0$ as $\Delta V = 0$

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

(iii)   If both are changing:-

   $\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$

*   Enthalpy is function of temperature i.e. changes with change in temperature.

   $H = U + PV$

   $= U + nRT$

*   Enthalpy is always defined at constant temperature and it varies with variation in temperature.

   $\Delta H = \Delta U + \Delta PV$

       $= \Delta n C_V T + \Delta n R T = \Delta n T (C_V + R)$

       $\Rightarrow \Delta H = \Delta n\, C_p T$

$$\boxed{\downarrow \text{Enthalpy at cons tan t pressure.}}$$

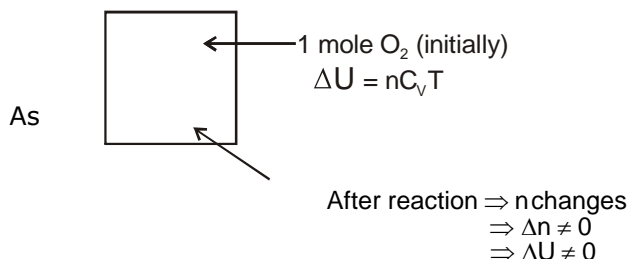$$\Delta H \quad = \quad \Delta E + \Delta nRT$$

Enthalpy at a constant pressure

Enthalpy at a constant Volume

Δn = no. of moles of gaseous product - no. of moles of gaseous reactant.

Note:-

In chemistry, At constant temp $\Delta U \neq 0$

1 mole O_2 (initially)

$$\Delta U = nC_V T$$

As

After reaction $\Rightarrow n$ changes
$\Rightarrow \Delta n \neq 0$
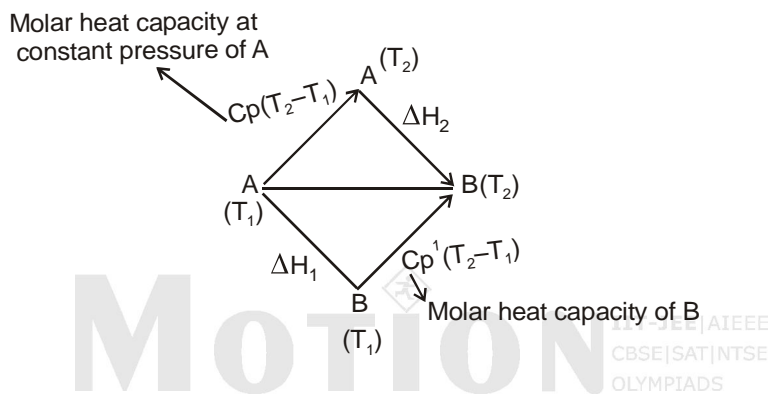$\Rightarrow \Delta U \neq 0$

Also as after the reaction the nature of substance formed changes which may have different value of internal energy at the same temp.

KIRCHOFF'S EQUATION

This gives the relation between enthalpy and temperature.
*   Physical state is changed at constant temperature.

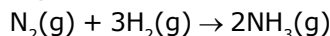Molar heat capacity at constant pressure of A

$A(T_2)$

$Cp(T_2-T_1)$ ΔH_2

A $B(T_2)$
(T_1)

ΔH_1 $Cp^1(T_2-T_1)$

B Molar heat capacity of B
(T_1)

According to Hess'Law

$$\Delta H_2 + Cp(T_2 - T_1) = \Delta H_1 + Cp^1 (T_2 - T_1)$$
$$\Delta H_2 - \Delta H_1 \quad = (Cp^1 - Cp)(T_2 - T_1)$$
$$\quad = \Delta Cp (T_2 - T_1)$$

$$\Rightarrow \quad \Delta Cp \quad = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

Where

ΔCp = Molar heat capacity of product –– Molar heat capacity of reactant

e.g.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
$$\Delta Cp = 2Cp(NH_3) - Cp(N_2) - 3Cp(H_2)$$

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* If the above formula (Kirchoff's eqⁿ) is to be written for molar heat capacity at constant volume then

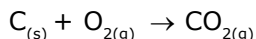$$\Delta C_V = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1}$$

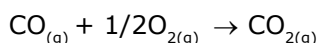* If ΔC_p is function of temperature

$\Delta C_p = T^2 + T$

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

HEAT OF FORMATION

Enthalpy change during the formation of 1 mole of a compound form its most stable common occurring form (also called reference states) of elements is called heat of formation.
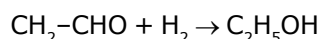
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta H = \Delta H_f(CO_2)$

$CO_{(g)} + 1/2 O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta H \neq \Delta H_f CO_2(g)$

(because CO_2 has not been formed form its element in their most stable form)

Similarly

$CH_2-CHO + H_2 \rightarrow C_2H_5OH$

$\Delta H \neq \Delta H_f(C_2H_5OH)$

Heat of reaction

Element	Most stable form
H	H_2(gas)
O	O_2(gas)
N	N_2(gas)
F	F_2(gas)
Cl	Cl_2(gas)
Br	Br_2(gas)
I	I_2(solid)
C	C(grapnite)
P	P(white)
S	S(rhombic)

