Thermochemistry

Thermochemistry

Thermochemistry deals with the energy changes involved in chemical reaction.

Thermochemical Reaction :

A chemical reaction which tells us about all the information like energy changes associated with a chemical reaction and phases of various reactants and products is called Thermochemical reactions.

Definition

The branch of chemistry concerned with the quantities of heat evolved or absorbed during chemical reactions is known as thermochemistry.

Ex.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

$$\Delta H = -285.91 \text{ kJ}$$

$$\underset{\text{(graphite)}}{C} + \underset{\text{(rhombic)}}{2S} \longrightarrow CS_2$$

$$\Delta H = +91.96 \text{ kJ}$$

The change in enthalpy during a chemical reaction occurs due to breaking and making of bonds,

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

Δn_g = Moles of gaseous products– Moles of gaseous reactants

R = Molar gas constant

T = Temperature in Kelvin

Concept Ladder

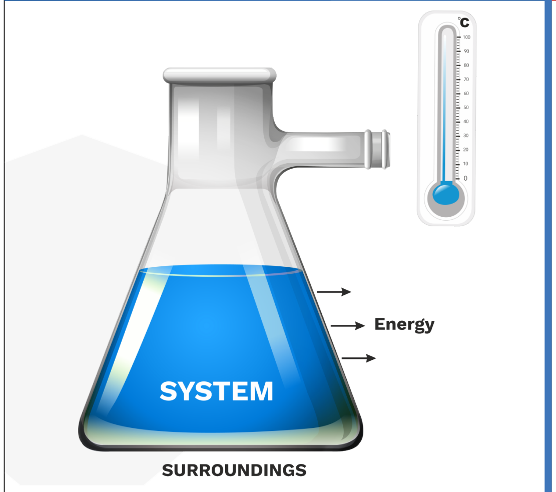
- If $\Delta n_g < 0$,then ΔH may be < 0
- If $\Delta n_g > 0$,then ΔH may be more than 0 means endothermic

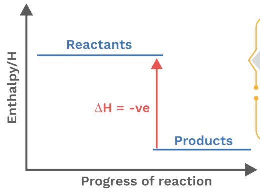
Ex.

Endothermic	Exothermic
1. $A + B \rightarrow C$; $\Delta H = +10$ KJ 2. $A + B + 10$ KJ $\rightarrow C$ 3. $A + B \rightarrow C - 10$ KJ	1. $A + B \rightarrow C$; $\Delta H = -10$ KJ 2. $A + B - 10$ KJ $\rightarrow C$ 3. $A + B \rightarrow C + 10$ KJ

EXOTHERMIC

An exothermic reaction occurs when the temperature of a system decreases due to the evolution of heat.



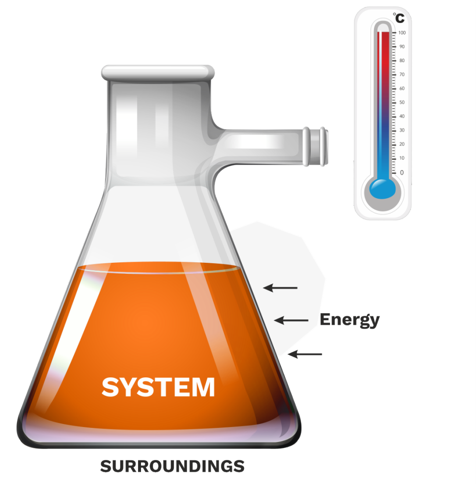


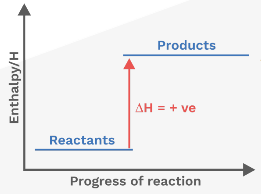
In an exothermic reaction, ΔH is negative because heat is given out to the surroundings.

$C(s) + O_2(g) \rightarrow CO_2(g)$ (ΔH= -393.5kJ)

ENDOTHERMIC

An endothemic reaction occurs when the temperature of an isolated system increases due to gain of heat.





In an endothermic reaction, ΔH is positive because heat is taken in, from the surroundings.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ (ΔH= +180.5kJ)

EXOTHERMIC	ENDOTHERMIC
Making ice cubes	Melting ice cubes
Formation of snow in clouds	Conversion of frost to water vapour
Condensation of rain from water vapour	Evaporation of water
A candle flame	Forming a cation from an atom in the gas phase
Mixing sodium sulphite and bleach	Baking bread
Rusting iron	Cooking an egg
Burning sugar	Producing sugar by photosynthesis
Forming ion pairs	Separating ion pairs
Combining atoms to make a molecule in the gas phase	Splitting a gas molecule apart
Mixing water and strong acids	Mixing water and ammonium nitrate

ENTHALPY :

When a chemical reactions are carried out at constant pressure (atmospheric pressure) then it has been found a new state function knows as Enthalpy (H).

Ex.

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \; ; \Delta H = -44 \text{ kcal}$$

$$H = U + PV$$

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

(At constant pressure)

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

(Combining with first law)

$$\Delta H = q_p$$

Hence, transfer of heat at constant pressure brings about a change in the enthalpy of the system

- We cannot exactly calculate enthalpy content of a substance only the change in enthalpy can be calculated when substance is taken from one state to other
- Let Enthalpy content initially be $H^0_{m,1}$ & finally enthalpy content be $H^0_{m,2}$.

Previous Year's Question

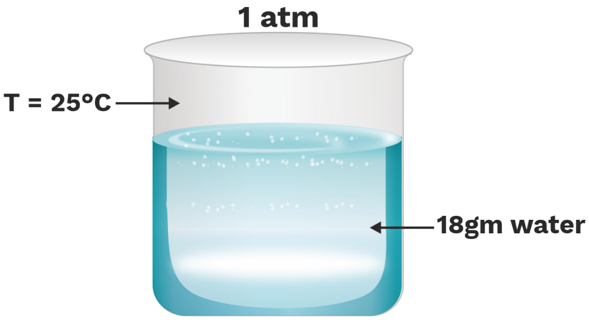
If ΔH is the change in enthalpy and ΔU, the change in internal energy accompoanying a gaseous reaction, then **[AIPMT]**

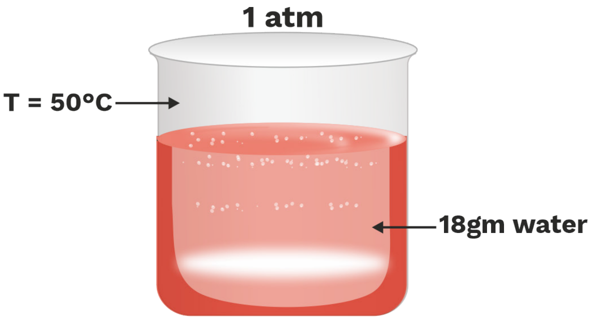
(1) ΔH is always greater than ΔU

(2) ΔH < ΔU only if the number of moles of the products is greater than the number of moles of the reactants

(3) ΔH is always less than ΔU

(4) ΔH < ΔU only if the number of moles of prdoucts is less than the numbe of moles of the reactants.





Then $\Delta H^\circ = H^0_{m,2} - H^0_{m,1}$

= heat added at constant pressure to change temperature from 25° C to 50°C

= $C_p\Delta T$ = 18 cal/mole × 25°C = 450 cal

Heat of Reaction :

- The heat change during a reaction is known as heat of reaction
- This process may be exothermic or endothermic.

Rack your Brain

For a reaction having ΔH = +ve and ΔE = −ve, what will be the classification as exothermic or endothermic?

