

## THERMOCHEMISTRY

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions. It is based on first law of thermodynamics.

### 1. ENTHALPY OF A SUBSTANCE :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- $H_m$ (substance) : For example molar enthalpy of water vapours at 398 K and 1 atm pressure may be represented as  $H_m$  ( $H_2O$ , g, 398 K, 1 atm). In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance. Standard state of any substance means.
  - For a GAS standard state means ideal gas at 1 bar partial pressure at any given temperature.
  - For a LIQUID – pure liquid at one bar pressure at 1 bar pressure at any given temperature.
  - For a PURE CRYSTALLINE SOLID – pure crystalline solid at 1 bar pressure and at any given temperature
  - For any SUBSTANCE or ION IN SOLUTION – the species should be in unit molality (can also be taken as 1M concentration), at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at 398 K will be represented as  $H^\circ(H_2O, g, 398 K)$  and molar standard enthalpy of liquid water at 398 K will be represented as  $H_m^\circ(H_2O, l, 398 K)$  (It is hypothetical but can be calculated).
- 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.

**For example :**



Let enthalpy content initially be  $H_{m,1}^0$  & finally enthalpy content be  $H_{m,2}^0$

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

$$\begin{aligned} &= \text{heat added at constant pressure to change temperature from } 25^\circ\text{C to } 50^\circ\text{C.} \\ &= C_p \Delta T = (18 \text{ cal/mole } ^\circ\text{C}) (25^\circ\text{C}) = 450 \text{ cal} \end{aligned}$$

### 2. ENTHALPY CHANGE OF REACTION, ( $\Delta_rH$ )

The enthalpy change accompanying a reaction is called the reaction enthalpy. It may also be defined as the amount of heat lost or gained in the chemical reaction, when all the reactants and products are maintained at the same temperature and pressure. The enthalpy change of a chemical reaction may be given as

$$\Delta_rH = (\text{sum of enthalpies of products}) - (\text{sum of enthalpy of reactants})$$



$$= \sum (\Delta H)_{\text{products}} - \sum (\Delta H)_{\text{reactants}}$$

### 1. Why does heat get released/absorbed during chemical reactions?

**Sol.** Because the reactants have a fixed enthalpy content before the reaction and when these are converted into the products which have a different enthalpy content. So, heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies  $\Delta U \neq 0$ .

$$\text{If } H_{\text{products}} > H_{\text{reactants}}$$

Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products

$$\text{and if } H_{\text{products}} < H_{\text{reactants}}$$

Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

Enthalpy change of a reaction :  $\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$

$$\begin{aligned} \Delta H^{\circ}_{\text{reactions}} &= H^{\circ}_{\text{products}} - H^{\circ}_{\text{reactants}} \\ &= \text{positive} : \text{endothermic} \\ &= \text{negative} : \text{exothermic} \end{aligned}$$

### 3. FACTORS AFFECTING $\Delta H$ OF THE REACTIONS ARE :

- (i) Physical states of reactants & products.
- (ii) Allotropic forms of elements.
- (iii) Reaction conditions.

$$\Delta H = \Delta U + \Delta n g RT$$

where  $\Delta H$  = Heat change of reaction at constant pressure or enthalpy change.

$\Delta U$  = Heat change of reaction at constant volume or internal energy change.

$\Delta n g$  = Total moles of gaseous products – total moles of gaseous reactants.

It should be noted that while computing  $\Delta n g$  of a reaction, only the stoichiometric numbers of gaseous is counted and those of liquids and solids are completely ignored.

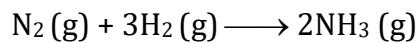
(iv) Temperature : Variation of  $\Delta H^{\circ}$  with temperature can be explained by **Kirchoff's equation**.

$$\Delta_r H_2^{\circ} = \Delta_r H_1^{\circ} + \int \Delta_r C_p \cdot dT$$

$$\Delta_r C_p = \sum (C_p)_{\text{products}} - \sum (C_p)_{\text{reactants}}$$

= Difference in molar heat capacities of products and reactants.

For example for the reaction



$$\Delta_r H_2^{\circ} = \Delta_r H_1^{\circ} + \Delta_r C_p (T_2 - T_1)$$

$$\text{where } \Delta_r C_p = 2C_{p,NH_3} - C_{p,N_2} - 3C_{p,H_2}$$

$$* \text{ for a constant volume reaction, } \Delta E_2^0 = \Delta E_1^0 + \int \Delta_r C_v \cdot dT$$

2. The molar heat capacities at constant pressure (assumed constant with respect to temperature) at A,B and C are in ratio of 3 : 1.5 : 2.0 The enthalpy change for the exothermic reaction A + 2B  $\rightarrow$  3C at 300 K and 310 K is  $\Delta_r H_{300}$  and  $\Delta_r H_{310}$  respectively then :



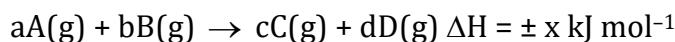
- (A)  $\Delta_r H_{300} > \Delta_r H_{310}$   
 (B)  $\Delta_r H_{300} < \Delta_r H_{310}$   
 (C)  $\Delta_r H_{300} = \Delta_r H_{310}$   
 (D) if  $T_2 > T_1$  then  $\Delta_r H_{310} > \Delta_r H_{300}$  and if  $T_2 < T_1$  then  $\Delta_r H_{310} < \Delta_r H_{300}$

**Ans.** (C)

**Sol.**  $\Delta_r C_p = 0, \therefore \Delta_r H_{300} = \Delta_r H_{310}$

#### 4. THERMOCHEMICAL EQUATIONS :

An equation which indicates the amount of heat change in the reaction. These can be added, subtracted or multiplied whenever required. It indicates the amount of heat change in the reaction, which is written on the extreme right of the reaction. for example :



#### 5. TYPES OF ENTHALPY CHANGES IN CHEMICAL REACTIONS :

##### 5.1 STANDARD ENTHALPY OF FORMATION :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built.

- “The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value”. The specified temperature is usually taken as 25°C.

A few examples are  $\Delta H_f^\circ (O_2, g) = 0$

$$\Delta H_f^\circ (\text{C, graphite}) = 0 \quad \Delta H_f^\circ (\text{C, diamond}) \neq 0$$

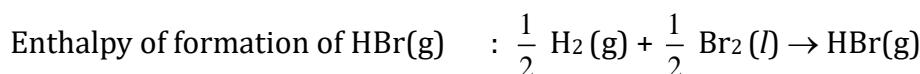
$$\Delta H_f^\circ (\text{Br}_2, \text{liquid}) = 0$$

$$\Delta H_f^\circ (\text{S, rhombic}) = 0 \quad \Delta H_f^\circ (\text{S, monoclinic}) \neq 0$$

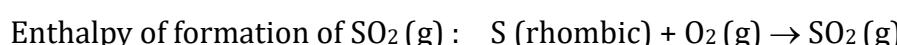
$$\Delta H_f^\circ (\text{P, white}) = 0 \quad \Delta H_f^\circ (\text{P, black}) \neq 0$$

- “The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed from its constituent elements taken in their standard or reference state”.

The chemical equations corresponding to enthalpy of formation of few substances are given below.



$$\Delta H_f^\circ(\text{HBr, g}) = H_m^0(\text{HBr, g}) - \frac{1}{2} H_m^0(\text{H}_2, \text{g}) - \frac{1}{2} H_m^0(\text{Br}_2, \text{l}) \quad \dots(1)$$



$$\Delta H_f^\circ(\text{SO}_2, \text{g}) = H_m^0(\text{SO}_2, \text{g}) - H_m^0(\text{S, rhombic}) - H_m^0(\text{O}_2, \text{g}) \quad \dots(B)$$

But above equations cannot be used for calculation of enthalpy of reaction as the molar enthalpies of different species can not be exactly known.

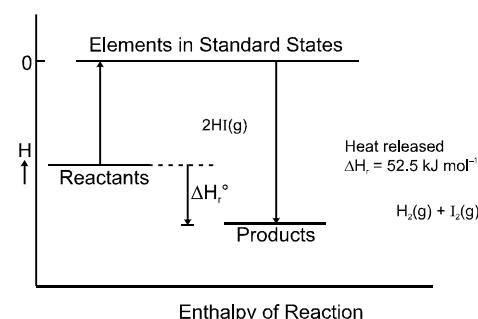
### 5.1.1 ENTHALPY OF REACTION FROM ENTHALPIES OF FORMATION:

The enthalpy of reaction can be calculated by

$$\Delta H_r^\circ = \sum v_B \Delta H_f^\circ, \text{products} - \sum v_B \Delta H_f^\circ, \text{reactants}$$

$v_B$  is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



3. Calculate the standard enthalpy of reaction  $\text{ZnO}(s) + \text{CO}(g) \rightarrow \text{Zn}(s) + \text{CO}_2(g)$ .

Given,  $\Delta H_f^\circ(\text{ZnO}, s) = -350 \text{ KJ/mole}$ ,  $\Delta H_f^\circ(\text{CO}_2, g) = -390 \text{ KJ/mole}$ ,  $\Delta H_f^\circ(\text{CO}, g) = -110 \text{ KJ/mole}$ .

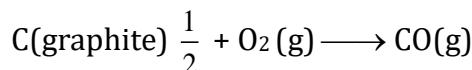
**Ans.** 7kJ.

**Sol.**  $\Delta H^\circ = \{\Delta H_f^\circ(\text{CO}_2, g) - (\Delta H_f^\circ(\text{ZnO}, s) + \Delta H_f^\circ(\text{CO}, g))\}$

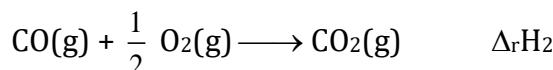
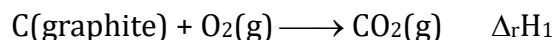
$$\Delta H^\circ_{\text{reaction}} = -390 - (-350 - 110) = 70 \text{ kJ}$$

### 5.1.2 HESS'S LAW OF CONSTANT HEAT SUMMATION :

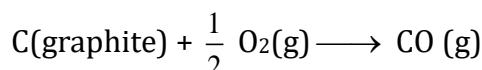
- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.
- Since  $\Delta_r H$  stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products are written on the left hand side and reactants on the right hand side), then the numerical value of  $\Delta_r H$  remains the same, but its sign changes.
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value  $\Delta_r H$  for the reaction



Which is difficult to determine experimentally, can be estimated from the following two reactions for which  $\Delta_r H$  can be determined experimentally.



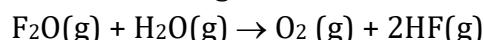
Substracting the latter from the former, we get



Consequently,  $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$



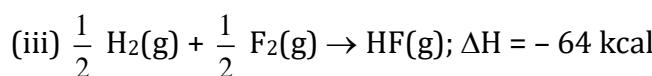
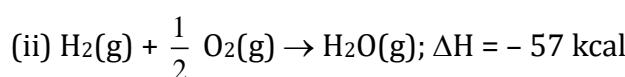
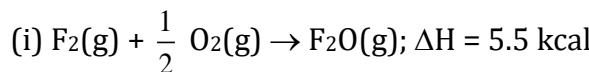
4. Calculate heat of the following reaction at constant pressure,



The heats of formation of  $\text{F}_2\text{O}$  (g),  $\text{H}_2\text{O}$ (g) and  $\text{HF}$  (g) are 5.5 kcal, -57kcal and -64 kcal respectively.