* All metal exist in solid form (reference states)

ENTHALPY AT STANDARD STATE :-(ΔH^o)

T = 25ºC = 298 K

P = 1 atm

Conc = 1M

ΔH^o = Heat of formation at standard state

If $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}$ is any reaction, Heat of reaction for any thermochemical equation can be written as
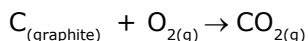
$\Delta H^o = \Delta H_f^o(product) - \Delta H_f^o(Reactant)$

If we use the above concept for the above given reaction then

$\Delta H^o = \Delta H_f^o{}_{(c)} + \Delta H_f^o{}_{(D)} - \Delta H_f^o{}_{(A)} + \Delta H_f^o{}_{(B)}$

Assumption :–

The heat of formation of most stable form of an element is taken as zero.

$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta H^o = \Delta H_f^o(CO_2) - \Delta H_f^o C_{(s)} - \Delta H_f^o(O_2)(g)$

$\Rightarrow \Delta H^o = \Delta H_f^o(CO_2)$ (As $\Delta H_f^o C_{(s)} = 0$ and $\Delta H_f^o O_2(g) = 0$)

Another example can be taken as

$H_2(g) + 1/2 O_2(g) \rightarrow H_2O_{(l)}$

$\Delta H^o = \Delta H_f^o(H_2O) - \Delta H_f^o(H_2) - 1/2 \Delta H_f^o(O_2)$

$$\quad\quad\quad\quad\quad\quad \| \quad\quad\quad\quad \|$$
$$\quad\quad\quad\quad\quad\quad O \quad\quad\quad\quad O$$
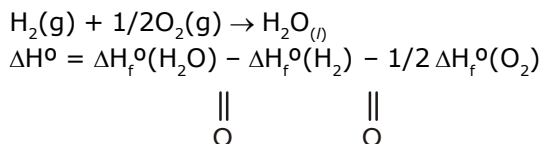
$\Delta H^o = \Delta H_f^o(H_2O)$

*   Heat of formation is always –ve as the process is exothermic.

Ex.1   *From the following data,*

$C_{(s, graphite)} + O_{2(g)} \rightarrow CO_{2(g)}$ *$\Delta H^o = -393.5$ kJ/mole*

$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$ *$\Delta H^o = -286$ kJ/mole*

$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_{2(g)} + 6H_2O(l)$ *$\Delta H^o = -3120$ kJ/mole*
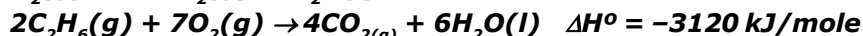
Calculate the standard enthalpy of formation of

$C_2H_6(g)$ (in kJ/mole)

Sol.   From eq^n(1) $\Delta H_f^o(CO_2) = -393.5$ kJ/mole

From eq^n(2) $\Delta H_f^o(H_2O) = -286$ kJ/mole

From eq^n (3) $\Delta_r H^o = 4 \Delta H_f^o(CO_2) + 6\Delta H_f^o(H_2O) - 2 \times \Delta H_f^o(C_2H_6) - 7 \times \Delta H_f^o O_2(g)$

$-3120 = 4 \times (-393.5) + 6 \times (-286) - 2 \times \Delta H_f^o(C_2H_6)$ (As $\Delta H_f^o O_2(g) = 0$)

$\Rightarrow -3120 = -1574 - 1716 - 2 \times \Delta H_f^o(C_2H_6)$

$\Rightarrow -3120 + 3290 = - 2 \times \Delta H_f^o(C_2H_6)$

$\Rightarrow 170 = - 2 \times \Delta H_f^o(C_2H_6)$

$\Rightarrow \Delta H_f^o = - 85$ kJ/mole

HEAT OF COMBUSTION

It is the enthalpy change (always –ve) when One mole of the substance undergo complete combustion.

$C_{(s)} + O_2 \rightarrow CO_2(g)$

$\Delta H^o = \Delta H_C^o C(s) = \Delta H_f^o(CO_2) - \Delta H_f^o C(s) - \Delta H_f^o(O_2)$

$\Delta H^o = = \Delta H_C^o C(s) = \Delta H_f^o(CO_2)$

Other example

$H_2 + 1/2 O_2 \rightarrow H_2O(g)$ $\overset{O}{\underset{\|}{}}$ $\overset{O}{\underset{\|}{}}$

$\Delta H^o = \Delta H_C^o (H_2) = \Delta H_f^o (H_2O) - \Delta H_f^o(H_2) - 1/2 \Delta H_f^o (O_2)$

$\Delta H^o = \Delta H_f^o (H_2) = \Delta H_f^o (H_2O)$
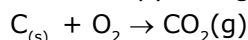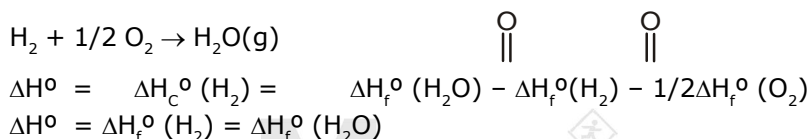
Note :–

Heat of combustion is always exothermic except N_2 and F_2.