Q.1 $C(s) + O_2(g) \rightarrow CO_2(g)$

Then related ΔH is known as

(1) HOF (Heat of formation)
(2) HOC (Heat of combustion)
(3) HOR (Heat of reaction)
(4) HOS (Heat of solution)

A.1 (3) Heat of reaction

Factors affecting heat of reaction :

1. Conditions of constant pressure and volume

(i) Heat at constant pressure is known as enthalpy change

$$q_p = \Delta H$$

(ii) Heat at constant volume is known as internal energy change

$$q_v = \Delta E \text{ or } \Delta U$$

Rack your Brain

On what basis we can classify the reactions as exothermic or endothermic?

Physical state of reactant and product :

1. Physical state of reactant

$$\underset{\text{(Diamond)}}{C} + O_2 \rightarrow CO_2; \quad \Delta H = -395 \text{ KJ}$$

$$\underset{\text{(Graphite)}}{C} + O_2 \rightarrow CO_2; \quad \Delta H = -393 \text{ KJ}$$

- According to above example one can say that heat of reaction depends on the physical state of reactant
- In endothermic reaction, obtained product is known as endothermic product and in exothermic reaction obtained product is known as exothermic product

2. Physical state of product :

According to example one can say that ΔH depends on the physical state of product

(i) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \Delta H = -68 \text{ Kcal}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g); \Delta H = -57 \text{ Kcal}$

Object: $H_2O(l) \rightarrow H_2O(g); \Delta H = 11 \text{ KJ}$

In the formation of H_2O (liq.) more heat is evolved in comparison to the formation of H_2O gas because some part of heat is used to convert liquid into gas

- Endothermic product is less stable than exothermic product

$C + O_2$; $\Delta H = -395.4$ KJ

Diamond

$C + O_2$; $\Delta H = -393.5$ KJ

Graphite

Rack your Brain

Can you guess what will be the effect of changing pressure to a reaction involving only ideal gas?

Previous Year's Question

Zn gives H_2 gas with H_2SO_4 and HCl but not with HNO_3 because

[AIPMT]

(1) Zn act as oxidising agent when react with HNO_3
(2) HNO_3 is weaker acid than H_2SO_4 and HCl
(3) In electrochemical series Zn is above hydrogen
(4) NO_3^- is reduced in preference to hydronium ion.

Concept Ladder

When state changes from lower energy to higher energy state, process is endothermic and vice versa for exothermic.

Effect of temperature

Kirchoff equation :

1. At constant pressure

Let at temperature T_1, heat of reaction ΔH_1 and at temperature T_2 heat of reaction is ΔH_2

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

$$\Delta C_p - (\Sigma C_p)_p - (\Sigma C_p)_R$$

$$\begin{tikzcd} A \arrow[r, "\Delta_r H"] \arrow[d, "\Delta_r H_1"'] & B \\ C \arrow[r, "\Delta_r H_2"'] & D \arrow[u, "\Delta_r H_3"'] \end{tikzcd}$$

$$\boxed{\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3}$$

2. At constant volume

$$\Delta U_2 - \Delta U_1 = \Delta C_V (T_2 - T_1)$$

$$\Delta C_v - (\Sigma C_V)_p - (\Sigma C_V)_R$$

Types of Heat of Reaction

1. Heat of formation (ΔH_f) :

i. This process may be exothermic or endothermic

ii. Standard condition :

P → 1 atm

T → Different for different reactions

If not given then we will consider it 25° C

iii. Standard enthalpy of substance is considered as standard heat of formation

iv. Heat of formation of reaction :

Concept Ladder

The standard condition are :

- Solid / liquid / gas hould be at 1 bar.
- For substance dissolved in solution concentration should be 1M.
- By convention, enthalpy of formation $\Delta_f H$, of an element in reference state is taken as zero.

Previous Year's Question

Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434, 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is

[AIPMT]

(1) -93 kJ mol^{-1}
(2) 245 kJ mol^{-1}
(3) 93 kJ mol^{-1}
(4) -245 kJ mol^{-1}

Definitions

The heat evolved or absorbed when 1 mole of a substance is formed from its constituent elements under constant pressure and temperature conditions is called enthalpy of formation. It is denoted by ΔH_f.

Example.

$$C(graphite) + O_2 \longrightarrow CO_2(g)$$

$$C(graphite) + 2H_2 \longrightarrow CH_4(g)$$

1. If heat of formation of different substances are given then to calculate ΔH of a reaction

$$\Delta H = \left(\sum H_f\right)_{Products} - \left(\sum H_f\right)_{Reactants}$$

- In standard condition

$$\Delta H^{\circ} = \left(\sum H_f^0\right)_{Products} - \left(\sum H_f^0\right)_{Reactants}$$

- If heat of combination of different substance are given

$$\Delta H^{\circ} = \left(\sum H_{comb}\right)_{Reactants} - \left(\sum H_{comb}\right)_{Products}$$

The reference state of commonly used elements are :

Elements	Reference state
C	C(graphite)
S	S_8(rhombic)
P	P_4 (white)
O	$O_2(g)$
H	$H_2(g)$
Br	$Br_2(l)$
Metal	$M_{(s)}$(except Hg(l))

Concept Ladder

Standard heat of formation of constituent particle is zero.
$\Delta_f H^0$ of O_2, H_2, Cl_2 , N_2 , Na, K, Fe, C (graphite) etc. = 0

Rack your Brain

The standard heat of formation at 101.3 kNm^{-2} and 298 K for which state of bromine is arbitrarily taken to be zero?

Previous Year's Question

The heat of combustion of carbon to CO_2 is -393.5 kJ mol. The heat released upon formation of 35.2g of CO_2 from carbon and oxygen gas is **[NEET]**

(1) +315 KJ (2) -630 kJ
(3) -3.15 kJ (4) -315 kJ

Q.2 1. $C + O_2 \rightarrow CO_2$ $\Delta H = -x$

2. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H = -y$

3. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -z$

Find $\Delta H_f(CH_4) = ?$

A.2 Multiply Equation (2) by 2

Now, Equation (1) + Equation (2) × 2 - Equation (3)

$C + 2H_2 \rightarrow CH_4$

$\Delta_f H^\circ(CH_4) = -x - 2y + z$

Q.3 The $\Delta_f H^\circ$ for N_2O_5 (g) in kJ/mol on the basis of the following data is :

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta_r H^\circ = -114$ kJ/mol

$4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g)$ $\Delta_r H^\circ = -102.6$ kJ/mol

$\Delta_f H^\circ$ NO(g) = 90.2 kJ/mol

(1) 15.1 (2) 30.2 (3) – 36.2 (4) None of these

A.3 (1)

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$ $\Delta_f H^\circ = 90.2$

$N_2(g) + O_2(g) \longrightarrow 2NO(g)$ $\Delta_r H^\circ = 90.2 \times 2$ ....(i)

$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$ $\Delta_r H^\circ = -114$ ....(ii)

$2NO_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O_5(g)$ $\Delta_r H^\circ = \frac{-102.6}{2} = -51.3$

Addition of (i),(ii) and (iii) equation

$N_2(g) + \frac{5}{2}O_2(g) \rightarrow N_2O_5(g)$

$\Delta_f H^\circ$ for $N_2O_5(g)$ = 15.1 kJ/mol

Q.4 In following which exothermic product is most stable

(1) A : ΔH = – 200 Kcal/mol
(2) A : ΔH = – 100 Kcal/mol
(3) A : ΔH = – 500 Kcal/mol
(4) A : ΔH = –50 Kcal/mol

A.4 (3)