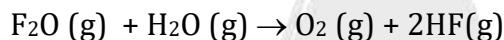
**Ans.** - 76.5 kcal.

**Sol.** Given that



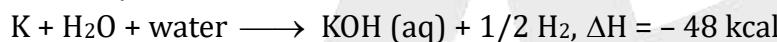
$\text{F}_2\text{O}$  and  $\text{H}_2\text{O}$  in eqns. (i) and (ii) and in the eqn. given in the problem are on the opposite sides, while  $\text{HF}$  in eqn. (iii) and in the eqn. given in the problem is on the same sides.

Thus applying, [2 × Eqn. (iii) – Eqn. (i) –Eqn. (ii)], we get



$$\Delta H = - 5.5 - (- 57) + 2 \times (- 64) = - 76.5 \text{ kcal}$$

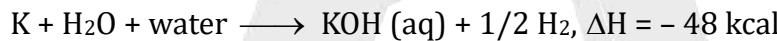
5. If  $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$ ,  $\Delta H = - 68 \text{ kcal}$



Find the heat of formation of KOH.

**Ans.** -102 kcal.

**Sol.** If  $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$ ,  $\Delta H = - 68 \text{ kcal}$

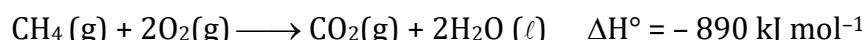


$$\Delta fH_{\text{KOH}} = (i) + (ii) - (iii) \quad \Delta fH_{\text{KOH}} = - 48 - 68 - (-14) = -102 \text{ kcal.}$$

## 5.2 STANDARD ENTHALPY OF COMBUSTION :

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

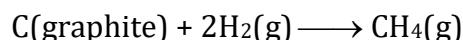
For example, the standard enthalpy of combustion of methane at 298 K is - 890 kJ mol<sup>-1</sup>. This implies the following reaction :



The standard enthalpy of combustion of methane at 298 K may be written as

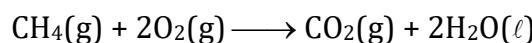
$$\Delta H_c^\circ (\text{CH}_4, \text{g}, 298 \text{ K}) = - 890 \text{ kJ mol}^{-1}$$

- The data on the enthalpy of combustion can be determined experimentally.
- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of  $\text{CH}_4(\text{g})$ :





First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane. Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :



$$\Delta H_c^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_f^\circ(\text{CH}_4, \text{g})$$

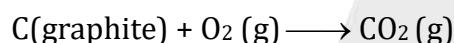
therefore  $\Delta H_f^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g})$

- The enthalpies of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the measured value of  $\Delta H_c^\circ(\text{CH}_4, \text{g})$ , the enthalpy of formation of  $\text{CH}_4$  can be calculated. The value is

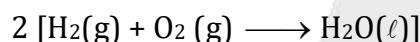
$$\Delta H_f^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g})$$

$$= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1}$$

or, equivalently, we may add the following three chemical equations.



$$\Delta cH^\circ = -393 \text{ kJ mol}^{-1}$$



$$\Delta_rH^\circ = 2(-285) \text{ kJ mol}^{-1}$$



$$\Delta_rH^\circ = -(-890) \text{ kJ mol}^{-1}$$



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$$\Delta_fH^\circ = -73 \text{ kJ mol}^{-1}$$

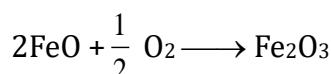
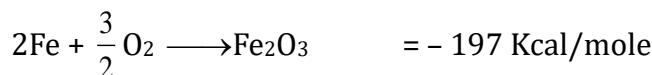
6. The standard enthalpy of formation of  $\text{FeO}$  &  $\text{Fe}_2\text{O}_3$  is  $-65 \text{ kcal mol}^{-1}$  and  $-197 \text{ kcal mol}^{-1}$  respectively. A mixture of two oxides contains  $\text{FeO}$  &  $\text{Fe}_2\text{O}_3$  in the mole ratio  $2 : 1$ . If by oxidation, it is changed into a  $1 : 2$  mole ratio mixture, how much of heat will be released per mole of the initial mixture ?

(A)  $13.4 \text{ kcal/mole}$  (B)  $14.6 \text{ kcal/mole}$  (C)  $15.7 \text{ kcal/mole}$  (D)  $16.8 \text{ kcal/mole}$

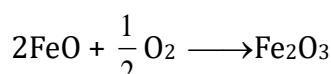
**Ans. (A)**

**Sol.**  $\text{FeO} + \text{Fe}_2\text{O}_3$

$2x \quad x$



$$\Delta H = -197 + 65 \times 2 \quad \Delta H = -67 \text{ Kcal/mole}$$



$$\frac{2}{3} \quad \frac{1}{3}$$

$$\frac{2}{3} - 2x \quad \frac{1}{3} + x$$

$$\frac{\frac{2}{3} - 2x}{\frac{1}{3} + x} = \frac{1}{2} \Rightarrow x = \frac{1}{5}$$

So, energy released =  $\frac{1}{5} \times 67 = 13.4 \text{ kcal/mole}$

### 5.1.2 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).

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, as shown in figure. 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.

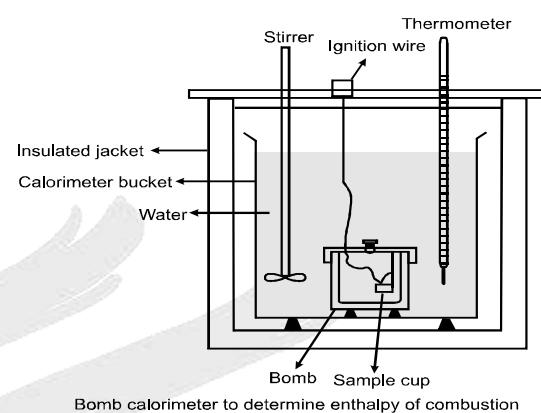
If total heat capacity of calorimeter and all of its contents = C, rise in temperature =  $\Delta T$  then heat released =  $q = C\Delta T$  of this heat is because of mass m of substance then :

$$\text{due to 1 mole, heat released} = \left( \frac{M}{m} \right) q = \Delta U c^\circ$$

(constant volume reaction).

Now,  $\Delta H^\circ$  can be calculated by using  $\Delta H^\circ = \Delta U^\circ + \Delta n g RT$ .

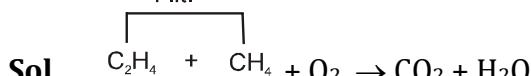
Where  $\Delta n g$  is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.



7. A gas mixture of 4 litres of ethylene and methane on complete combustion at 25°C produces 6 litres of CO<sub>2</sub>. Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are – 1464 and –976 kJ mol<sup>-1</sup> at 25°C.

**Ans.** – 50 kJ.

4 lit.



x lit. (4 – x) lit. 6 lit.

(say)

or x moles (4 – x) moles 6 moles

Applying POAC for C atoms,

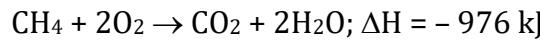
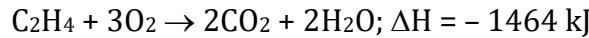
$$2 \times x + 1 \times (4 - x) = 1 \times 6 ; x = 2 \text{ lit.}$$

Thus, the volume of C<sub>2</sub>H<sub>4</sub> = 2 lit., and volume of CH<sub>4</sub> = 2 lit.



volume of  $C_2H_4$  in a 1 litre mixture =  $2/4 = 0.5$  lit.  
and volume of  $CH_4$  in a 1 litre mixture =  $1 - 0.5 = 0.5$  lit.

Now, thermochemical reactions for  $C_2H_4$  and  $CH_4$  are



As  $\Delta H$  values given are at  $25^\circ\text{C}$ , let us first calculate the volume occupied by one mole of any gas at  $25^\circ\text{C}$  (supposing pressure as 1 atm)

$$\text{Volume per mole at } 25^\circ\text{C} = \frac{298}{273} \times 22.4 = 24.4 \text{ lit.}$$

$$\text{Thus, heat evolved in the combustion of } 0.5 \text{ lit. of } C_2H_4 = -\frac{1464}{24.4} \times 0.5 = -30 \text{ kJ}$$

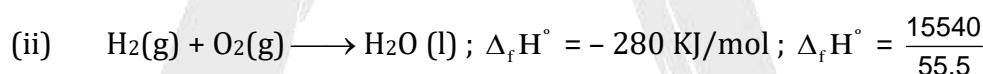
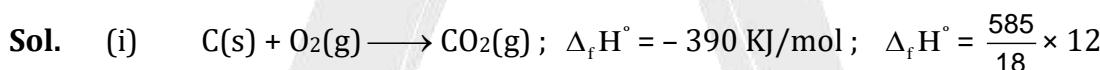
$$\text{and heat evolved in the combustion of } 0.5 \text{ lit. of } CH_4 = \frac{976}{24.4} \times 0.5 = -20 \text{ kJ.}$$

$$\therefore \text{total heat evolved in the combustion of 1 litre of the mixture} = -30 + (-20) = -50 \text{ kJ.}$$

- 8.** Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data. (in KJ/mole).

- (i) 18 g of graphite on complete combustion evolve 585 KJ heat
- (ii) 15540 KJ heat is required to dissociate all the molecules of 1 litre water into  $H_2$  and  $O_2$ .
- (iii) The heat of formation of liquid benzene is 48 kJ/mol
- (iv) Density of  $C_6H_6$  (l) = 0.87 g/ml

**Ans.** 36 kJ



$$\Delta H^\circ = [6(-390) + 3(-280)] - 48 = -3228 \text{ KJ/mol}$$

$$\text{Mass of benzene is } 0.87 \times 100 = 87 \text{ g}$$

$$\text{Heat evolved from 87 g benzene} = 3600 \text{ KJ.}$$

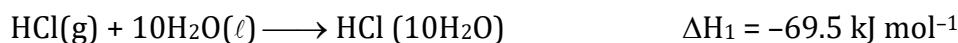
$$\text{Hence, } q = 3600 \text{ kJ.}$$

### 5.3 INTEGRAL ENTHALPY OF SOLUTION :

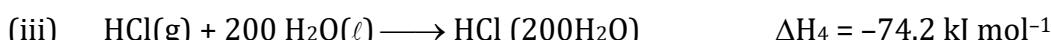
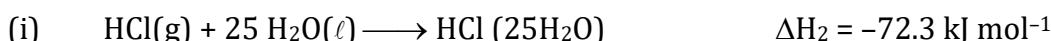
The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.



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 ; Thus



indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are



Whenever amount of solvent is not specified then take its amount to be very large just like in equation no.