* $N_2 + O_2 \rightarrow 2NO$
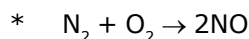
      (It is an endothermic reaction)

* $O_2 + F_2 \rightarrow OF_2$
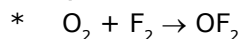
      (Since O has normally tendency to accept electron and opposite is happening above hence reaction is is considered endothermic)

*   Heat of reaction for any thermochemical equation can be written as (in form of heat of combustion)

      ΔH_r^o = Heat of combustion of reactant – Heat of combustion of reactant .

      $\Delta H_r^o = \Delta H_C^o$ (Reactant) $- \Delta H_C^o$ (Product)

Ex.2   *The enthalpy change for the reaction*

$C_3H_8(g) + H_2(g) \rightarrow C_2H_6(g) + CH_4(g)$ at 25ºC is – 55.7 kJ/mole calculate the enthalpy of combustion of $C_2H_{6(g)}$. The enthalpy of combustion of H_2, and CH_4 are – 285.8 and – 890.0 kJ/mole respectively. Enthalpy of combustion of propane is –2220 KJmol^{-1}.

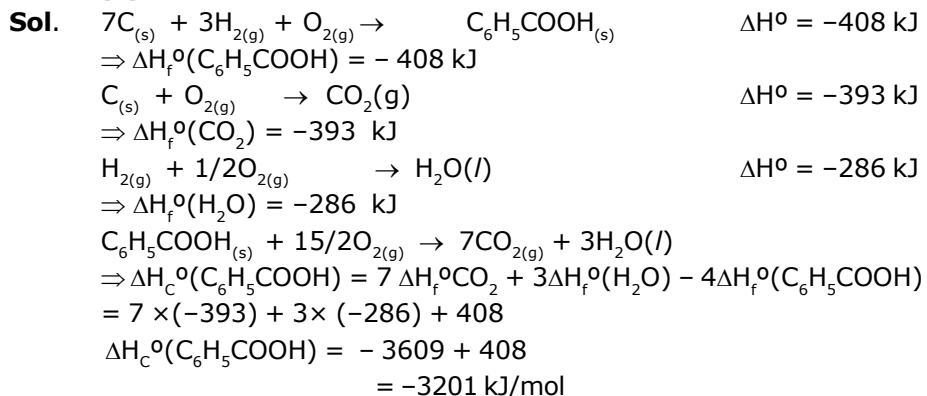**Sol**.   As we know any thermochemical eq^n can be written in terms of heat of combustion as follows

$\Delta H_r^o = \Delta H_C^o$ (Reactant) $- \Delta H_C^o$ (Product)

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$\Delta H_r^o = \Delta H_c^o (C_3H_8) + \Delta H_C^o (H_2) - \{\Delta H_c^o(C_2H_6) + \Delta H_c^o(CH_4) \}$

$- 55.7 = (-2220 - 285.8) - \{-890 + \Delta H_c^o(C_2H_6) \}$

$\Rightarrow \Delta H_c^o(C_2H_6) (g) = -1560.1 \text{ kJmol}^{-1}$

Problems Based on Both HOC and HOF :

Ex.3 *At 300K, the standard enthalpies of formation of $C_6H_5COOH_{(s)}$, $CO_2(g)$ and $H_2O(l)$ are −408, −393 and −286 kJmol⁻¹ respectively. Calculate the enthalpy of combustion of benzoic acid at*

(i) constant pressure

(ii) constant volume.

Sol. $7C_{(s)} + 3H_{2(g)} + O_{2(g)} \rightarrow \quad C_6H_5COOH_{(s)}$ $\Delta H^o = -408$ kJ

$\Rightarrow \Delta H_f^o(C_6H_5COOH) = -408$ kJ

$C_{(s)} + O_{2(g)} \quad \rightarrow CO_2(g)$ $\Delta H^o = -393$ kJ

$\Rightarrow \Delta H_f^o(CO_2) = -393$ kJ

$H_{2(g)} + 1/2O_{2(g)} \quad\quad \rightarrow H_2O(l)$ $\Delta H^o = -286$ kJ

$\Rightarrow \Delta H_f^o(H_2O) = -286$ kJ

$C_6H_5COOH_{(s)} + 15/2O_{2(g)} \rightarrow 7CO_{2(g)} + 3H_2O(l)$

$\Rightarrow \Delta H_C^o(C_6H_5COOH) = 7 \Delta H_f^o CO_2 + 3\Delta H_f^o(H_2O) - 4\Delta H_f^o(C_6H_5COOH)$