Q.5 In following reactions whose ΔH indicates the heat of formations

1. $C_{diamond} + O_2 \rightarrow CO_2$
2. $C + 2H_2 \rightarrow CH_4$
3. $CaO + CO_2 \rightarrow CaCO_3$
4. $2C + O_2 \rightarrow 2CO$
5. $2H_2 + O_2 \rightarrow 2H_2O$
6. $K + \frac{1}{2}Cl_2 + O_3 \rightarrow KClO_3$

A.5 (2)

Q.6 The standard heats of formation at 298 K for CCl_4(g), H_2O (g), CO_2(g) and HCl (g) are -25.5, -57.8, -94.1 and -22.1 kcal mol^{-1} respectively, Calculate $\Delta H^\circ_{298\ K}$ for the reaction :

$$CCl_4(g) + 2H_2O(g) \longrightarrow CO_2(g) + 4HCl(g)$$

A.6

$$\begin{aligned}\Delta_f H &= \left[\Delta_f H(CO_2) + 4\,\Delta_f H(HCl)\right] - \left[\Delta_f H(CCl_4) + 2\Delta_f H(H_2O)\right] \\ &= \left[-94.1 + 4\times(-22.1)\right] - \left[-25.5 + 2\times(-57.8)\right] \\ &= -41.4\,\text{kcal}\end{aligned}$$

Q.7 Standard heat of formation of CO & CO_2 is –26.4 & –94.1 Kcal/mol, Then find out heat of combustion of CO (In Kcal per mol)

A.7

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$\Delta H = \left(\sum H_f^0\right)_p - \left(\sum H_f^0\right)_R = [-94.1-(-26.4)]$$

= –67.7 Kcal/mol

Heat of combustion of CO is -67.7 kcal/mol

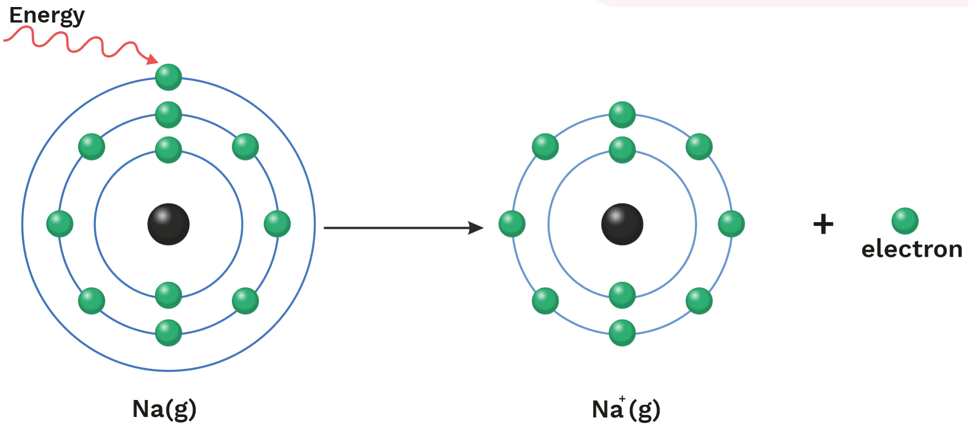
Ionisation Enthalpy ($\Delta_i H$)

It is the enthalpy change when an electron is removed from an isolated gaseous atom or in its ground state under conditions of constant temperature and pressure.

$X(g) \longrightarrow X^+(g) + e^-$

Rack your Brain

Do the Ionisation energy and ionisation enthalpy are same for noble gases.?



Electron gain Enthalpy ($_{\Delta eg}H$)

It is the enthalpy change when an electron is added to a neutral gaseous atom to convert. It into a negative ion under conditions of constant temperature and pressure

$X(g) + e^- \longrightarrow X^-(g)$

Lattice Enthalpy ($\Delta_{lattice}H$) :

At constant temperature and pressure, when one mole of an ionic compound dissociates into its ions in gaseous state the change in enthalpy of an ionic compound is known as Lattice Enthalpy.

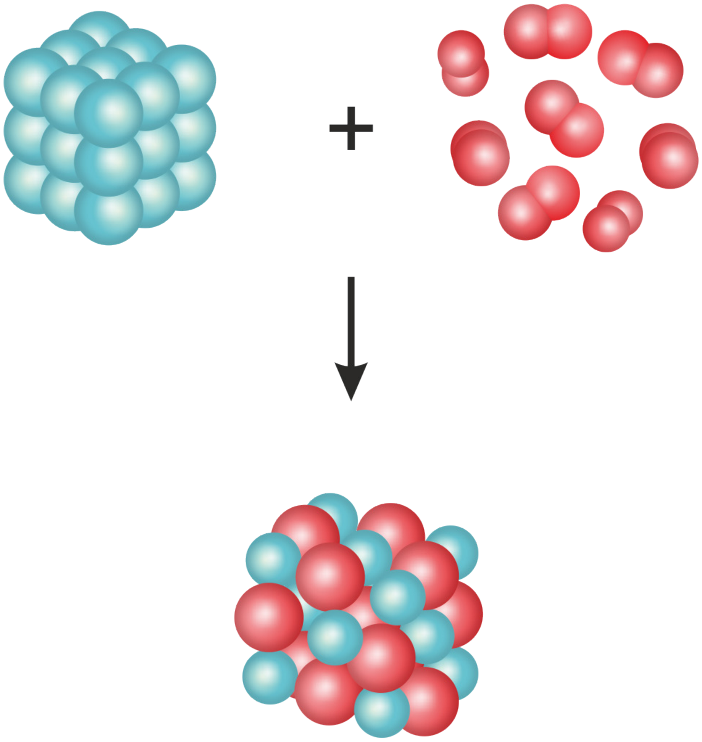
$Na^+Cl^-(s) \longrightarrow Na^+(g) + Cl^-(g)$;

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

Lattice enthalpy can also be defined for the reverse process. In that case the value of $\Delta_{lattice}H$ will be negative.

Concept Ladder

Ionisation energy is measured in terms of eV where as ionisation enthalpy is per mole of substance.



Heat of combustion

1. When 1 mole of compound is completely burnt, the heat evovled in the process is termed as Heat of combustion.

Ex.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O; \Delta H = -890.3\,kJ$$

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l); \quad \Delta H = -1367.4\,kJ$$

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l); \ \Delta H = -745.6\ kcal$$

2. This Process is always exothermic
3. Among hydrocarbon as number of carbon atom increases heat of combustion increases if number of carbon atoms are same then more number of hydrogen atom indicates more heat of combustion.
4. In heat of combustion process substance is completely oxidized

Definitions

The amount of heat required to raise the temperature of a body through 1°C is called Specific Heat.

5. Following process do not consider in heat of combustion

E.g 1. $N_2 + O_2 \rightarrow 2NO$; $\Delta H = +ve$

2. $N_2 + 1/2\ O_2 \rightarrow NO$; $\Delta H = +ve$

3. $F_2 + 1/2\ O_2 \rightarrow OF_2$; $\Delta H = +\ ve$

Because in (1) and (2) reaction nitrogen show incomplete oxidation while in 3rd reaction fluorine show reduction.

Measurement of Enthalpy of Combustion :

Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure. The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.

If total heat capacity of calorimeter and all of its contents = C, rise in temperature = ΔT then heat released = $q = C\Delta T$ of this heat is because of mass m of substance then : due to 1 mole, heat released $= \left(\frac{M}{m}\right) q = \Delta E_C^0$ (constant volume)

Now, ΔH_C^0 can be calculated by using

$$\Delta H_C^0 = \Delta E_C^0 + \Delta n_g RT$$

Where Δn_g is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.

Rack your Brain

The combustion of a substance is always exothermic or endothermic?