9. Calculate the free energy change when 1 mole of NaCl is dissolved in water at 25°C. Lattice energy of NaCl = 777.8 kJ mol<sup>-1</sup> ; ΔS for dissolution = 0.043 kJ mol<sup>-1</sup> and hydration energy of NaCl = -774.1 kJ mol<sup>-1</sup>.

**Sol.**  $\Delta H_{\text{dissolution}} = \text{Lattice energy} + \text{Hydration energy}$   
 $= 777.8 - 774.1 = 3.7 \text{ kJ mol}^{-1}$

Now  $\Delta G = \Delta H - T\Delta S$   
 $= 3.7 - 298 \times 0.043 = 3.7 - 12.814$   
 $\Delta G = -9.114 \text{ kJ mol}^{-1}$

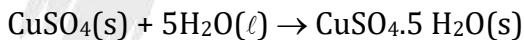
### 5.3.1 ENTHALPY OF HYDRATION :

Enthalpy of hydration is used in following two ways.

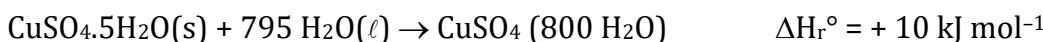
- Enthalpy of hydration of anhydrous or partially hydrated salts :

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

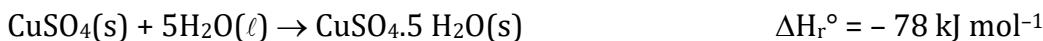
For example, the hydration of anhydrous cupric sulphate is represented by



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



by subtraction, we get

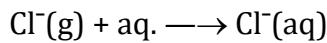


### 5.3.2 ENTHALPY OF HYDRATION OF GASEOUS IONS :

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqueous ion.

By convention, the standard enthalpy of formation of H<sup>+</sup>(aq) is taken to be zero.

Enthalpy of hydration of Cl<sup>-</sup> gaseous ions will be represented by :



$$\Delta H_r^\circ = \Delta H_f^\circ (\text{Cl}^-, \text{aq})$$

### 5.1.3 ENTHALPY OF FORMATION OF IONS :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as.  $\frac{1}{2} \text{Cl}_2(\text{g}) + \text{aq.} \longrightarrow \text{Cl}^-(\text{aq}) \quad \Delta H_r^\circ = \Delta H_f^\circ (\text{Cl}^-, \text{aq})$

By convention, the standard enthalpy of formation of  $\text{H}^+(\text{aq})$  is taken to be zero.

We have seen that  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta_r H^\circ = -57.1 \text{ kJ mol}^{-1}$

For this reaction,  $\Delta H_r^\circ = \Delta H_f^\circ (\text{H}_2\text{O}, \text{l}) - \{\Delta H_f^\circ (\text{H}^+, \text{aq}) + \Delta H_f^\circ (\text{OH}^-, \text{aq})\}$

Hence, at  $25^\circ\text{C}$ , we get  $\Delta H_f^\circ (\text{H}^+, \text{aq}) + \Delta H_f^\circ (\text{OH}^-, \text{aq}) = \Delta H_f^\circ (\text{H}_2\text{O}, \text{l}) - \Delta H_r^\circ$

so  $\Delta H_f^\circ (\text{OH}^-, \text{aq}) = \{-286.1 - (-57.1)\} \text{ kJ mol}^{-1} = -229.00 \text{ kJ mol}^{-1}$

- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with  $\text{H}^+$  or  $\text{OH}^-$ . for example, the enthalpy of formation of  $\text{Na}^+$  can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of  $\text{NaOH}$ . The two values are :

- The chemical equation for the formation of infinite dilute solution of  $\text{NaOH}(\text{s})$  is



Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus

$$\Delta H^\circ_{\text{sol}}(\text{NaOH}, \text{s}) = \Delta_f H^\circ(\text{Na}^+, \text{aq}) + \Delta_f H^\circ(\text{OH}^-, \text{aq}) - \Delta_f H^\circ(\text{NaOH}, \text{s})$$

$$\text{or} \quad \Delta_f H^\circ(\text{Na}^+, \text{aq}) = \Delta H^\circ_{\text{sol}}(\text{NaOH}, \text{s}) - \Delta_f H^\circ(\text{OH}^-, \text{aq}) + \Delta_f H^\circ(\text{NaOH}, \text{s})$$

$$= [-44.50 - (-229.99) + (-425.61)] \text{ kJ mol}^{-1} = -240.12 \text{ kJ mol}^{-1}$$

- Similarly, from  $\text{NaCl}(\text{aq})$  or  $\text{HCl}(\text{aq})$ , the enthalpy of formation of  $\text{Cl}^-(\text{aq})$  can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.

- 10.** Calculate the enthalpy change when one mole of  $\text{HCl}(\text{g})$  is dissolved in a very large amount of water at  $25^\circ\text{C}$ . The change in state is :  $\text{HCl}(\text{g}) + \text{aq.} \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

Given :  $\Delta_f H^\circ(\text{HCl}, \text{g}) = -92 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$

**Ans.**  $-75 \text{ kJ mol}^{-1}$

**Sol.** For the reaction,  $\text{HCl}(\text{g}) + \text{aq.} \longrightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$

we have  $\Delta H^\circ = \Delta_f H^\circ(\text{Cl}^-, \text{aq}) - \Delta_f H^\circ(\text{HCl}, \text{g})$

$$\Delta H^\circ = [-167 - (-92)] \text{ kJ mol}^{-1} = -75 \text{ kJ mol}^{-1}$$

### 5.4 ENTHALPY OF NEUTRALIZATION :

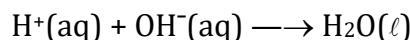
The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

Enthalpy of neutralization is defined as the enthalpy change when one mole of  $\text{H}^+$  in dilute solution combines with one mole of  $\text{OH}^-$  to give rise to undissociated water, i.e.



$$\Delta H = -57.1 \text{ kJ/mol} = -13.7 \text{ kcal/mol}$$

Remember :

- For Strong Acid + Strong Base, heat of neutralisation is always equal to  $-13.7 \text{ kcal/mol}$  or  $-57.1 \text{ kJ/mol}$ .
- For any other combination of acid and base this heat is less than  $-13.7 \text{ kcal/mol}$  or  $-57.1 \text{ kJ/mol}$ .

#### 5.4.1 ENTHALPY OF IONIZATION :

Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than  $57.1 \text{ kJ mol}^{-1}$ .

It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing these acids and bases. This heat is known as enthalpy of ionization. Examples are :



The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,



The complete reaction is obtained by adding the above two steps. Thus



Obviously,  $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2$

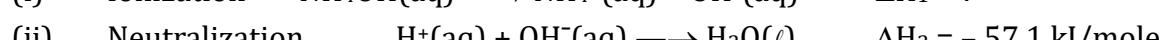
$$\Delta H^\circ_1 = \Delta H^\circ - \Delta H^\circ_2 = [-45.1 - (-57.1)] = 12 \text{ kJ/mol}$$

- Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.
- 11. Enthalpy of neutralization of HCl by NaOH is  $-57.1 \text{ kJ/mol}$  and by  $\text{NH}_4\text{OH}$  is  $-51.1 \text{ kJ/mol}$ . Calculate the enthalpy of dissociation of  $\text{NH}_4\text{OH}$ .

**Ans.**  $6.0 \text{ kJ/mol}$

**Sol.** Given that,  $\text{H}^+(\text{aq}) + \text{NH}_4\text{OH}(\text{aq}) \longrightarrow \text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\ell) \quad \Delta H = -51.1 \text{ kJ/mol}$

We may consider neutralization in two steps.



$$\text{Thus, } \Delta H = \Delta H_1 + \Delta H_2$$

$$\text{Therefore, } \Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1} = 6.0 \text{ kJ/mol}$$

12. The enthalpy of formation of  $\text{H}_2\text{O(l)}$  is  $-285 \text{ kJ mol}^{-1}$  and enthalpy of neutralization of a strong acid and a strong base is  $-55 \text{ kJ mol}^{-1}$ . What is the enthalpy of formation of  $\text{OH}^-$  ions?

**Ans.**  $-230 \text{ kJ mol}^{-1}$

**Sol:** Given that,  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(\ell) \quad \Delta_f H = -285 \text{ kJ mol}^{-1}$

$$\Delta_{\text{neut}} H = \Delta_f H(\text{H}_2\text{O}, \ell) - \Delta_f H(\text{OH}^-, \text{aq})$$



$$\begin{aligned}\text{Hence } \Delta_f H(\text{OH}^-, \text{aq}) &= \Delta_f H(\text{H}_2\text{O}, \ell) - \Delta_{\text{neut}} H \\ &= [-285 - (-55)] \text{ kJ mol}^{-1} = -230 \text{ kJ mol}^{-1}\end{aligned}$$

- 13.** 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution's temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mole of HCl. (Assuming density of sol. = 1 g/ml & specific heat of water is 4.2 J/g-K) is

**Ans.**  $-2.52 \times 10^2 \text{ kJ/mole}$ .

**Sol.** Assuming density of solution is 1g/cc  
and specific heat is 4.2 J/g-K

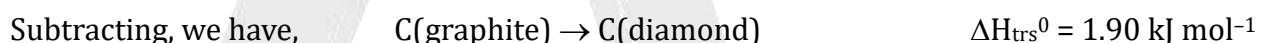
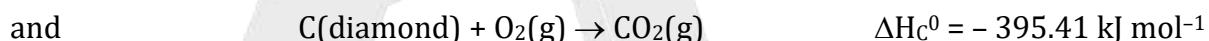
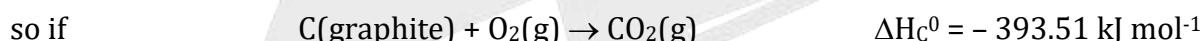
$$q = ms\Delta T = 100 \times 4.2 \times 3$$

millimoles of acid neutralized = 5

$$\Delta H = -\frac{100 \times 4.2 \times 3}{5 \times 10^{-3}} = -168 \text{ kJ/mole.}$$

### 5.5 ENTHALPY OF TRANSITION :

Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.



### 5.6 ENTHALPY OF PRECIPITATION :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.



- 14.** Calculate  $\Delta H^\circ$  for the reaction,  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$  at 25°C.