$= 7 \times(-393) + 3\times (-286) + 408$

$\Delta H_C^o(C_6H_5COOH) = -3609 + 408$

         $= -3201$ kJ/mol

$\Rightarrow$ enthalpy of combustion at constant pressure $= -3201$ kJ mol⁻¹

Also

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

$-3201 = \Delta U + (-0.5) \times 8.31 \times 10^{-3} \times 300$

         (As $\Delta n = 0.5$, $R = 8.314 \times 10^{-3}$ kJ)

$\Rightarrow \Delta U = -3201 + 1.2471$

    $\Delta U = -3199.7529$

$\Rightarrow$ enthalpy of combustion at constant volume $= -3199.7529$

<div align="center">

BOND ENERGY
</div>

It is defined for gaseous molecules. "The enthalpy change during the breaking of one mole of bond into isolated gaseous atoms is called bond energy of the compound"

e.g. $H_2(g) \rightarrow 2H(g)$
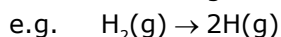
$\Delta H^o = \sum H - H$

*   हम किसी भी reaction को Heat of formation of product – Heat of formation of Reactant के form में लिख सकते हें और अगर उपर वाले eq^n को भी वैसे ही लिखा जाये तो

$\Delta H^o = \sum H - H = 2\Delta H_f^o H(g) - \Delta H_f^o(H_2)$

$\Rightarrow \sum H - H = 2\Delta H_f^o H(g)$ $\Rightarrow \Delta H_f^o H(g) = \dfrac{\sum H - H}{2}$

Similarly

$\Delta H_f^o O(g) = \dfrac{\sum O = O}{2}$

$\Delta H_f^o N(g) = \dfrac{\sum N \equiv N}{2}$

  *   Let us consider the similar bond breaking In CH_4

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$$CH_4(g) \rightarrow C_{(g)} + 4H_{(g)}$$
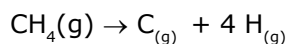
$$\Delta H = 4\sum C-H = \Delta H_f^oC(g) + 4\Delta H_f^oH(g) - \Delta H_f^o(CH_4)$$

** Enthalpy of reaction in terms of bond energy for a thermochemical eq^n can be written as

$$\Delta H_f^o = B.E._{(Reactant)} - B.E._{(products)}$$

Ex.4 *Using the bond enthalpy data given below, calculate the enthalpy change for the reaction*
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$
Data :
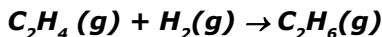
Bond	*C – C*	*C = C*	*C – H*	*H – H*
Bond Enthalpy	*336.81*	*606.68*	*410.87*	*431.79*
	(kJ/mol)	*(kJ/mol)*	*(kJ/mol)*	

Sol. $\Delta_r H^o = \sum reactant - \sum product$

$$\Delta H_r^o = \sum C=C + 4\sum C-H + \sum H-H - \sum C-C - 6\sum C-H$$

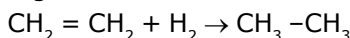$\Delta H_r^o = 606.68 + 4 \times 410.87 + 431.79 - 336.81 - 6 \times 410.87$

$= 2681.95 - 2802.03$

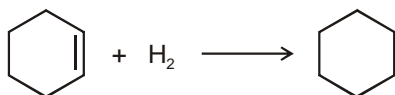$\Delta H_r^o = -120.08$ kJ/mol

HEAT OF HYDROGENATION

"Enthalpy change during the addition of 1 mole of H_2 to an unsaturated compound. is called heat of hydrogentation."

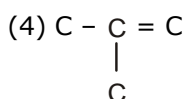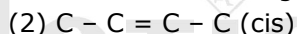Hydrogenation is an exothermic process. of therefore heat of hytdrogentaiton is always –ve.

e.g.

$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3$

$\Delta H_r^o = \Delta H^o_{(Hydrogenation)} (CH_2 = CH_2)$

$\therefore \quad \Delta H_r^o = \Delta H^o_{(Hydrogenation)}$ of cyclohexene

Ex.5 Compare the heat of hydrogenation of the following alkene

(1) C – C – C = C   (2) C – C = C – C (cis)   (3) C – C = C – C (trans)

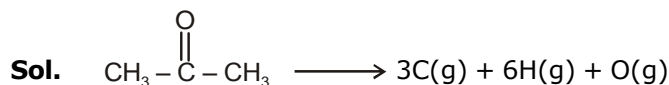(4) C – C = C
       |
       C   (5) C = C – C = C

Sol. Stability of alkene $\alpha \dfrac{1}{Heat\,of\,hydrogenation}$

The above concept is true as long as no. of double bonds are equal as heat of hydrogenation is defined for per mole of double bond. It will be certainly larger for higher number of double bonds irrespective of their stability.