Concept Ladder

Elements	Combustion Products
$C_{(graphite)}$	CO_2
H	$H_2O_{(l)}$ or $H_2O_{(g)}$(depends on condition)
S	$SO_{2(g)}$

Rack your Brain

Can you relate electron gain enthalpy ($\Delta_{eg}H$) and electron affinity?

Q.8 Reaction :

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $\Delta H = 800$ kJ/mol

Then find out the amount of heat evolved on the combustion of 4 gm CH_4

(1) 150 kJ (2) 200 kJ (3) 220 kJ (4) 180 kJ

A.8 No. of moles of 4g of CH_4 = 4/16

1 Mole of CH_4 evolve heat during combustion = 800kJ

4/16 mole fo CH_4 evolve heat = 800×4/16

= 3200/16 = 200 kJ

Q.9 Heat of combustion of glucose is –2520 kJ/mol then calculate the moles of required O_2 when amount of heat evolved is 504 kJ ?

(1) 1.5 mol (2) 2.2 mol (3) 1.8 mol (4) 1.2 mol

A.9 During complete combustion of 1 mole of gluclose, 6 mole of O_2 is required which yields -2520 kJ of energy

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + 6H_2O$; $\Delta H = -2520$ kJ/mol.

so, number of moles of O_2 required when 504 kJ of energy is released

$$= \frac{6 \times 504}{2520} = 1.2 \text{ mol}$$

Q.10 Heat of formation of CO_2,H_2O and propene

= –393.5 kJ, –285.8 kJ, +20.4 kJ are respectively,

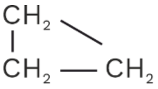
And heat of iso-merisation of cyclopropane to propene is –33 kJ then calculate heat of combustion of cyclo-propene (In kJ per mole)

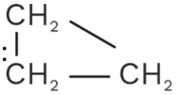
(1) –2091.3 (2) –2391 (3) –2019 (4) –2319.6

A.10 (1)

1. $C + O_2 \rightarrow CO_2$; $\Delta H = -393.5$ kJ

2. $H_2 + 1/2O_2 \rightarrow H_2O_2$; $\Delta H = -285.5$ kJ
3. $3C + 3H_2 \rightarrow C_3H_6$; $\Delta H = -20.4$ kJ

4.  $\longrightarrow C_3H_6$; $\Delta H = (-33)$

Object:  $+ \frac{9}{2} O_2 \rightarrow 3CO_2 + 3H_2O$

(1) × 3+ 3 × (2) + (4) –(3); $\Delta H = (-393.5) \times 3 + 3(-285.8) + (-33) - (20.4)$

$\Delta H = -2091.3$ kJ/mole

Q.11 In a Gobar gas plant, gobar gas is formed by bacterial fermentation of animal refuse. It mainly contains methane and its heat of combustion is -809 kJ mol^{-1} according to following equation:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O; \qquad \Delta H = -809\,kJ$$

How much gobar gas would have to be produced per day for a small village of 50 families, if it is assumed that each family requires 20000 kJ of energy per day? The methane content in gobar gas is 80% by mass.

A.11 Energy consumption of 50 families per day

$= 50 \times 20000$ kJ $= 1 \times 10^6$ kJ

809 kJ of energy is obtained by burning methane = 16g

1×10^6 kJ of energy will be obtained by burning methane

$$= \frac{16}{809} \times 10^6 = 1.98 \times 10^4 g \qquad = 19.8\,kg$$

Since, methane content in gobar gas is 80% by mass, hence, the mass of gobar gas needed

$$= \frac{100}{80} \times 19.8 = 24.75\,kg$$

Q.12 Standard heat of formation of CH_4, CO_2 and H_2O are -80, -400 and -240 kJ/mole, then calculate heat of combustion of CH_4 (in KJ per mole)

(1) –800 KJ/mol

(2) –720 KJ/mol

(3) –880 KJ/mol

(4) –680 KJ/mol

A.12 (1)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$\Delta H = -400 + 2(-240) - (-80)$

$= -400 - 480 + 80$

$= -400 - 400$

$= -800$ kJ /mol

Q.13 If in above question 1m^3 CH_4 is burnt at NTP then find out the amount of heat evolved :

(1) 33.5×10^3 (2) 37.3×10^3 (3) 35.3×10^3 (4) 36.5×10^3

A.13 1 m^3 of CH_4 means 1000 L of CH_4

22.4 litre of CH_4 during cmbustion gives 800 kJ of energy

1 litre of CH_4 during cmbustion gives 800/22.4 kJ

1000 of CH_4 during cmbustion gives $\frac{800}{22.4} \times 1000$ kJ

$= 35.3 \times 10^3$ kJ

Q.14

1. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H = -283$ KJ

2. $CO + \frac{1}{2}O_2 \rightarrow CO_2$; $\Delta H = -241.8$ KJ

Then find out the amount of heat evolved on the combustion of 112 lit. water gas at NTP

(1) 1213 kJ (2) 1123 kJ (3) 1321 kJ (4) 1312 kJ

A.14 (4)

$(CO + H_2) + O_2 \rightarrow CO_2 + H_2O$

(1) + (2)

$\Delta H = -241.8 + (-283) = -524.8$

44.8 lit then amount of heat evolved = 524.8

112 lit then amount of heat evolved = $\frac{112 \times 524.8}{44.8} = 1312$ kJ

Calorific value

1. Amount of heat evolved on the complete combustion of 1g substance.

Example

When CH_4 undergoes complete combustion, it releases 800 kJ of energy.

then its calorific value is calculated as follows

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $\Delta H = -800$ KJ/mol

16g gives 800 KJ/g

1g gives = $\frac{800}{16} = 50$ kJ/g

Definitions

Enthalpy change accompanied by combustion of l g solid or 1 g liquid or 1 cc gas is called calorific value.

2. More calorific value indicate more fuel efficiency
3. If food;
   Highest caloric value — fats
   Least caloric value — Carbohydrates
4. Among gases; highest calorific value — H_2 i.e 150 KJ/g

Rack your Brain

Hydrogen has the highest calorific value. However, it is not used as domestic or industrial fuel. Why?

Q.15 Heat of combustion of CH_4 and C_4H_{10} are – 880 & –2800 KJ/mol respectively. Then find out the calorific value of each and which one is best fuel.

(1) 55, 48.27 C_4H_{10}	(2) 55, 48.27, CH_4
(3) 52, 46.24, C_4H_{10}	(4) 52, 46.24 CH_4

A.15 Caloric value of methane = $\dfrac{-880}{16} = -55\,\text{kJ / g}$

Caloric value of $C_4H_{10} = \dfrac{-2800}{58} = -48.27\,\text{kJ / g}$

More calorific value indicate more fuel efficiency so, CH_4 is the best fuel.

Q.16 On the combustion of 5 gm coke obtained heat is used to raise the temperature of 1 kg of water from 10°C to 47° C then calculate the fuel value of coke while specific heat of water is 1 cal $K^{-1}g^{-1}$

(1) 7200 cal/gm (2) 7300 cal/gm (3) 7600 cal/ gm (4) 7400cal/ gm

A.16 (4)

$\Delta H = mC_pdT$

$= 1000 \times 1 \times (47–10) = 37000$ cal

Caloric value = $\dfrac{37000}{5}$ = 7400 cal/g

Concept Ladder

Heat exchange = Heat capacity × Temperature change (heat exchange—when no chemical change or state change occurs)

Enthalpy of Neutralisation $\Delta_{neut}H$:

1. It is the heat released or absorbed when one equivalent of an acid undergoes neutralisation with one equivalent of a base.
   Example :
   $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$;
   $\Delta_{neut}H = -\ 57.7\ \text{kJ eq}^{-1}$

2. The value of enthalpy of neutralisation for strong acid and strong base is always constant (– 57.7 kJ eq^{-1}), independent from the acid and base taken.
3. The magnitude of enthalpy change of neutralization decreases when any one of the acid or base taken is weak.
4. Heat of neutralisation is < –13.7 kcal because some amount of heat is used to ionise the weak electrolyte.
5. Heat of ionisation is endothermic and it will be maximum for weak acid and weak base because both are weak electrolyte.