Given  $\Delta_f H^\circ(\text{Ag}^+, \text{aq}) = 105 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(\text{Cl}^-, \text{aq}) = -167 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(\text{AgCl}, \text{s}) = -127 \text{ kJ mol}^{-1}$

**Ans.**  $-65 \text{ kJ mol}^{-1}$

**Sol.** For the reaction  $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$

$$\begin{aligned}\Delta H^\circ &= \Delta_f H^\circ(\text{AgCl}, \text{s}) - \Delta_f H^\circ(\text{Ag}^+, \text{aq}) - \Delta_f H^\circ(\text{Cl}^-, \text{aq}) \\ &= [-127 - 105 - (-167)] \text{ kJ mol}^{-1} = -65 \text{ kJ mol}^{-1}\end{aligned}$$



## DO YOURSELF - 1

1. Benzene burns according to the following equation at 300 K ( $R = 25/3 \text{ J mole}^{-1}\text{K}^{-1}$ )
 
$$2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \longrightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \quad \Delta H^\circ = -6547.5 \text{ KJ}$$
 What is the  $\Delta U^\circ$  for the combustion of 1.5 mol of benzene  
 (A) -3271 kJ      (B) -9813 kJ      (C) -4905 kJ      (D) -9810 kJ
2. When 1.0 g of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is burned in a bomb calorimeter whose heat capacity is 8.75 kJ/K, the temperature increases by 0.312 K. The enthalpy of combustion of oxalic acid at  $27^\circ\text{C}$  is :  
 (A) -245.7 kJ/mol    (B) -244.4 kJ/mol    (C) -241.9 kJ/mol    (D) 246.9 kJ/mol
3. The heat of combustion of ethyl alcohol is -300 kcal. If the heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are -94.3 and -68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.
4. The standard enthalpy of decomposition of the yellow complex  $\text{H}_3\text{NSO}_2$  into  $\text{NH}_3$  and  $\text{SO}_2$  is  $+40 \text{ kJ mol}^{-1}$ . Calculate the standard enthalpy of formation of  $\text{H}_3\text{NSO}_2$ .  $\Delta H^\circ_f(\text{NH}_3) = -46.17 \text{ kJ mol}^{-1}$ ,  $\Delta H^\circ_f(\text{SO}_2) = -296.83$
5. When 12.0 g of carbon (graphite) reacted with oxygen to form CO and  $\text{CO}_2$  at  $25^\circ\text{C}$  and constant pressure, 252 kJ of heat was released and no carbon remained. If  $\Delta H^\circ_f(\text{CO}, \text{g}) = -110.5 \text{ kJ mol}^{-1}$  and  $\Delta H^\circ_f(\text{CO}_2, \text{g}) = -393.5 \text{ kJ mol}^{-1}$ , calculate the mass of oxygen consumed.
6. The standard enthalpy of neutralization of KOH with HCN and HCl in dilute solution is -2480 cal. $\text{mol}^{-1}$  and  $-13.68 \text{ kcal mol}^{-1}$  respectively. Find the enthalpy of dissociation of HCN at the same temperature.

## 5.5 BOND ENTHALPIES :

The bond enthalpy is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While bond dissociation enthalpy is the enthalpy required to dissociate a given bond of some specific compound, for example the enthalpy of dissociation of the O-H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.



However, to break the O-H bond in the hydroxyl radical required a different quantity of heat :



The bond enthalpy,  $\Delta H_{\text{OH}}$ , is defined as the average of these two values, that is :

$$\Delta H_{\text{OH}} = \frac{501.87 \text{ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

In the case of diatomic molecules, such as  $\text{H}_2$ , the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.

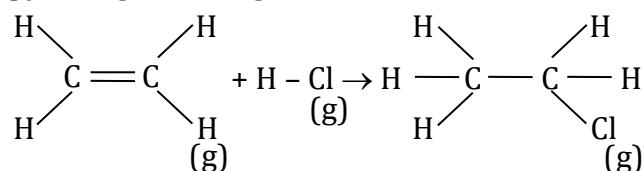




Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

### O Estimation of Enthalpy of a reaction from bond Enthalpies :

Let the enthalpy change for the gaseous reaction



be required from the bond enthalpy data. This may be calculated as follows :

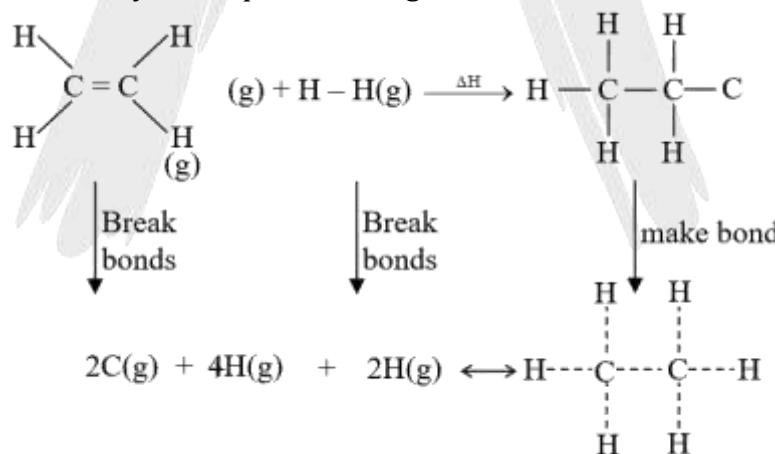
$$\begin{aligned} \Delta H &= \left( \begin{array}{l} \text{Enthalpy required to break reactants} \\ \text{into gases atoms} \end{array} \right) - \left( \begin{array}{l} \text{Enthalpy required to form products} \\ \text{from the gases atoms} \end{array} \right) \\ &= [4\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}]_{\text{R}} + [-5\Delta H_{\text{C-H}} - \Delta H_{\text{C-C}} - \Delta H_{\text{C-Cl}}]_{\text{P}} \\ &= (\Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}) - (\Delta H_{\text{C-H}} + \Delta H_{\text{C-C}} + \Delta H_{\text{C-Cl}}) \end{aligned}$$

15. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

Data :	Bond	Bond enthalpy
	C – C	336 kJ mol <sup>-1</sup>
	C = C	606 kJ mol <sup>-1</sup>
	C – H	410 kJ mol <sup>-1</sup>
	H – H	431 kJ mol <sup>-1</sup>

**Ans.** – 119 kJ/mol.

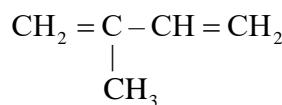
**Sol.** Diagrammatically, we represent the given reaction as follows :



$$\begin{aligned} \Delta H_r &= (4\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}}) - (6\Delta H_{\text{C-H}} + \Delta H_{\text{C-C}}) \\ &= (4 \times 410 + 606 + 431) - (6 \times 410 + 336) \\ &= 2677 - 2796 \\ &= -119 \text{ kJ/mol.} \end{aligned}$$



16. Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



Data Bond enthalpy of C – H bond = 413.38 kJ mol<sup>-1</sup>

Bond enthalpy of C – C bond = 347.69 kJ mol<sup>-1</sup>

Bond enthalpy of C = C bond = 615.05 kJ mol<sup>-1</sup>

Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol<sup>-1</sup>

Enthalpy of dissociation of H<sub>2</sub>(g) = 435.97 kJ mol<sup>-1</sup>

**Ans.**  $\Delta_f H = 103.31 \text{ kJ mol}^{-1}$

**Sol.** For isoprene, we have to form

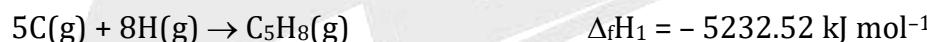
2C – C bonds ; 2C = C bonds and 8C – H bonds

**Method-1** For which energy released is

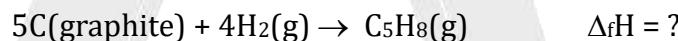
$$[2(+347.69) + 2(+615.05) + 8(+413.38)] \text{ kJ mol}^{-1} = 5232.52 \text{ kJ mol}^{-1}$$

that is,  $\Delta H$  (from gaseous atoms) = + 5232.52 kJ mol<sup>-1</sup>

The reaction corresponding to this is



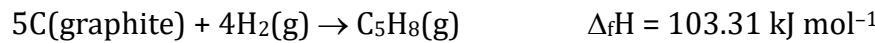
But we want  $\Delta_f H$  corresponding to the following equation



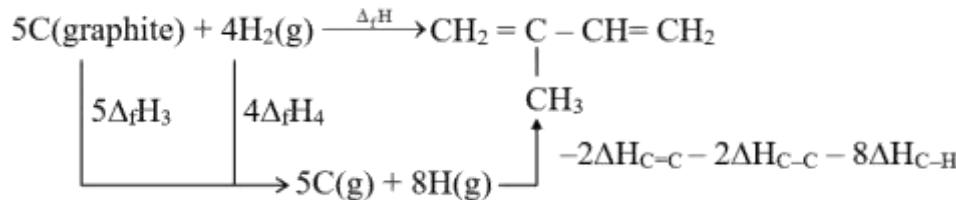
This can be obtained by the following manipulations :



Adding, we get



**Method-2** Diagrammatically, the above calculations may be represented as follows.



Applying Hess's law, we get

$$\Delta_f H = 5\Delta H_3 + 4\Delta H_4 - 2\Delta H_{\text{C=C}} - 2\Delta H_{\text{C-C}} - 8\Delta H_{\text{C-H}}$$



$$= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38) \text{ kJ mol}^{-1}$$

$$\Delta_f H = 103.31 \text{ kJ mol}^{-1}$$

### 5.7 Resonance Energy :

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$$\Delta H^\circ_{\text{resonance}} = \Delta H^\circ_{f, \text{experimental}} - \Delta H^\circ_{f, \text{calculated}}$$

$$= \Delta H^\circ_{\text{combustion, calculated}} - \Delta H^\circ_{\text{combustion, experimental}}$$

- 17.** Calculate the heat of formation of benzene from the following data, assuming no resonance.

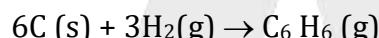
Bond energies :

$$\text{C} - \text{C} = 83 \text{ kcal}, \text{C} = \text{C} = 140 \text{ kcal}, \text{C} - \text{H} = 99 \text{ kcal}$$

$$\text{Heat of atomisation of C} = 170.9 \text{ kcal}$$

$$\text{Heat of atomisation of H} = 52.1 \text{ kcal}$$

**Sol.** We have to calculate  $\Delta H$  for the reaction



For reactants :

$$\text{Heat of atomisation of 6 moles of C} = 6 \times 170.9 \text{ kcal}$$

$$\text{heat of atomisation of 6 moles of H} = 6 \times 52.1 \text{ kcal}$$

For products :

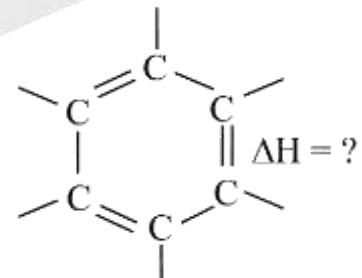
$$\text{Heat of formation of 6 moles of C - H bonds} = -6 \times 99$$

$$\text{Heat of formation of 3 moles of C-C} = -3 \times 83$$

$$\text{Heat of formation of 3 moles of C = C bonds} = -3 \times 140$$

on adding, we get heat of formation of  $\text{C}_6\text{H}_6$ , i.e.,

$$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75 \text{ kcal}$$



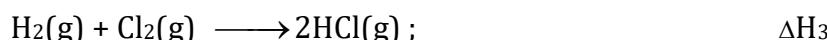
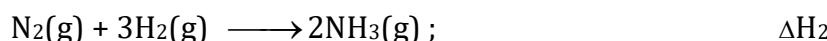
### DO YOURSELF - 2

- Calculate the bond energy of Cl-Cl bond from the following data :  
 $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g}); \Delta H = -100.3 \text{ kJ}$ . Also the bond enthalpies of C-H, C-Cl, H-Cl bonds are 413, 326 and 431  $\text{kJ mol}^{-1}$  respectively.
- Calculate  $\Delta H^\circ_r$  for the reaction  $\text{CH}_2\text{Cl}_2(\text{g}) \longrightarrow \text{C}(\text{g}) + 2\text{H}(\text{g}) + 2\text{Cl}(\text{g})$ . The average bond enthalpies of C-H and C-Cl bonds are  $414 \text{ kJ mol}^{-1}$  and  $330 \text{ kJ mol}^{-1}$ .
- Calculate the enthalpy change ( $\Delta H$ ) of the following reaction



$2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$  given average bond enthalpies of various bonds, i.e., C-H, C≡C, O=O, C=O, O-H as 414, 814, 499, 724 and 640 kJ mol<sup>-1</sup> respectively.