(1)   C – C – C = C (2 × H)

(2)   C – C = C – C (6 × H)
            (cis)

(3)   C – C = C – C (6 × H)
            (trans)

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(4) C = C   (6 × H)

(5) C = C – C = C   (2 double bonds)

As we know trans > cis (stability)

$\Rightarrow$ Heat of hydrogen (trans) < Heat of hydrogenation (cis)

$CH_3 – CH = CH – CH_3 \longleftrightarrow CH_3 – \overset{\ominus}{C}H – CH = \overset{\overset{\oplus}{H}}{CH_2}$

(less stable)   (+ I of CH_3 reduce the stability)

(more stable)   (more stable as nothing is
                       trying to reduce its stability)

of therefore decreasing order of heat of hydrogenation of alkene

5 > 1 > 2 > 3 > 4 >

Ex.6 *Find ΔH_f of HCl(g) if bond energies of H_2, Cl_2 and HCl are 104, 58, 103 kcal/mole respectively.*

Sol.   H – Cl $\rightarrow$ H(g) + Cl(g)

$\sum H-Cl = \Delta H_f^o H(g) + H_f^o Cl(g) – \Delta H_f^o HCl(g)$

$103 = \frac{1}{2}\sum H-H + \frac{1}{2}\sum Cl-Cl – \Delta H_f^o HCl(g)$

$103 = \frac{1}{2}\times 104 + \frac{1}{2}\times 58 – \Delta H_f^o HCl(g)$

$\Rightarrow \Delta H_f^o HCl(g) = – 22$ kcal/mol.

HEAT OF ATOMISATION

" When one mole of any substance is converted into gaseous atoms enthalpy change during the process is called heat of atomisation." It is always + ve due to endothermic nature of the process.

HEAT OF SUBLIMATION

Enthalpy change during the conversion of one mole of solid to 1 mole of gaseous phase directly without undergoing into liquid phase is called enthalpy of sublimation or heat of sublimation,

It is always + ve due to endothermic nature of the process.

e.g.

$C_{(s)} \rightarrow C_{(g)}$

$\Delta H^o = \Delta H_{sub}^o C(s) = \Delta H_f^o C(g) – \Delta H_f^o C(s)$

$\qquad\qquad\qquad\qquad\qquad\quad \overset{\|}{O}$

$\Rightarrow \Delta H_{sub}^o C(s) = \Delta H_f^o C(g)$

$\Rightarrow \Delta H_{sub}^o C(s) = \Delta H_f^o C(g) = \Delta H_{atmosation}^o C(g)$

Ex.7 *Using the given data, calculate enthalpy of formation of acetone(g) [All values in kJmol^{-1}]*

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bond enthalpy of C–H = 413.4,   C – C = 347.0 (C = O) = 728.0
(O = O) = 495.0 ,   H – H = 435.8 $\Delta_{sub}H$ of C = 718.4

Sol. $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 \longrightarrow 3C(g) + 6H(g) + O(g)$

$6 \sum C-H + \sum C=O + 2\sum C-C = 3\Delta H_f^o C(g) + 6\Delta H_f^o H(g) + \Delta H_f^o O(g) - \Delta H_f^o (CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3)$

$6 \times 413.4 + 728 + 2 \times 347 = 3 \times 718.4 + \dfrac{6}{2} \times 435.8 + \dfrac{1}{2} \times 495.0 - \Delta H_f^o (CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3)$

$\Rightarrow \Delta H_f^o (CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3) = -192.3 \ kJmol^{-1}$

Ex.8 *The enthalpy of combustion of acetylene is 312 kcal. If enthalpy of formation of CO_2 and H_2O are −94.38 and −68.38 kcal respectively*
Calculate $C \equiv C$ bond enthalpy.
Given that enthalpy of atomisation of 150 kcal and H − H bond enthalpy and C − H bond enthalpy are 103 kcal and 93.64 kcal respectively.

Sol. $HC \equiv CH + \dfrac{5}{2} O_2 \rightarrow 2CO_2 + H_2O$
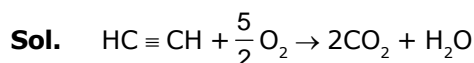
$\Delta H_C^o (CH \equiv CH) = 2\Delta H_f^o (CO_2) + \Delta H_f^o (H_2O) - \Delta H_f^o (C_2H_2)$
$- 312 = 2 \times (-94.38) + (-68.38) - \Delta H_f^o (C_2H_2)$
$\Delta H_f^o (C_2H_2) = 54.86$
$CH \equiv CH \rightarrow 2C(g) + 2H(g)$
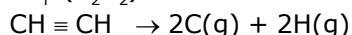
$\sum C \equiv C + 2\sum C-H = 2\Delta H_f^o C(g) + 2\Delta H_f^o H(g) - \Delta H_f^o (CH \equiv CH)$

$\sum C \equiv C + 2 \times 93.64 = 2 \times 150 + 2 \times \dfrac{1}{2} \times 103 - 54.86 \quad \Rightarrow \sum C \equiv C = 160.86 \ kJmol^{-1}$
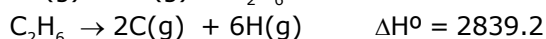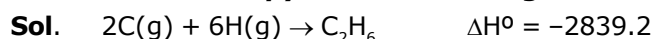
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RESONANCE ENERGY

</div>

"The energy difference between resonance hybrid and most stable canonical structure is called resonance energy".
Resonance energy is always −ve as nature of the process is exothermic.