Concept Ladder

Heat of neutralisation of weak acid-strong base is not constant.

Q.17 Reaction

$H^+ + OH^- \rightarrow H_2O + 13.7$ Kcal

Then find out heat of neutralisation in following process

1. 0.25 mol H_2SO_4 + 4g NaOH were mixed
2. 100 ml 0.1 M H_2SO_4 + 100 ml 0.1 M NaOH were mixed

A.17 1. Equivalent of $H_2SO_4 = 0.25 \times 2 = 0.5$
Equivalent of NaOH = 4/10 × 1 = 0.1
Heat of Neutralistion = -13.7 × 0.1 = - 1.37 kcal

2. Equivalent of $H_2SO_4 = 1 \times 2 \times (100/1000) = 0.02$
Equivalent of NaOH = 1 × 0.1 × (100/1000) = 0.01
Heat of Neutralisation = -13.7 × 0.01 = 0.137 kcal

Enthalpy of Solution, $\Delta_{sol}H$:

1. It is the enthalpy change when one mole of a substance is dissolved in a specified amount of solvent under conditions of constant temperature and pressure.

Example :

$NaCl(s) \longrightarrow NaCl(aq)$; $\Delta_{sol}H = + 4kJ\ mol^{-1}$

$NaCl(s) \longrightarrow Na^+ (aq) + Cl^-(aq)$; $\Delta_{sol}H = + 4kJ\ mol^{-1}$

Concept Ladder

The heat of solution of NaCl is very small as the heat of ionisation is nearly equal to the heat of hydration.

2. When large volume of solvent is taken, the enthalpy change is called enthalpy of solution at infinite dilution.
3. This process may be exothermic and endothermic
4. In heat of solution process solid finally convert into aqueous.If it can crystalise the water molecule then first of all water molecule crystallise after it. It will convert into aqueous and if it cannot crystallise the water molecule then it will direct convert from solid to aqueous .

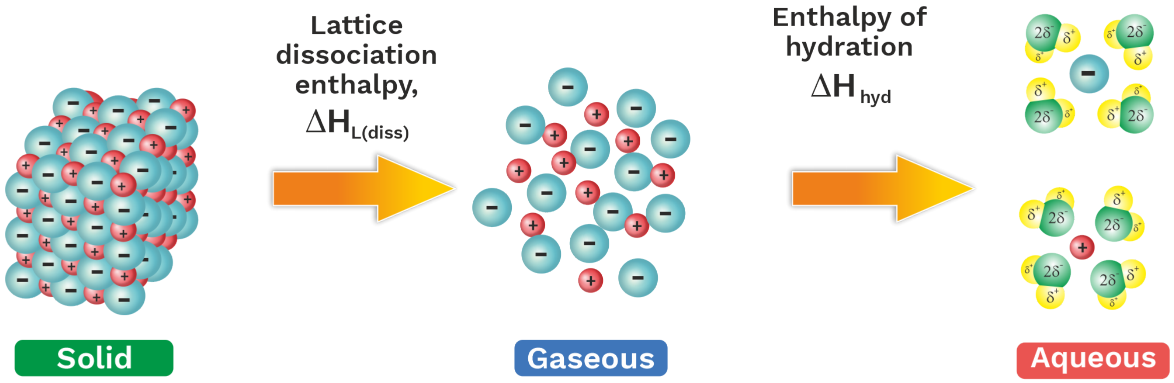
$CuSO_4$ (s) + aq $\rightarrow$ $CuSO_4.5H_2O$(aq); $\Delta H = -ve$

KCl (s) + aq $\rightarrow$ KCl (aq); $\Delta H = -ve$

Concept Ladder

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved.

Enthalpy Of Solution



Q.18 Heat of solution of $CuSO_4$(s) is – 15.9 kcal/mol and heat of solution of $CuSO_4.5H_2O$(s) is 2.8 kcal/mol then find out heat of hydration of $CuSO_4$(s) (In kcal per mole)

(1) –18.7 (2) –16.8 (3) –13.1 (4) –14.7

A.18 (1)

(1) $CuSO_4(s) + aq \rightarrow CuSO_4.5H_2O(aq)$; $\Delta H = -15.9$ kcal/mol

(2) $CuSO_4.5H_2O(s) + aq \rightarrow CuSO_4.5H_2O(aq)$; $\Delta H = 2.8$ kcal/mol

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

Equations (1)–(2) = –15.9–2.8 ; $\Delta H = -18.7$ kcal/mol

Enthalpy of Hydration, $\Delta_{hyd}H$:

It is the enthalpy change when one mole of an anhydrous (or partially hydrated) compound combines with the required number of moles of water to form a specific hydrate at the specified temperature and pressure. For example :

$CuSO_4\ (s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s)$;

$\Delta_{(hyd)}H = -\ 78.20\ kJ\ mol^{-1}$

Concept Ladder

During dissolution, physical state of the compound changes while during hydration, there is no change in the physical state of the compound.

Q.19 Heat of solution $MgCl_2(s)$ is –25 Kcal/mol and heat of hydration of $MgCl_2(s)$ –30Kcal/mol then find out heat of solution of $MgCl_2.2H_2O(s)$ (in Kcal/mol)

(1) –5 (2) –55 (3) 5 (4) 55

A.19 (3)

$MgCl_2(s) + aq \rightarrow MgCl_2.2H_2O\ (aq)$; $\Delta H = -\ 25Kcal$

$MgCl_2(s) + aq \rightarrow MgCl_2.2H_2O\ (s)$; $\Delta H = -\ 30Kcal$

$MgCl_2.2H_2O\ (s) + aq \rightarrow MgCl_2.2H_2O(aq)$

Equations (1) – (2)

Heat of solution = –25 + 30 = 5 Kcal/mol

Enthalpy of Atomisation, Δ_aH :

1. It is the enthalpy change when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition.
2. This process is always endothermic

For Example :

$H_2(g) \longrightarrow 2H(g)$; $\Delta_aH = 435.0\ kJ\ mol^{-1}$

$CH_4(g) \longrightarrow C(g) + 4H(g)$; $\Delta_aH = 1665\ kJ\ mol^{-1}$

Concept Ladder

Heat of combustion of organic substances and heat of hydrogenation are determined in Bomb calorimeter.

Heat of Hydrogenation

- Heat evolved when 1 mole unsaturated combines with fix number of hydrogen molecule & convert into saturated hydrocarbon

  $C_2H_2 + 2H_2 \rightarrow C_2H_6$; $\Delta H = -ve$
- This process is always exothermic

Q.20 Heat of combustion of cyclohexane, cyclohexene and H_2 are –3920, – 3800, –241 KJ /mol. Then calculate heat of hydrogenation of cyclohexene (C_6H_{10})

(1) –133 KJ / mol
(2) –125 KJ / mol
(3) –141 KJ/ mol
(4) –121 KJ / mol

A.20 (4)

$C_6H_{10} + H_2 \longrightarrow C_6H_{12}$

Heat of hydrogenation

= (–3800–241) –(–3920)

=–4041 + 3920

Heat of hydrogenation of cyclohexene = –121 KJ/mol

Heat of sublimation :

- Heat required to convert 1 mole solid directly into gas is known as heat of sublimation

$$(\Delta H)_{\text{sublimation}} = (\Delta H)_{\text{fusion}} + (\Delta H)_{\text{vapourisation}}$$

- This process always endothermic.
  Ex. $I_2(s) \longrightarrow I_2(g)$; ΔH = +14.9 kcal

Heat of Transition

- Heat evolved or absorbed to convert 1 mole substance from 1 allotropic form to another is known as heat of transition.
- This process may be exothermic or endothermic.