4. Estimate the average S-F bond enthalpy in SF<sub>6</sub>. The values of standard enthalpy of formation of SF<sub>6</sub>(g), S(g) and F(g) are : - 1100, 274 and 80 kJ mol<sup>-1</sup> respectively.

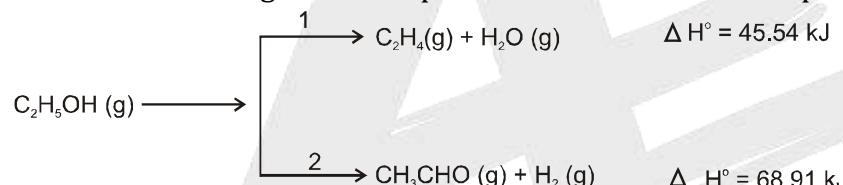


The heat of formation of NCl<sub>3</sub>(g) in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is

(A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$       (B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$

(C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$       (D) None

6. Ethanol can undergoes decomposition to form two sets of products.



If the molar ratio of C<sub>2</sub>H<sub>4</sub> to CH<sub>3</sub>CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethanol is

- (A) 65.98kJ      (B) 48.137 kJ      (C) 48.46 kJ      (D) 57.22 kJ

7. Find the bond enthalpy of S – S bond from the following data :



### ANSWER KEY

### DO YOURSELF - 1

1. (C)

Sol. From given reaction  $Dn_g = 12 - 15 = -3$

$$\text{so } \Delta U^\circ = \Delta H^\circ - \Delta n_g RT = -6542 + 3RT$$

$$\text{for 1.5 mole, } \Delta U^\circ = \{-6542 + 3RT\} = 6534.5 \text{ kJ}$$

2. (C)

Sol. H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(l) + O<sub>2</sub>(g)  $\longrightarrow$  H<sub>2</sub>O(l) + 2CO<sub>2</sub>(g);

$$\Delta n_g = 3/2$$

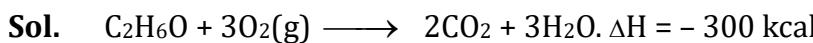
$$\Delta U_c = -8.75 \times 0.312 \times 90 = -245.7 \text{ kJ/mol}$$

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



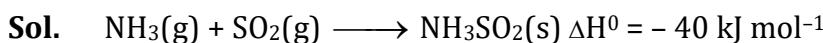
$$= -245.7 + \frac{1.5 \times 8.314 \times 300}{1000} = -241.947 \text{ kJ/mol.}$$

**3.** (-94.1 kcal)



$$\Delta H_{\text{comb}} = 2\Delta H_{f,\text{CO}_2}^{\circ} + 3\Delta H_{f,\text{H}_2\text{O}}^{\circ} - \Delta H_{f,\text{C}_2\text{H}_6\text{O}}^{\circ} = 2(-94.3) + 3(-68.5) + 300 = -94.1 \text{ Kcal}$$

**4.**  $-383 \text{ kJ mol}^{-1}$



$$\Delta H^{\circ} = \Delta H_f^{\circ}(\text{NH}_3\text{SO}_2, \text{S}) - \Delta H_f^{\circ}(\text{NH}_3, \text{g}) - \Delta H_f^{\circ}(\text{SO}_2, \text{g})$$

Solving for  $\Delta H_f^{\circ}(\text{NH}_3\text{SO}_2, \text{S})$

$$\Delta H_f^{\circ} = (\text{NH}_3\text{SO}_2, \text{S}) - \Delta H_f^{\circ}(\text{NH}_3, \text{g}) + \Delta H_f^{\circ}(\text{SO}_2, \text{g}) + \Delta H^{\circ}$$

$$= (-46.17 - 296.83 - 40) \text{ KJ mol}^{-1} = -383 \text{ kJ mol}^{-1}$$

**5.** **24 g**

**Sol.** We have

$$\text{Amount of carbon} = \frac{12.0\text{g}}{12.0 \text{ g mol}^{-1}} = 1 \text{ mol}$$

The equations to be considered are



Let the amount x of carbon be converted into CO and the remaining (i.e.  $1.0 \text{ mol} - x$ ) into  $\text{CO}_2$ . we will have  $[x(-110.5) + (1.0 \text{ mol} - x)(-393.5)] \text{ kJ mol}^{-1} = -313.8 \text{ kJ}$

Which gives  $x = \text{mol} = 0.5 \text{ mol}$

$$\text{Amount of oxygen needed} = \left[ \frac{0.5}{2} + (1.0 - 0.5) \right] \text{ mol} = 0.75 \text{ mol}$$

$$\text{Mass of oxygen needed} = (0.75 \text{ mol})(32 \text{ g mol}^{-1}) = 24 \text{ g}$$

**6.** 11.2 Kcal



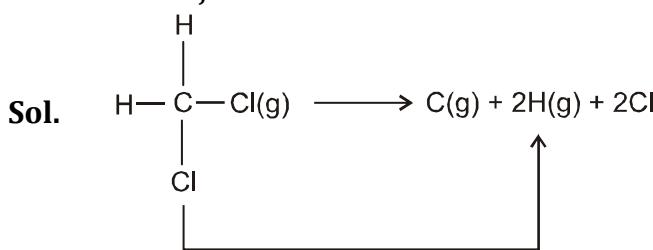
$$\Delta H_{\text{diss}}(\text{HCN}) = +13.68 - 2.48 = 11.2 \text{ Kcal}$$

### DO YOURSELF - 2

**1.**  $243.7 \text{ kJ mol}^{-1}$

**Sol.**  $\Delta H = 4\Delta H_{\text{C-H}} + \Delta H_{\text{Cl-Cl}} - 3\Delta H_{\text{C-H}} - \Delta H_{\text{C-Cl}} - \Delta H_{\text{H-Cl}}$   
 $= -100.3 = (4 \times 413) + x - (3 \times 413) - 326 - 431$   
 $x = 243.7 \text{ KJ mol}^{-1}$

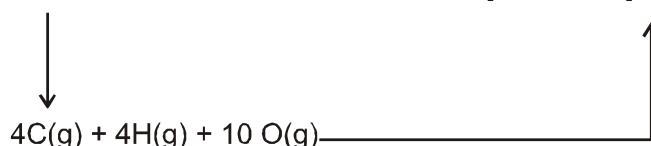
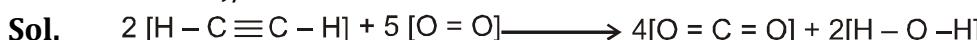
**2.**  $1488 \text{ kJ mol}^{-1}$ .



$$\Delta H_r = 2\Delta H_{\text{C-H}} + 2\Delta H_{\text{C-Cl}} = 2 \times 414 + 2 \times 330 = 828 + 660 = 1488 \text{ kJ/mol.}$$



3. - 2573 kJ/mole

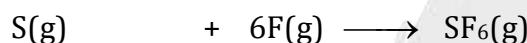


$$\Delta H_r = 2[\Delta H_{\text{C}\equiv\text{C}} + 2\Delta H_{\text{C-H}}] + 5\Delta H_{\text{O=O}} - 4[2\Delta H_{\text{C=O}}] - 2[2\Delta H_{\text{O-H}}]$$

$$\Delta H_r = 2[814 + 2 \times 414] + 5[499] - [8 \times 724] - 4[640] = 3284 + 2495 - 5792 - 2560 = -2573 \text{ kJ/mole.}$$

4. 309 kJ mol<sup>-1</sup>

Sol. To calculate the average S-F bond enthalpy, we determine the enthalpy change for the following reaction.



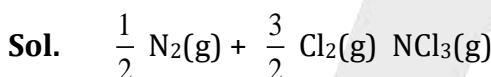
$$\Delta H_f^0 \text{ SF}_6\text{(g)} = 275 \text{ kJ mol}^{-1} \quad 80 \text{ kJ mol}^{-1} \quad 1100 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0 = \Delta H_f^0(\text{SF}_6\text{,g}) - [\Delta H_f^0(\text{S,g}) + 6\Delta H_f^0(\text{F,g})]$$

$$= [-1100 - (274 + 6 \times 80)] \text{ kJ mol}^{-1}$$

$$\text{Hence } \Delta H_{(\text{S-F})} = \frac{-\Delta H_f^0(\text{SF}_6\text{,g})}{6} = \frac{1854 \text{ kJ mol}^{-1}}{6} = 309 \text{ kJ mol}^{-1}$$

5. (B)

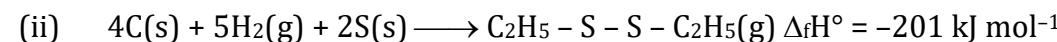
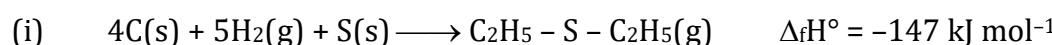


$$\Delta H = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$$

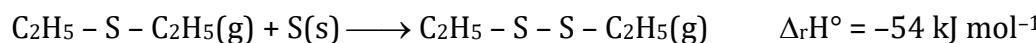
6. (B)

Sol.  $\Delta_r H = \frac{8}{9} \times 45.54 + \frac{1}{9} \times 68.91 = 48.137 \text{ kJ.}$

7. Given that



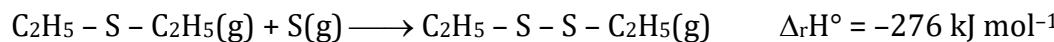
Subtracting Eq. (i) from Eq. (ii), we get



Adding to this, the following equation



We get



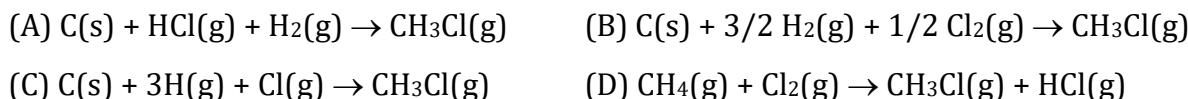
In the last equation 276 kJ of heat evolved because of the S-S bond formation.

Hence, the bond enthalpy of S - S is 276 kJ mol<sup>-1</sup>.