Ex.9 *The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are −2839.2,*
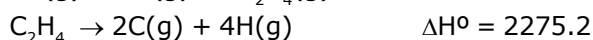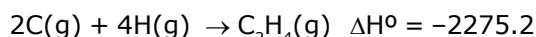*−2275.2 and −5506 kJmol⁻¹ respectively. Calculate the resonance energy of benzene. The bond enthalpy of C − H bond is given as equal to + 410.87 kJ/mol.*

Sol. $2C(g) + 6H(g) \rightarrow C_2H_6 \qquad \Delta H^o = -2839.2$
$C_2H_6 \rightarrow 2C(g) + 6H(g) \qquad \Delta H^o = 2839.2$
$\sum C - C + 6\sum C - H = 2839.2 \qquad \Delta H^o = 2839.2$
$\sum C - C + 6 \times 410.87 = 2839.2$
$\Rightarrow \sum C - C = 373.98 \qquad ... (1)$
$2C(g) + 4H(g) \rightarrow C_2H_4(g) \quad \Delta H^o = -2275.2$
$C_2H_4 \rightarrow 2C(g) + 4H(g) \qquad \Delta H^o = 2275.2$
$\sum C = C + 4\sum C - H = 2275.2$
$\sum (C = C) = 631.72 \qquad ...(2)$

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$6C(g) + 6H(g) \rightarrow C_6H_6$ $\Delta H^o = -5506$

$\Rightarrow C_6H_6 \rightarrow 6C(g) + 6H(g)$ $\Delta H^o = 5506$

$\Rightarrow 3\sum C = C + 3\sum C - C + 6\sum C - H + x = 5506$
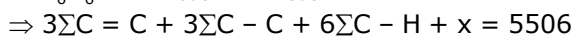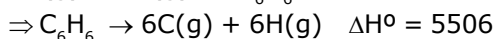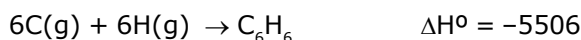
Putting all the values from eq^n, 1, & (2) we get x = 23.68

$\Rightarrow$ Resonance energy of benzene = − 23.68 kJ/mole

BOMB CALORIMETER

$\downarrow O_2$ gas

$\dfrac{w}{M}$ mole $\Leftarrow$ w $\rightarrow$ m gm of water
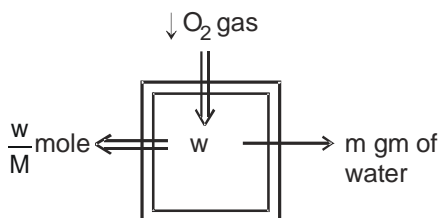
Heat evolved = $ms\Delta t + C\Delta t$

         $\downarrow$

     Heat capacity of container

Heat of combustion = $- \dfrac{[ms\Delta t + C\Delta t]}{\left(\dfrac{w}{M}\right)}$

$= -\dfrac{M}{w}[ms\Delta t + C\Delta t] = -\dfrac{M}{w} \times \Delta t[ms + C]$ $= -\dfrac{M}{w} \times \Delta t[C' + C]$

                                                                           $\downarrow$ $\searrow$

                                                   Heat capacity   Heat capacity
                                                   of water   of container

$\Rightarrow \quad \Delta H = -\dfrac{M}{w} \times \Delta t \times C \rightarrow$ Heat capacity of system

Ex.10 *When 1.0 gm of fructose $C_6H_{12}O_6$ (s) is burnt in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56ºC. If the heat capacity of the calorimeter and its contents is 10.0 kJ/ºC. Calculate the enthalpy of combustion of fructose at 298 K.*

Sol. Heat capacity of the system

$\Delta H_C = \dfrac{-M}{w}[C \times \Delta t]$

$= \dfrac{-180}{1}[10 \times 1.56] = -2808$ kJ/mole

HEAT OF SOLUTION

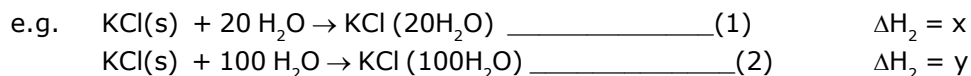Enthalpy change during the dissolution of 1 mole of salt in excess of solvent.

$KCl(s) + aq \rightarrow KCl (aq)$
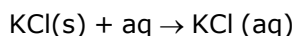
 ΔH^o = Heat of sol^n of KCl (s)

Note :-

(1)   Heat of solution is always exothermic for the anhydrous form of salts which can form their hydrates.

e.g. $CuSO_4$, Na_2SO_4, $FeSO_4$, $ZnSO_4$, $CaCl_2$, $LiCl$ etc.

       $CuSO_4(s) + aq \rightarrow CuSO_4(aq)$ $\Delta H < 0$

(2)   Heat of solution is endothermic for the hdyrated form of the salt.