Heat of Fusion :

- Heat required to convert 1 mole solid into liquid is known as heat of fusion
  $H_2O(s) \rightarrow H_2O(l)$; ΔH = +1.44 kcal

Heat of vapourisation

- Heat required to convert 1 mole liquid into gas is known as heat of vapourisation.
  $H_2O(l) \rightarrow H_2O(g)$; ΔH = 10.5 kcal
- This process is always endothermic.

Rack your Brain

C (Diamond) ⟶ C (Graphite) + x kJ. The heat change in this process is called ?

Concept Ladder

Allotropic transitions are also phase transformations.

Q.21 Calculate heat of transition when diamond convert into graphite

1. $C_{(diamond)} + O_2 \rightarrow CO_2 \quad \Delta H = -395$ KJ/mol

2. $C_{(graphite)} + O_2 \rightarrow CO_2 \quad \Delta H = -393$ KJ/mol

(1) −2 KJ (2) +2 KJ (3) +4 KJ (4) −4 KJ

A.21 (1)

Heat of transition when diamond convert into graphite
Now, substract equation (2) from (1)
$\Delta H = -\ 395 - (-393) = -2KJ$

- **Free energy change for an irreversible reaction**

  $$\Delta G = \left(\sum G_f\right)_P - \left(\sum G_f\right)_R$$

  In standard condition

  $$\Delta G^\circ = \left(\sum G_f^0\right)_P - \left(\sum G_f^0\right)_R$$

  G_f – free energy of formation

- **Free energy change for a reversible reaction**

  $$\Delta G = \Delta G^0 + 2.303\ RT \log Q$$

Concept Ladder

The values of change in Gibbs free energy (ΔG) and change in enthalpy (ΔH), depend upon entropy change (ΔS) for a thermochemical reaction.

Q.22 Reaction

1. $C + O_2 \rightarrow CO_2 \quad ; \Delta G = -380$ KJ
2. $4Al + 3O_2 \rightarrow 2Al_2O_3 \quad ; \Delta G = -2250$ KJ

Reduction of Al_2O_3 in presence of carbon is possible or not ?

(1) −555 KJ (2) −745 KJ (3) +555 KJ (4) + 745 KJ

A.22 (3)

Now Multiply equation (1) by 3/2

$$\frac{3}{2}C + \frac{3}{2}O_2 \longrightarrow \frac{3}{2}CO_2; \Delta G = -380 \times \frac{3}{2}kJ$$

Multiply Eqation 1/2 and written as

$$Al_2O_3 \longrightarrow 2\,Al + \frac{3}{2}O_2; \Delta G = \frac{2250}{2}kJ$$

On adding above equations
$Al_2O_3 + 3/2\ C \rightarrow 2Al + 3/2\ CO_2;\ \Delta G = +555$ kJ
Reduction of Al_2O_3 in presence of carbon is not possible.

Q.23 Reaction :

$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO$ at 300 K temperature, $\Delta H° = 90$ KJ

$\Delta S°$ for N_2, O_2 and NO are 180, 206 and 210 $JK^{-1}mol^{-1}$

Then find out the standard free energy change :

(1) 94.8 KJ (2) 98.4 KJ (3) 89.8 KJ (4) 84.9 KJ

A.23 (4)

$\Delta S° = (\Sigma S°)_p - (\Sigma S°)_R$

$= [210] - \left[\frac{1}{2} \times 180 + \frac{1}{2} \times 206\right]$

$= 17$ J/K

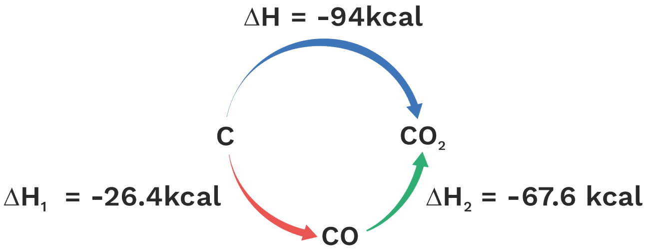
$\Delta G° = \Delta H° - T\Delta S°$

$= 90 - 300 \times \frac{17}{1000}$

$\Delta G° = 84.9$ KJ

Hess's Law :

1. Heat of reaction always remain same whether the reaction completes in one step or more than one step



Ex. Carbon is first converted into $CO_2(g)$ and then CO(g) into $CO_2(g)$, ie., conversion has been carried in two steps:

Concept Ladder

(Laplace and Lavoisour Law)

Heat of formation of a substance = heat of decomposition of that substance but with opposite sign

$C + O_2 \rightarrow CO_2; \Delta H = -x$

$CO_2 \rightarrow C + CO_2; \Delta H = +x$

$$C(s)+\frac{1}{2}O_2 \longrightarrow CO(g) \quad ; \Delta H = -26.4\,\text{kcal}$$

$$CO(g)+\frac{1}{2}O_2 \longrightarrow CO_2(g) \; ; \Delta H = -67.6\,\text{kcal}$$

Total enthalpy change C(s) to $CO_2(g)$
ΔH = -94.0 kcal

2. Heat of reaction doesn't depend on the number of step in which a reaction completes
3. Hess's law is based on FLOT
4. Doesn't give information about time in which a reaction completes
5. Hess's law is a theoretical form in which given reactions are added subtracted and multiplied with a constant value to obtain a object reaction.

Concept Ladder

- ΔH or ΔE is not proportional to the path of a reaction.
- ΔH or ΔE is a state function which depends only on initial and final states (first law of thermodynamics).

Rack your Brain

Bond energy of N–H, H–H, and N≡N bonds are Q_1 , Q_2 and Q_3 ; $\Delta_f H$ (NH_3) for
$N_2 + 3H_2 \longrightarrow 2NH_3$ is:

Q.24 Calculate the heat of formation of acetic acid from the following data:

$$CH_3COOH(l)+2O_2(g) \longrightarrow 2CO_2(g)+2H_2O(l);\ \Delta H = -207.9\ \text{kcal} \quad ....(1)$$

$$C(s)+O_2(g) \longrightarrow CO_2(g)\ ;\ \Delta H = -94.48\,\text{kcal} \quad ....(2)$$

$$H_2(g)+\frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -68.4\,\text{kcal} \quad ....(3)$$

A.24 $2C(s)+2H_2(g)+O_2(g) \longrightarrow CH_3COOH(l);\ \Delta_f H(CH_3COOH) = ?$

$\Delta_f H$ (CH_3COOH)
= 2 × (-94.48) + 2 (-68.4) + 207.9
= -325.76 + 207.9
= - 117.86 kcal

Bond Energy

1. Bond energy means bond dissociation energy.
2. Bond dissociation process → Endothermic.
3. Bond formation process → Exothermic.
4. In diatomic molecule.
   Heat required to dissociate 1 mole bond and convert it into 2 separate gaseous atom is known as bond energy.

   $$Cl-Cl(g)\longrightarrow 2Cl(g);\ \Delta H=+242.5\,kJ/mol$$

   $$H-H(g)\longrightarrow 2H(g);\ \Delta H=+433\ kJ/mol$$
5. Bond dissociation energy is equal to bond formation energy but with opposite sign

Concept Ladder

In polyatomic molecule we always calculate average bond energy

$$\text{Average bond energy} = \frac{\text{Total energy related with all bonds}}{\text{Number of bonds dissociate}}$$

Q.25 The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl (g).