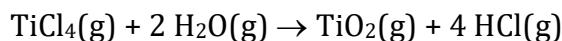


**EXERCISE # 0-I**  
**ENTHALPY OF FORMATION**

1. Which of the following equations represents a reaction that provides the heat of formation of CH<sub>3</sub>Cl?



2. Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction:



$$\Delta H^\circ_f \text{ TiCl}_4(\text{g}) = -763.2 \text{ kJ/mole}$$

$$\Delta H^\circ_f \text{ TiO}_2(\text{g}) = -944.7 \text{ kJ/mole}$$

$$\Delta H^\circ_f \text{ H}_2\text{O}(\text{g}) = -241.8 \text{ kJ/mole}$$

$$\Delta H^\circ_f \text{ HCl}(\text{g}) = -92.3 \text{ kJ/mole}$$

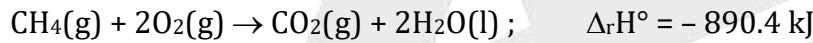
$$(\text{A}) -278.1 \text{ kJ}$$

$$(\text{B}) +369.2 \text{ kJ}$$

$$(\text{C}) +67.1 \text{ kJ}$$

$$(\text{D}) -67.1 \text{ kJ}$$

3. Using the following information calculate the heat of formation of CH<sub>4</sub>.



$$\Delta H^\circ_f \text{ CO}_2(\text{g}) = - 393.5 \text{ kJ/mole}$$

$$\Delta H^\circ_f \text{ H}_2\text{O}(\text{l}) = - 285.9 \text{ kJ/mole}$$

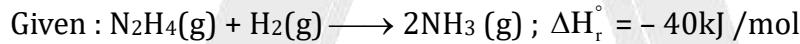
$$(\text{A}) - 98.6 \text{ kJ}$$

$$(\text{B}) - 65.5 \text{ kJ}$$

$$(\text{C}) - 74.9 \text{ kJ}$$

$$(\text{D}) - 43.5 \text{ kJ}$$

4. The standard enthalpy of formation of ammonia gas is -



$$\Delta H_f^\circ [\text{N}_2\text{H}_4(\text{g})] = - 120 \text{ kJ/mol}$$

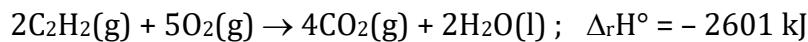
$$(\text{A}) -60 \text{ kJ}$$

$$(\text{B}) -180 \text{ kJ}$$

$$(\text{C}) 40 \text{ kJ}$$

$$(\text{D}) -80 \text{ kJ}$$

5. The heats of formation of CO<sub>2</sub>(g) and H<sub>2</sub>O(l) are -394 kJ/mole and -285.8 kJ/mole respectively  
Using the data for the following reaction, calculate the heat of formation of C<sub>2</sub>H<sub>2</sub>(g).



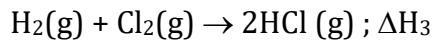
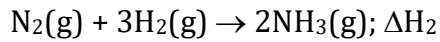
$$(\text{A}) - 238.6 \text{ kJ}$$

$$(\text{B}) 253.2 \text{ kJ}$$

$$(\text{C}) 238.7 \text{ kJ}$$

$$(\text{D}) 226.7 \text{ kJ}$$

6. NH<sub>3</sub>(g) + 3Cl<sub>2</sub>(g) → NCl<sub>3</sub>(g) + 3HCl (g); -ΔH<sub>1</sub>



The enthalpy of formation of NCl<sub>3</sub>(g) in the terms of ΔH<sub>1</sub>, ΔH<sub>2</sub> and ΔH<sub>3</sub> is

$$(\text{A}) \Delta H_f = - \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$$

$$(\text{B}) \Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$$



(C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3$       (D)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} + \frac{3}{2} \Delta H_3$

7. Study the following thermochemical equations :



The correct order of enthalpies of formation of A, B and C is -

- (A) A < B < C    (B) A < C < B    (C) C < A < B    (D) B < C < A

### ENTHALPY OF COMBUSTION

8. The heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-394 \text{ kJ/mole}$  and  $-285.8 \text{ kJ/mole}$  respectively &  $\Delta H_{\text{Combustion}}^{\circ} [\text{C}_3\text{H}_8(\text{g})] = -2221.6 \text{ kJ}$ . Then calculate the heat of formation of  $\text{C}_3\text{H}_8(\text{g})$ .

- (A) 212.2 kJ    (B) -143.3 kJ    (C) 185.4 kJ    (D) -103.6 kJ

9. What amount of heat energy (kJ) is released in the combustion of 12.0 g of  $\text{C}_3\text{H}_4$ ?

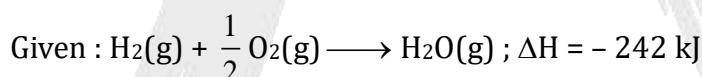
(Atomic weights: C = 12, H = 1, O = 16).



$$\Delta H^\circ = -1939.1 \text{ kJ}$$

- (A) 725    (B) 504    (C) 783    (D) 581.73

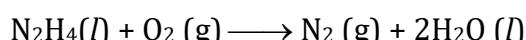
10. What is the ratio of the enthalpy change on combustion of hydrogen atoms to steam to the enthalpy change on combustion of an equal mass of hydrogen molecules to steam?



$$\text{B.E. } (\text{H} - \text{H}) = 436 \text{ kJ}$$

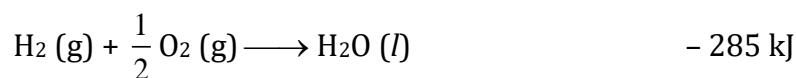
- (A) 0.80 : 1    (B) 1 : 0.80    (C) 1.80 : 1    (D) 2.80 : 1

11. Hydrazine, a component of rocket fuel, undergoes combustion to yield  $\text{N}_2$  and  $\text{H}_2\text{O}$ .



What is the enthalpy change of combustion of  $\text{N}_2\text{H}_4$  (kJ/mole)

Given Reaction	$\Delta H/\text{kJ}$
$2\text{NH}_3(\text{g}) + 3\text{N}_2\text{O}(\text{g}) \rightarrow 4\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	- 1011 kJ
$\text{N}_2\text{O}(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow \text{N}_2\text{H}_4(\text{l}) + \text{H}_2\text{O}(\text{l})$	- 317 kJ
$4\text{NH}_3(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$	- 286 kJ



- (A) -620.5      (B) -622.75      (C) 1167.5      (D) +622.75

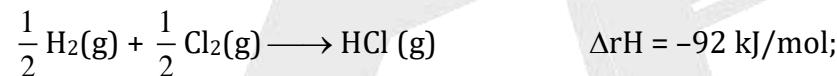
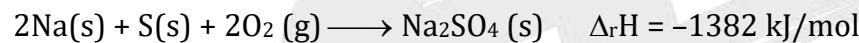
### ENTHALPY OF REACTION AND RELATION BETWEEN $\Delta H$ AND $\Delta U$

12. Find  $\Delta_r U^\circ$  for the reaction  $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$  at 300 K. Assume all gases are ideal.

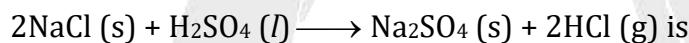


- (A) 111.5 kJ/mole    (B) -109.01 kJ/mole    (C) -111.5 kJ/mole    (D) None

13. The enthalpy changes of the following reactions at 27°C are



from these data, the heat change of reaction at constant volume (in kJ/mol) at 27°C for the process ( $R = 8.3 \text{ J/K-mol}$ )



- (A) 67      (B) 62.02      (C) 71.98      (D) 50

14.  $2\text{NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$

$$\Delta U_f^\circ [\text{N}_2\text{O}_4(\text{g})] = 2 \text{ kcal/mole}$$

and  $\Delta U^\circ_{\text{reaction}} = -16 \text{ kcal/mol}$  then calculate  $\Delta H^\circ_{\text{formation}}$  of  $\text{NO}_2$  at 727°C

- (A) 9 kcal/mol    (B) 4.5 kcal/mol    (C) 8 kcal/mol    (D) 10 kcal/mol

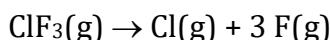
### BOND ENTHALPY, ENTHALPY OF ATOMISATION, ENTHALPY OF VAPOURISATION

15. The bond dissociation energy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58 and 103 kcal mol<sup>-1</sup> respectively. The enthalpy of formation for  $\text{HCl}$  gas will be :-

- (A) -44.0 kcal    (B) -22.0 kcal    (C) 22.0 kcal    (D) 44.0 kcal



16. The enthalpy change for the following reaction is 513 kJ. Calculate the average Cl – F bond energy.



- (A) 1542 kJ      (B) 88 kJ      (C) 171 kJ      (D) 514 kJ

17. The reaction  $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$  has  $\Delta H = -25$  kcal.

Bond	Bond Enthalpy kcal
$\in_{\text{C-Cl}}$	84
$\in_{\text{H-Cl}}$	103
$\in_{\text{C-H}}$	X
$\in_{\text{Cl-Cl}}$	Y
$x : y = 9 : 5$	

From the given data, what is the bond enthalpy of Cl—Cl bond

- (A) 70 kcal      (B) 80 kcal      (C) 67.75 kcal      (D) 57.75 kcal

18. If  $x_1$ ,  $x_2$  and  $x_3$  are enthalpies of H–H, O=O and O–H bonds respectively, and  $x_4$  is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of  $\text{H}_2(\text{g})$

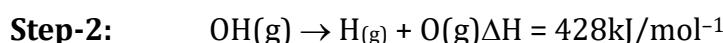
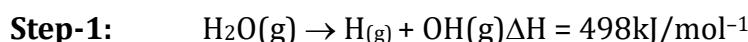
(A)  $x_1 + \frac{x_2}{2} - 2x_3 + x_4$

(B)  $x_1 + \frac{x_2}{2} - 2x_3 - x_4$

(C)  $x_1 + \frac{x_2}{2} - x_3 + x_4$

(D)  $2x_3 - x_1 - \frac{x_2}{2} - x_4$

19. The enthalpy change at 298K for decomposition is given in following steps-



Then value of mean bond enthalpy of O–H bond will be -

- (A) 498 kJ/mol      (B) 463 kJ/mol      (C) 428 kJ/mol      (D) 70 kJ/mol

20. If bond enthalpy of C–C and C = C are 348 kJ /mole and 615 kJ/mole respectively then calculate enthalpy change (in kJ/mole) which occurs during the isomerisation of cyclopropane (g) into propene (g)

- (A) 19      (B) 81      (C) 1      (D) 20



## HYDRATION ENTHALPY, ENTHALPY OF SOLUTION, HYDRATION AND DILUTION

21. The lattice enthalpy of solid NaCl is  $772 \text{ kJ mol}^{-1}$  and enthalpy of solution is  $2 \text{ kJ mol}^{-1}$ . If the hydration enthalpy of  $\text{Na}^+(\text{g})$  &  $\text{Cl}^-(\text{g})$  ions are in the ratio of 3:2.5, what is the enthalpy of hydration of chloride ion?  
 (A)  $-140 \text{ kJ mol}^{-1}$     (B)  $-350 \text{ kJ mol}^{-1}$     (C)  $-351.81 \text{ kJ mol}^{-1}$     (D) None
22. Enthalpy of dilution of 4M HCl to 2M HCl is  $-2.5 \text{ kJ/mol}$ . Find enthalpy change when 500 ml of HCl is diluted from 4M to 2M  
 (A)  $-2.5 \text{ kJ/mol}$     (B)  $-5 \text{ kJ/mol}$     (C)  $-10 \text{ kJ/mol}$     (D)  $-1.25 \text{ kJ/mol}$