       $CuSO_4 . 5H_2O + aq \rightarrow CuSO_4(aq)$ $\Delta H > 0$

(3)   Heat of sol^n is endothermic for the salts which do not form their hydrates.

e.g. $NaCl$, $NaNO_3$, KCl etc.

INTEGRAL HEAT OF SOLUTION

Enthalpy change when 1 mole of salt is dissolved in given amount of solvent.

e.g. $KCl(s) + 20 H_2O \rightarrow KCl (20H_2O)$ _____(1) $\Delta H_2 = x$

       $KCl(s) + 100 H_2O \rightarrow KCl (100H_2O)$ _____(2) $\Delta H_2 = y$

HEAT OF DILUTION

Reversing the eq^n (1) and adding in (2)

$KCl(20H_2O) + 80H_2O \rightarrow KCl(100H_2O)$
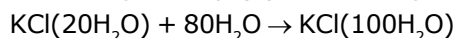
                $\Delta H = y - x$

enthalpy change when the conc. of salt changes from one to another on the basis of dilution
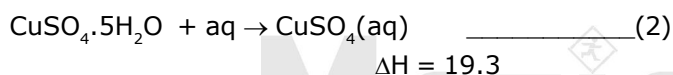
$\Rightarrow \Delta H = y - x =$ Heat of dilution

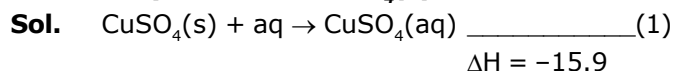## HEAT OF HYDRATION

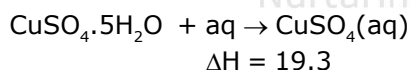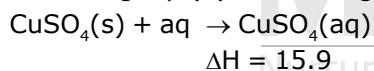Ethalpy change during the formation of hdyrated form of salt from its anhydrous form. It is always exothermic.

$CuSO_4(s) + 5H_2O \rightarrow CuSO_4.5H_2O$
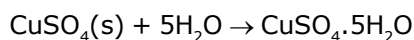
        $\Delta H =$ Heat of hydration of $CuSO_4(s)$

Ex.11 *Heat of sol^n of $CuSO_4(s)$ and $CuSO_4.5H_2O$ is 15.9 and 19.3 kJ/mol respectively. Find the heat of hydration of $CuSO_4(s)$*

Sol. $CuSO_4(s) + aq \rightarrow CuSO_4(aq)$ _____(1)

                $\Delta H = -15.9$

       $CuSO_4.5H_2O + aq \rightarrow CuSO_4(aq)$ _____(2)

                $\Delta H = 19.3$

       Reversing eq^n (1) and adding (2)

       $CuSO_4(s) + aq \rightarrow CuSO_4(aq)$

                $\Delta H = 15.9$

       $CuSO_4.5H_2O + aq \rightarrow CuSO_4(aq)$

                $\Delta H = 19.3$

_____

$CuSO_4.5H_2O \rightarrow CuSO_4(s)$

                $\Delta H = 35.2$

$\Rightarrow$ $CuSO_4(s) \rightarrow CuSO_4.5H_2O$
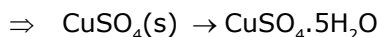
                $\Delta H = -35.2$
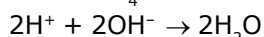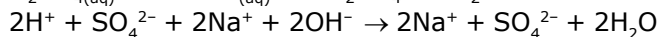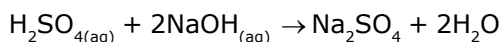
$\Rightarrow$ Heat of hydration of $CuSO_4(s) = -35.2$ kJ/mol

HEAT OF NEUTRALISATION

Enthalpy change during neutralisation of 1 gm equivelant of Acid with 1 gm equivelant of base in

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dilute $soln$ is called heat of neutralisation.

$HCl(aq) + NaoH(aq) \rightarrow NaCl + H_2O$

$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(aq)}$

   $\Delta H^o = -13.7$ Kcal

$H_2SO_{4(aq)} + 2NaOH_{(aq)} \rightarrow Na_2SO_4 + 2H_2O$

$2H^+ + SO_4^{2-} + 2Na^+ + 2OH^- \rightarrow 2Na^+ + SO_4^{2-} + 2H_2O$
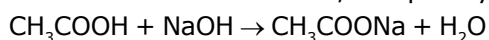
$2H^+ + 2OH^- \rightarrow 2H_2O$
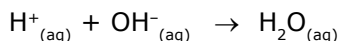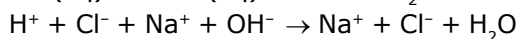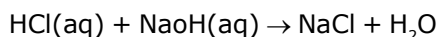
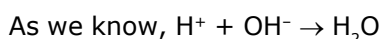$\Rightarrow \Delta H = -13.7 \times 2$

Note :-

In case of weak Acid or weak bases the observed value is little lower because of a part of it is used in dissociating weak Acid or weak base which is not at all completely ionised at dilute solution unditions.
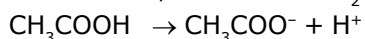
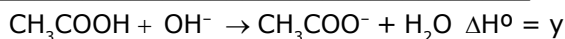   These are however, completely ionised at infinite dilution. e.g.