A.25

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\longrightarrow HCl(g);\quad \Delta H=?$$

$$\Delta H=\left[\frac{1}{2}\Delta H_{H-H}+\frac{1}{2}\Delta H_{Cl-Cl}\right]-\left[\Delta H_{H-Cl}\right]$$

$$=\frac{1}{2}\times 104+\frac{1}{2}\times 58-103$$

$$=-22\,kcal\ mol^{-1}$$

Q.26 Ratio of bond enthalpy of A_2, B_2, AB are 1 : 0.5 : 1. Heat of formation of AB is –100 KJ/mol, then calculate the bond enthalpy of A_2

(1) 400 KJ (2) 350 KJ (3) 300 KJ (4) 450 KJ

A.26 (1)

$$\frac{1}{2}A_2+\frac{1}{2}B_2\rightarrow AB$$

$$\Delta H=(\Sigma BE)_R-(\Sigma BE)_P \quad -100=\left(\frac{1}{2}x+\frac{1}{4}x\right)-(x) \quad -100=\frac{3}{4}x-x=-\frac{x}{4}$$

x = 400

B.E of A_2 = 400 KJ

6. If different bond energy are given then calculate ΔH of a reaction.

$\Delta H = \Sigma$ Bond energy (Reactants) - Σ Bond energy (products)

Resonance energy :

When two or more double bond are in conjugation, there is possibility of delocalization of electron through conjugation. This phenomenon is called resonance.

Determination of resonance energy

When a compound shows resonacne, there is considerable difference between the heat of formation as calculate from bond energies and that determined experimentally.

Resonance energy = Experimetnal or actual heat of formation - calculated heat of formation

Concept Ladder

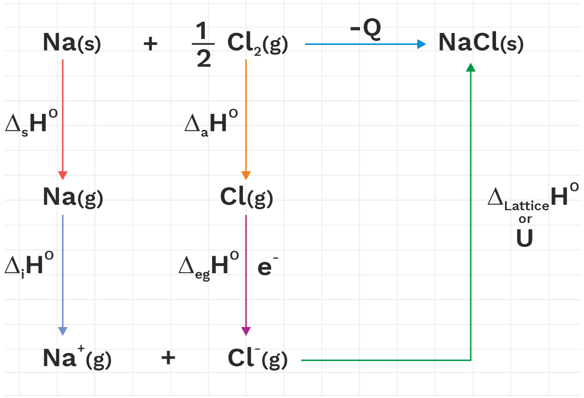
When resonance hybrid is formed from any of its resonating structures, energy will be released.

BORN– HABER CYCLE FOR NaCl :

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the compound is formed by interaction of constituent gaseous cations and gaseous anions.

$$A^{+}(g) + B^{-}(g) \longrightarrow \underset{\text{1 mole}}{A^{+}B^{-}} + \underset{\text{(Lattice Energy)}}{\text{Energy}}$$

It is represented by the symbol **"U"**. It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as Born-Haber cycle which is based on Hess's law. The cycle can be easily explained by taking the example of the formation of sodium chloride (NaCl). The formation of sodium chloride can be schematically represented as;



The various steps in the formation of NaCl are the following: In case step, either energy is absorbed or released.

S.No	Steps involved	Energy change
1	Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $Na(s) \xrightarrow{\Delta_s H^\circ} Na(g)$	$+\Delta_s H^\circ$
2	Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed. $Na(g) \xrightarrow{\Delta_i H^\circ} Na^+(g) + e$	$+\Delta_i H^\circ$
3	Half mole of molecular chlorine dissociation into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociaton energy is absorbed. $\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_a H^\circ} Cl(g)$	$\frac{1}{2}\Delta_a H^\circ$
4	Gaseous chlorine atoms change into chloride ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $Cl(g) + e^- \xrightarrow{-\Delta_{eg} H^\circ} Cl^-(g)$	$-\Delta_{eg} H^\circ$
5	Sodium and chlrine ions are held together by electrostatic forces to form Na^+Cl^-. the energy equivalent to lattice energy is released.	$\Delta_{lattice} H^\circ/U$

Total energies involved in the above five steps

$$= \Delta_s H^\circ + \frac{1}{2}\Delta_a H^\circ + \Delta_i H^\circ - \Delta_{eg} H^\circ + U$$

DIFFERENT TYPES OF STANDARD ENTHALPY CHANGES (BASED ON IUPAC RECOMMENDATIONS)

S.no	Transition Enthalpy	Example	Defination	Symbol
1	Enthalpy of formation	$K(s) + \frac{1}{2}Cl_2(g) \rightarrow KCl(s)$	One mole of the compound formed from its elements	$\Delta_f H^\circ$ Or ΔH_f^0
2	Enthalpy of combustion	$C_2H_6(g) + O_2 \rightarrow CO_2(g) + 3H_2O(l)$	One mole of the compound (fuel) is burnt completely in oxygen	$\Delta_C H^0$ Or ΔH_C^0
3	Enthalpy of fusion	$H_2O(s) \rightarrow H_2\,O(\ell)$	One mole of the liquid is formed from the solid without a change in temperature	$\Delta_{fus} H^\circ$ Or $\Delta_{fus} H_{fus}^\circ$
4	Enthalpy of vaporisation	$H_2O(\ell) \rightarrow H_2\,O(g)$	One mole of the vapour formed from the liquid without a change in temperature	$\Delta_{vap} H^\circ$ Or ΔH°_{vap}
5	Enthalpy of sublimation	$I_2(s) \rightarrow I_2(g)$	One mole of the vapour formed the solid	$\Delta_{sub} H^\circ$ Or ΔH°_{sub}
6	Enthalpy of atomisation	$H_2(g) \rightarrow 2H(g)$	One mole of the substance broken into isolated atoms in the gas phases	$\Delta_{at} H^\circ$ Or ΔH°_{at}
7	Enthalpy of reaction	$A \rightarrow B$	Enthalpy change taking place in a reaction	$\Delta_r H^\circ$ Or $\Delta_r H^\circ_f$
8	Enthalpy of neutralisation	$HCl(aq) + NaOH(aq) \rightarrow H_2O + NaCl(aq)$	One mole of water formed by the neutralisation of an acid by a base	$\Delta_n H^\circ$ Or ΔH°_n
9	Enthalpy of ionisation	$Na(g) \rightarrow Na^+(g) + e^-$	One mole atoms ionised all species in gaseous phase	$\Delta_{ion} H^\circ$ Or ΔH°_{ion}
10	Electron gain enthalpy	$X(g) + e^- \rightarrow X^-(g)$	One mole of anions beings formed all species in the gaseous phase	$\Delta_{e.g} H^\circ$ Or $\Delta H^\circ_{e.g}$

S.no	Transition Enthalpy	Example	Defination	Symbol
11	Lattice enthalpy	$NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$	One mole of a crystal completely separated into isolated particle in the gaseous phase	$\Delta_L H^\circ$ Or ΔH°_L or U
12	Bond dissociation enthalpy (bond A–B)	$HCl(g) \rightarrow H(g) + Cl(g)$	One mole of bonds broken-all produce in the gaseous phase	ΔH°_{A-B} or ε_{A-B}
13	Enthalpy of solution	$NaCl(g) + H_2O$ (excess) $\rightarrow$ $NaCl(aq)$	One mole of the solute dissolved in excess of solvent so that further dilution produces no enthalpy change	$\Delta_{sol} H^\circ$ Or ΔH°_{sol}
14	Enthalpy of hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	One mole of the ion in gaseous phase is hydrated	$\Delta_{hyd} H^\circ$ Or ΔH°_{hyd}
15	Enthalpy of mixing	Pure substance → mixture	One mole each of the two or more substances is mixed	$\Delta_{mix} H^\circ$ Or ΔH°_{mix}