## RESONANCE ENERGY &amp; ENTHALPY OF NEUTRALISATION

23. If enthalpy change for hydrogenation of ethylene is  $-132 \text{ kJ/mole}$  and enthalpy of formation 1,3-butadiene (g) and butane (g) are  $115 \text{ kJ}$  and  $-140 \text{ kJ/mole}$  respectively then calculate resonance energy of 1,3-butadiene (in kJ).  
 (A) 9 kJ    (B) 18 kJ    (C) 4 kJ    (D) 10 kJ
24. Magnitude of enthalpy of neutralization is minimum for :  
 (A)  $\text{HCN} + \text{KOH}$     (B)  $\text{HCl} + \text{KOH}$     (C)  $\text{HCl} + \text{NH}_4\text{OH}$     (D)  $\text{HCN} + \text{NH}_4\text{OH}$
25. Enthalpy of neutralization of  $\text{NaOH}$  with  $\text{H}_2\text{SO}_4$  is  $-57.3 \text{ KJ eq}^{-1}$  and ethanoic acid  $-55.2 \text{ KJ eq}^{-1}$ . which of the following is the best explanation of this difference -  
 (A) Ethanoic acid is a weak acid and thus requires less  $\text{NaOH}$  for neutralization  
 (B) Ethanoic acid is only partly ionised, neutralization is therefore incomplete  
 (C) Ethanoic acid is monobasic while  $\text{H}_2\text{SO}_4$  is dibasic  
 (D) Some heat is used to ionize ethanoic acid completely
26. 0.2 M ; 100 ml  $\text{NaOH}$  is mixed with 0.4 M ; 100 ml  $\text{HCl}$  solution. Determine energy released during the reaction.

Given :  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \longrightarrow \text{H}_2\text{O}(l)$  ;

$$\Delta H = -57.5 \text{ KJ mol}^{-1}$$

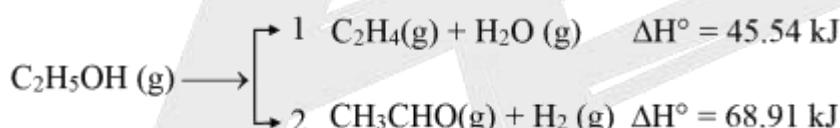
- (A) 1150 J    (B) 1150 KJ    (C) 2300 J    (D) 2300 KJ



27. Enthalpy of neutralization of  $\text{H}_2\text{C}_2\text{O}_4$  acid is  $-109 \text{ kJ/mol}$  using  $\text{NaOH}$ . If enthalpy of neutralization of  $\text{HCl}$  by  $\text{NaOH}$  is  $-57 \text{ kJ/mol}$ . Calculate  $\Delta H_{\text{ionization}}$  of  $\text{H}_2\text{C}_2\text{O}_4$  into its ions
- (A)  $50.84 \text{ kJ/mol}$     (B)  $5 \text{ kJ/mol}$     (C)  $2.5 \text{ kJ/mol}$     (D)  $10 \text{ kJ/mol}$
28.  $\Delta H_f^0$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^0$  of  $\text{OH}^-$  ion will be
- (A)  $-228.5 \text{ kJ mol}^{-1}$     (B)  $228.5 \text{ kJ mol}^{-1}$     (C)  $114.25 \text{ kJ mol}^{-1}$     (D)  $-114.25 \text{ kJ mol}^{-1}$

### KIRCHOFF EQUATION & SOME MIXED QUESTIONS

29. The molar heat capacities at constant pressure (assume constant with respect to temperature) of A, B and C are in ratio of **1.5 : 3.0 : 2.0**. If enthalpy change for the exothermic reaction  $\text{A} + 2\text{B} \longrightarrow 3\text{C}$  at  $300 \text{ K}$  is  $-10 \text{ kJ/mol}$  &  $C_{p,m}(\text{B})$  is  $300 \text{ J/mol}$  then enthalpy change at  $310 \text{ K}$  is:
- (A)  $-8.5 \text{ kJ/mol}$     (B)  $8.5 \text{ kJ/mol}$     (C)  $-11.5 \text{ kJ/mol}$     (D) none of these
30. Ethanol can undergoes decomposition to form two sets of products



if the molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  is  $8 : 1$  in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is

- (A)  $65.98 \text{ kJ}$     (B)  $48.137 \text{ kJ}$     (C)  $48.46 \text{ kJ}$     (D)  $57.22 \text{ kJ}$

31. Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,



In an experiment there was an absorption of  $0.44 \text{ kCal}$  when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of  $\text{HCl}$  . What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$  ?

- (A)  $0.5 \%$     (B)  $0.6 \%$     (C)  $5 \%$     (D)  $50 \%$

32.  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

$$\Delta G_f^\circ [\text{PCl}_5(\text{g})] = -74 \text{ kcal /mol}$$

$$\Delta G_f^\circ [\text{PCl}_3(\text{g})] = -60 \text{ kcal /mol}$$

then calculate value of equilibrium constant for dissociation of  $\text{PCl}_5(\text{g})$  at  $727^\circ\text{C}$  temperature ?

$$(\ln 2 = 0.7)$$

(A)  $2^{10}$

(B)  $2^{-10}$

(C) 2-20

(D)  $2^{+20}$

33. For the allotropic change represented by the equation  $C(\text{graphite}) \rightarrow C(\text{diamond})$ ,  $\Delta H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $\text{CO}_2$ , the enthalpy liberated in first case is

(A) less than in the second case by 1.9 kJ      (B) more than in the second case by 11.4 kJ  
(C) more than in the second case by 0.95 kJ      (D) less than in the second case by 11.4 kJ



## EXERCISE # S-I

## ENTHALPY OF FORMATION AND COMBUSTION

1. From the following data at 25°C, Calculate the standard enthalpy of formation of FeO(s) and of Fe<sub>2</sub>O<sub>3</sub>(s).

Reaction	$\Delta_rH^\circ$ (kJ/mole)
(A) Fe <sub>2</sub> O <sub>3</sub> (s) + 3C(graphite) → 2Fe (s) + 3CO(g)	492
(B) FeO (s) + C(graphite) → Fe(s) + CO(g)	155
(C) C(graphite) + O <sub>2</sub> (g) → CO <sub>2</sub> (g)	-393
(D) CO(g) + 1/2 O <sub>2</sub> (g) → CO <sub>2</sub> (g)	-282

2. When 2 moles of C<sub>2</sub>H<sub>6</sub>(g) are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of C<sub>2</sub>H<sub>6</sub>(g) . Given  $\Delta_fH$  for CO<sub>2</sub>(g) & H<sub>2</sub>O (l) are - 395 & - 286 kJ respectively.
3. Calculate standard enthalpies of formation of carbon-di-sulphide (l). Given the standard enthalpy of combustion of carbon (s), sulphur (s) and carbon-di-sulphide (l) are : - 393, - 293 and - 1108 kJ mol<sup>-1</sup> respectively.
4. The enthalpy changes for the reaction C<sub>3</sub>H<sub>8</sub>(g) + H<sub>2</sub>(g) → C<sub>2</sub>H<sub>6</sub>(g) + CH<sub>4</sub>(g) at 25° C is - 55.7 kJ/mol. Calculate the enthalpy of combustion of C<sub>2</sub>H<sub>6</sub>(g). The enthalpy of combustion of H<sub>2</sub>, & CH<sub>4</sub> and propane are -285.8, -890.0 kJ/mol and -2220 kJ mol<sup>-1</sup> respectively.
5. A cylinder of gas is assumed to contains 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion,  $\Delta H = - 2658$  kJ/mole for butane.

ENTHALPY OF REACTION AND RELATION BETWEEN  $\Delta H$  AND  $\Delta U$ 

6. At 300 K, the standard enthalpies of formation of C<sub>6</sub>H<sub>5</sub>COOH(s), CO<sub>2</sub>(g) & H<sub>2</sub>O (l) are; - 408, -393 & -286 kJ mol<sup>-1</sup> respectively.

Calculate the heat of combustion of benzoic acid at:

- (i) constant pressure
- (ii) constant volume.



### BOMB CALORIMETER, BOND ENTHALPY , ENTHALPY OF ATOMISATION, ENTHALPY OF VAPOURISATION

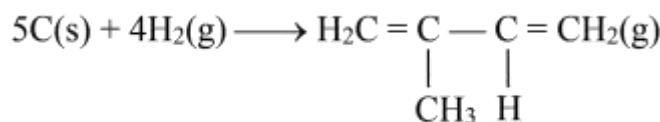
7. 0.16 g of methane was subjected to combustion at 27°C in a bomb Calorimeter. The temperature of Calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at  
 (i) constant volume    (ii) constant pressure.  
 The thermal capacity of Calorimeter system is 17.7 kJ K<sup>-1</sup>. ( $R = 8.313 \text{ mol}^{-1} \text{ K}^{-1}$ )
8. 1.00 L sample of a mixture of CH<sub>4</sub>(g) & O<sub>2</sub>(g) measured at 27°C & 760 torr was allowed to react at constant pressure in a Calorimeter which together with its contents had a heat capacity of 1200 Cal/K. The complete combustion of methane to CO<sub>2</sub> & H<sub>2</sub>O caused a temperature rise, in the Calorimeter, of 0.25K. What was the mole percent of CH<sub>4</sub> in the original mixture?  
 $\Delta H_{\text{comb}}^{\circ} (\text{CH}_4) = -200 \text{ k Cal mol}^{-1}$
9. XeF<sub>2</sub> (g) + H<sub>2</sub>(g) → 2HF(g) + Xe(g)  $\Delta H^{\circ} = -430 \text{ kJ}$   
 using the following bond energies: H-H = 435 kJ/mol  
 H-F = 565 kJ/mol  
 Calculate the average bond energy of Xe-F in XeF<sub>2</sub>.
10. For the reaction  
 $\text{N}_2\text{H}_4(\text{g}) \rightarrow \text{N}_2\text{H}_2(\text{g}) + \text{H}_2(\text{g}) \quad \Delta_r H^{\circ} = 109 \text{ kJ /mol}$   
 Calculate the bond enthalpy of N=N.  
 Given: B.E.(N-N) = 163 kJ/mol, B.E.(N-H) = 391 kJ/mol, B.E. (H-H) = 436 kJ/mol
11. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.  
 $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

**Data:**

Bond	C-C	C=C	C-H	H-H
Bond Enthalpy	336 kJ/mol	606 kJ/mol	410 kJ/mol	431 kJ/mol



12. Using bond enthalpy data, calculate enthalpy of formation of isoprene.



Given :  $\text{C} - \text{H} = 98.8 \text{ k Cal}$  ;  $\text{H} - \text{H} = 104 \text{ k Cal}$  ;  
 $\text{C} - \text{C} = 83 \text{ k Cal}$  ;  $\text{C} - \text{C} = 147 \text{ k Cal}$  &  
 $\text{C(s)} \rightarrow \text{C(g)} = 171 \text{ k Cal.}$

13. Compute the enthalpy of formation of liquid methyl alcohol in  $\text{kJ mol}^{-1}$ , using the following data.

Enthalpy of vaporisation of liquid  $\text{CH}_3\text{OH} = 38 \text{ kJ/mol}$ .