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

                    $\Delta H = -13.7 + x$

As we know, $H^+ + OH^- \rightarrow H_2O$ $\Delta H = -13.7$ kcal   _____(1)

$CH_3COOH \rightarrow CH_3COO^- + H^+$ $\Delta H^o = x$ _____(2)

Add eqn (1) + (2)

_____

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O \quad \Delta H^o = y$

Ex.12 *100 ml 0.5M H_2SO_4(strong Acid) is neutralised by 200 ml 0.2 M NH_4OH. In a constant pressure calorimeter which results in temperature rise of 1.4ºC. If heat capacity of calorimeter constant is 1.5 kJ/ºC.*

Which statement is/are correct.

Given: $HCl + NaOH \rightarrow NaCl + H_2O + 57$ kJ

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O + 48.1$ kJ
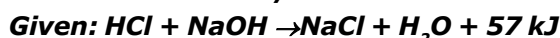
(A) Ethalpy of neutralisation of HCl v/s NH_4OH is −52.5 kJ/mol

(B) Ethalpy of dissociation (ionisation) of NH_4OH is 4.5 kJ/mol

(C) Ethalpy of dissociation of CH_3COOH is 4.6 kJ/mol

(D) ΔH for $2H_2O(l) \rightarrow 2H^+(aq) + 2OH^-(aq)$ is 114 kJ

Sol. (A) Total heat evolved due to the neutralization $= C \times \Delta t = 1.5 \times 1.4 = 2.1$

M. eq of $H_2SO_4 = 100 \times 0.5 = 50$

M.eq of $NH_4OH = 20 \times 0.2 = 40$

Since NH_4OH is limiting hence energy will evolved according to it.

$\Rightarrow 0.04$ gm eq produces 2.1 kJ

1 gm eq produces $= \dfrac{2.1}{0.04} \times 1 \quad = \dfrac{210}{4} = 52.5$

$\Rightarrow$ Heat of neutralisation $= -52.5$ kJ

(B) $-57 + x = -52.5$

$\Rightarrow x = -52.5 + 57 = 4.5$

$\Rightarrow$ Enthalpy of dissociation of $NH_4OH = 4.5$ kJ/mol

(C) $57 - (x + y) = 48.1$
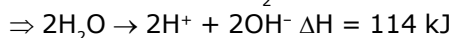
$\Rightarrow x + y = 8.9$

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$\Rightarrow 4.5 + y = 8.9 \Rightarrow y = 4.4$

$\Rightarrow$ enthalpy of dissociation of CH_3COOH = 4.4 kJ/mol

(D)   As we know

$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -57$

$\Rightarrow 2H^+ + 2OH^- \rightarrow 2H_2O \qquad \Delta H = -57 \times 2$

$\Rightarrow 2H_2O \rightarrow 2H^+ + 2OH^- \; \Delta H = 114$ kJ
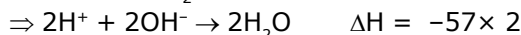
$\Rightarrow$ Option A, B, and D are correct.

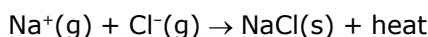## BORN HABER CYCLE

Ionisation Energy :-

The minimum amount of energy required to remove one electron form the outermost shell of an isolated gaseous atom is called ionisation energy of the element.

Electron affinity:-

Amount of energy released when an extra electron is added to an isolated gaseous atom.

Lattice Energy :

Amount of energy released when 1 mole of gaseous cation and 1 mole gaseous anion combine to each other and form 1 mole of ionic compound is called lattice energy.
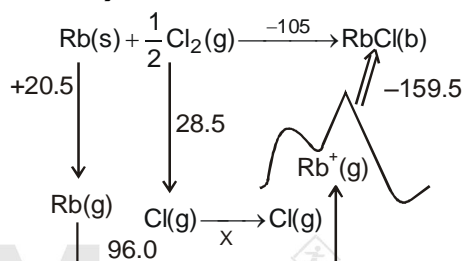
$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) + heat$$
$$\downarrow$$
$$\text{Lattice energy}$$

$$\Delta H_{lattice} \; \alpha \; \frac{q_1 q_2}{\left(r^+ + r^-\right)^2}$$

Ex.13 The born-Haber cycle for formation of rubidium chloride ((RbCl) is given bellow (the enthalpies are in kcal mol^{-1})

$$Rb(s) + \frac{1}{2}Cl_2(g) \xrightarrow{\;-105\;} RbCl(b)$$

+20.5   28.5 -159.5

$Rb^+(g)$

$Rb(g) \qquad Cl(g) \xrightarrow{\;X\;} Cl(g)$

96.0

find the value of X?

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