Q.27 The molar heat of formation of $NH_4NO_3(s)$ is –367.54 kJ and those of $N_2O(g)$, $H_2O(l)$ are 81.46 and –285.8 kJ respectively at 25°C and 1 atmosphere pressure. Calculate ΔH and ΔU of the reaction $NH_4NO_3(s) \xrightarrow{} N_2O(g) + 2H_2O(l)$

A.27 We have to find ΔH for

$NH_4NO_3(g) \xrightarrow{} N_2O(g) + 2HO(l);\ \Delta H = ?$

$\Delta H_{reaction} = \Delta H_{products} - \Delta H_{Reactants}$

$$= \Delta H_{N_2O} + \Delta H_{H_2O} \times 2 - \Delta H_{NH_4NO_3}$$

Given, $\Delta H_{N_2O} = +81.46\text{ kJ},\ \Delta H_{H_2O} = -285.8\text{ kJ},\ \Delta H_{NH_4NO_3} = -367.54\text{ kJ}$

$\therefore \quad \Delta H_{N_2O} = +81.46\text{ kJ},\ \Delta H_{H_2O} = 285.8\text{ kJ},\ \Delta H_{NH_4NO_3} = -367.54\text{ kJ}$

$\Delta H_{reaction} = +81.46 + 2(-285.8) - (-367.54)$

Further

$\Delta H = \Delta U + \Delta nRT$

$\therefore \quad -122.6 \times 10^3 = \Delta U + 1 \times 8.314 \times 298$

$\therefore \quad \Delta U = -125077$ Joule

$= 125.077$ kJ

Q.28 Enthalpy of neutralization of HCl by NaOH is –57.32 kJ mol^{-1} and by NH_4OH is –51.34 kJ mol^{-1} . Calculate the enthalpy of dissociation of NH_4OH.

A.28 Given that

$H^+(aq) + NH_4OH(aq) \xrightarrow{} NH_4^+(aq) + H_2O(l) \qquad \Delta_rH = -51.34\text{ kJ mol}^{-1}$

We may consider neutralisation in two steps :

(i) Ionization

$NH_4OH(aq) \xrightarrow{} NH_4^+(aq) + OH^-(aq)\ \Delta_rH$

(ii) Neutralization

$H^+(aq) + OH^-(aq) \xrightarrow{} H_2O(l) \qquad \Delta_rH_2 = -57.32\text{ kJ mol}^{-1}$

Thus, $\Delta_rH = \Delta_rH_1 + \Delta_rH_2$

Therefore, $\Delta_rH_1 = \Delta_rH - \Delta_rH_2$

$= -51.34 + 57.32 = 5.98\text{ kJ/mol}^{-1}$

Q.29 The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5536 kJ mol^{-1} respectively. Calculate the resonance energy of benzene, compared with Kekule structure. The bond enthalpy of C–H bond is 410.87 kJ mol^{-1}.

A.21 Bond enthalpy of C–C bond

= Enthalpy required to break C_2H_6 into gaseous atoms –6 × bond enthalpy of C–H bond

= 2839.2 kJ mol^{-1} – 6 × 410.87 kJ mol^{-1}

= 373.98 kJ mol^{-1}

Bond enthalpy of C=C bond = Enthalpy required to break C_2H_4 into gaseous atoms –4 × bond enthalpy of C–H bond

= 2275.2 kJ mol^{-1} – 4 × 410.87 kJ mol^{-1}

= 631.72 kJ mol^{-1}

To form benzene having Kekule structure, we have to form 3C–C bonds, 3C=C bonds and 6 C–H bonds for which enthalpy released is

[3(–373.98) + 3(–631.72) + 6(–410.87)]

= 5482.32 kJ mol^{-1}

But the given value of $\Delta_f H$ is $\Delta_f H$ (actual) – $\Delta_f H$ (Kekule structure)

Hence resonance energy compared to Kekule structure

= $\Delta_r H$ (actual) – $\Delta_f H$ (Kekule structure)

= (–5536 + 548.2) = –53.68 kJ mol^{-1}

Q.30 Calculate the lattice energy forthe reaction,

$$Li^+(g) + Cl^-(g) \longrightarrow LiCl(s)$$

From the following data:

$\Delta_s H^\circ(Li) = 160.67\,kJ\ mol^{-1}$; $\frac{1}{2}\Delta_a H^\circ(Cl_2) = 122.17\,kJ\ mol^{-1}$

$\Delta_i H^\circ(Li) = 520.07\,kJ\ mol^{-1}$; $\Delta_{eg} H^\circ(Cl) = -365.26\,kJ\ mol^{-1}$

and $\Delta_f H^\circ(LiCl) = -401.66\,kJ\ mol^{-1}$

A.30 Applying the equation

$$-Q = \Delta_s H^\circ + \frac{1}{2}\Delta_a H^\circ + \Delta_i H^\circ - \Delta_{eg} H^\circ + U$$

and substituting the respective values

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31\,kJ mol^{-1}$$

Chapter Summary

1. Enthalpy (H) : It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content (H=E+PV)
2. Enthalpy change (ΔH) : It is the measure of heat change taking place during the process at constant temperature and constant pressure.
   $q_P = \Delta H$
   Enthalpy ΔH and internal energy change (ΔU) are related as
   $\Delta H = \Delta U + P\Delta V$
   $\Delta H = \Delta U + \Delta n_g RT$
   Where Δn_g = Gaseous moles of product – gaseous moles of reactants
3. Enthalpy of reactions ($\Delta_r H$) : The enthalpy change accompanying a chemical reactions when the number of moles of reactants react to give the products as given by the balanced chemical equation.
4. Standard enthalpy of formation ($\Delta_f H$) : The enthalpy change accompanying the formation of one mole of the compound from its elements at standard conditions and all the substances being the their standard states
   As a convention, the $\Delta_f H^\circ$ of every element is assumed to be zero
5. Enthalpy of combustion ($\Delta_c H$) : The amount of heat change when 1 mole of the substance is completely burnt in excess of O_2 or air. $\Delta_c H$ is always negative.
6. Enthalpy of solution ($\Delta_{sol} H$) : The enthalpy change when 1 mole of a substance will be dissolved in large excess of solvent so that further dilution does not give any further enthalpy change.
7. Enthalpy of hydration : This is the enthalpy change during the hydration of 1 mole of anhydrous salt to a specific hydrate
8. Hess's law : The enthalpy change in a particular reaction is the same whether in the reaction takes place in 1 step or in a number of steps.
9. Bond enthalpy : When one mole of the bonds of a particular type in gaseous molecule is breaked than the amount average amount of energy required is termed as bond enthalpy.
10. $\Delta S = \frac{q_{rev}}{T}$
11. $\Delta_r S^\circ = \sum \Delta S^\circ(\text{Products}) - \sum \Delta S^\circ(\text{reactants})$
    Ie. $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$ must be positive
12. Resonance Energy : Many compound exhibit resonance. Due to resonance they exist in a structure which is different from the expected one and more stable.
    Resonance energy = $\Delta H_f^0(\text{actual}) - \Delta H_f^0(\text{calculated})$