Enthalpy of formation of gaseous atoms from the elements in their standard states are



Bond Enthalpies

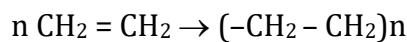


14. The enthalpy of atomization of  $\text{PH}_3$  is  $954 \text{ kJ mol}^{-1}$  and that of  $\text{P}_2\text{H}_4$  is  $1485 \text{ kJ mol}^{-1}$ . What is the bond enthalpy of the P-P bond?

15. Find the enthalpy of S-S bond from the following data.

(i) $\text{C}_2\text{H}_5 - \text{S} - \text{C}_2\text{H}_5 \text{ (g)}$	$\Delta_f H^\circ = -150 \text{ kJ/mol}$
(ii) $\text{C}_2\text{H}_5 - \text{S} - \text{S} - \text{C}_2\text{H}_5 \text{ (g)}$	$\Delta_f H^\circ = -200 \text{ kJ/mol}$
(iii) $\text{S(g)}$	$\Delta_f H^\circ = 225 \text{ kJ/mol}$

16. The polymerisation of ethylene to linear polyethylene is represented by the reaction



where  $n$  has a large integral value. Given that the average enthalpies of bond dissociation for  $\text{C}=\text{C}$  &  $\text{C}-\text{C}$  at  $298 \text{ K}$  are  $+590$  &  $+331 \text{ kJ mol}^{-1}$  respectively. Calculate the enthalpy of polymerisation per mole of ethylene at  $298 \text{ K}$ .

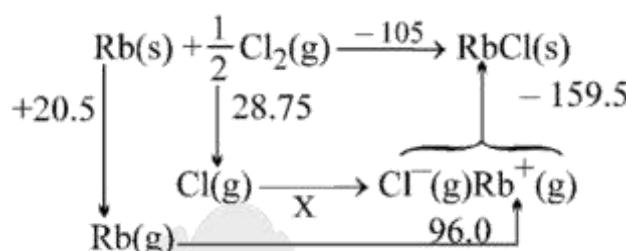
### BORN HABER CYCLE AND LATTICE ENTHALPY

17. Calculate the enthalpy change for the reaction  $\text{XeF}_4 \longrightarrow \text{Xe}^+ + \text{F}^- + \text{F}_2 + \text{F}$ .

The average  $\text{Xe}-\text{F}$  bond enthalpy is  $34 \text{ kcal/mol}$ , first I.E. of  $\text{Xe}$  is  $279 \text{ kcal/mol}$ , electron affinity of  $\text{F}$  is  $85 \text{ kcal/mol}$  & bond dissociation enthalpy of  $\text{F}_2$  is  $38 \text{ kcal/mol}$ .



18. Calculate the electron gain enthalpy of fluorine atom using the following data. Make Born – Haber's cycle. All the values are in  $\text{kJ mol}^{-1}$  at  $25^\circ \text{C}$ .  $\Delta H_{\text{diss}}(\text{F}_2) = 160$ ,  $\Delta_f H(\text{NaF(s)}) = -571$ , I.E.  $[\text{Na(g)}] = 494$ ,  $\Delta H_{\text{vap}}[\text{Na(s)}] = 101$ , Lattice enthalpy of  $\text{NaF(s)} = 894$ .
19. The Born–Haber cycle for formation of rubidium chloride ( $\text{RbCl}$ ) is given below (the enthalpies are in  $\text{k Cal mol}^{-1}$ )



Find the value of  $X$ .

20. By using the following data draw an appropriate enthalpy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.  
 Comment on the difference in their values.  
 enthalpy change of solution of  $\text{NaCl(s)} = -2 \text{ kJ/mol}$ .  
 enthalpy change of solution of  $\text{NaI(s)} = +2 \text{ kJ/mol}$ .  
 enthalpy change of hydration of  $\text{Na}^+(\text{g}) = -390 \text{ kJ/mol}$ .  
 lattice enthalpy of  $\text{NaCl} = 772 \text{ kJ/mol}$ .  
 lattice enthalpy of  $\text{NaI} = 699 \text{ kJ/mol}$ .

### HYDRATION ENTHALPY, ENTHALPY OF SOLUTION , HYDRATION AND DILUTION.

#### OTHER TYPES OF ENTHALPIES OF REACTION

21. The enthalpy of solution of anhydrous  $\text{CuSO}_4(\text{s})$  is  $-16 \text{ kCal}$  and that of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  is  $3 \text{ kCal}$ . Calculate the enthalpy of hydration of  $\text{CuSO}_4(\text{s})$ .
22. If the enthalpy of formation of  $\text{HCl(g)}$  and  $\text{Cl}^-(\text{aq})$  are  $-90 \text{ kJ/mole}$  and  $-170 \text{ kJ/mol}$ , find the enthalpy of solution of hydrogen chloride gas.

#### RESONANCE ENERGY

23. Calculate resonance enthalpy of  $\text{CO}_2(\text{g})$  from following data

$$\Delta H_{\text{combustion}}^0 [\text{C}_{\text{graphite}}] = -390 \text{ kJ/mol}$$

$$\Delta H_{\text{atomisation}}^0 [\text{C}_{\text{graphite}}] = 715 \text{ kJ/mol}$$



$$\Delta H_{\text{B.E.}}^0 [\text{O} = \text{O}] = 500 \text{ kJ/mol}$$

$$\Delta H_{\text{B.E.}}^0 [\text{C} = \text{O}] = 675 \text{ kJ/mol}$$

24. Use the following data to answer the questions below :



Calculate the resonance energy of anthracene,

25. Calculate enthalpy of combustion of propane [C<sub>3</sub>H<sub>8</sub> (g)] in **kJ/mol** at 298 K.

Given : B.E. (O = O) = 498 kJ/mole ; B.E. (C = O) = 804 kJ/mole

B.E. (C-H) = 410 kJ/mole ; B.E. (O-H) = 464 kJ/mole

B.E. (C-C) = 345 kJ/mole ; Resonance energy of

CO<sub>2</sub> (g) = - 143 kJ/mole

$\Delta H_{\text{vaporization}} (\text{H}_2\text{O}, l) = 41 \text{ kJ/mol}$

### ENTHALPY OF NEUTRALISATION

26. The enthalpies of neutralization of NaOH & NH<sub>4</sub>OH by HCl are -13680 Cal and -12270 Cal respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH<sub>4</sub>Cl in solution ? Assume that NH<sub>4</sub>OH and NaCl are quantitatively obtained.

27.  $\text{H}^+ + \text{OH}^- \longrightarrow \text{H}_2\text{O} ; \Delta H^\ominus = -57 \text{ kJ/mol}$

$$\Delta H_{\text{ionisation}}^0 [\text{HCN}] = 45 \text{ kJ/mol}$$

If 200 ml , 1/10 M Ba(OH)<sub>2</sub> solution is mixed with 500 ml , 1/10M HCN, then find out the heat evolved.

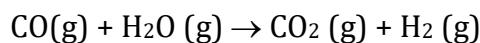
28. Two solutions initially at 25°C were mixed in an adiabatic constant pressure Calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm<sup>3</sup>, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the Calorimeter.



29. Calculate the enthalpy change when infinitely dilute solution of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  are mixed  
 $\Delta_f H^\circ$  for  $\text{Ca}^{2+}$  (aq),  $\text{CO}_3^{2-}$  (aq) and  $\text{CaCO}_3$  (s) are  $-129, -161, -288 \text{ kcal mol}^{-1}$  respectively.

### KIRCHOFF EQUATION

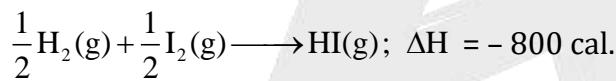
30. Determine  $\Delta H$  for the following reaction at 500K and constant pressure :



use the following data :

Substance	$C_p$ (J/mol K)	$\Delta_f H(298\text{K})$ (kJ/mol)
CO	29	-110
$\text{H}_2\text{O}$	33	-241
$\text{CO}_2$	37	-393
$\text{H}_2$	29	0

31. The heat of formation of one mole of HI from hydrogen and iodine vapour at  $27^\circ \text{C}$  is  $-8000 \text{ cal}$ .



Calculate the heat of formation at  $127^\circ \text{C}$ . Given

$$C_p = 7 + 6 \times 10^{-3} T \text{ for hydrogen (g) (Cal/mol/K)}$$

$$C_p = 7 + 4 \times 10^{-3} T \text{ for iodine (g) (Cal/mol/K)}$$

$$C_p = 7 + 3 \times 10^{-3} T \text{ for HI (g) (Cal/mol/K)}$$

### Misc

32. Froms the given table answer the following questions:

	$\text{CO(g)}$	$\text{CO}_2\text{(g)}$	$\text{H}_2\text{O(g)}$	$\text{H}_2\text{(g)}$
$(\Delta_f H^\circ)_{298}$ (kcal/mole)	-26	-94	-57	0
$(\Delta_f G^\circ)_{298}$ (kcal/mole)	-32	-94	-54	0
$S^\circ_{298}$ (Cal/K/mole)	47	51	?	31



(1) Calculate  $\Delta r H_{298}^\circ$

(ii) Calculate  $\Delta r G_{298}^\circ$

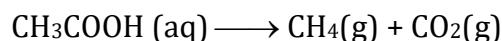
(iii) Calculate  $\Delta r S_{298}^\circ$

(iv) Calculate  $\Delta r U_{298}^\circ$

(v) Calculate  $S_{298}^\circ$  [H<sub>2</sub>O(g)]



33. At temperatures above 85 K, decarboxylation of acetic acid becomes a spontaneous process under standard state conditions. What is the standard entropy change (**in J/K-mol**) of the reaction.

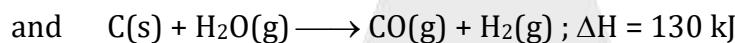
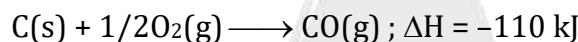


Given :  $\Delta H_f^0 [\text{CH}_3\text{COOH} \text{ (aq)}] = -484 \text{ kJ/mol}$

$$\Delta H_f^0 [\text{CO}_2(\text{g})] = -392 \text{ kJ/mol}$$

$$\Delta H_f^0 [\text{CH}_4(\text{g})] = -75 \text{ kJ/mol}$$

34. From the following data of  $\Delta H$  of the following reactions



The mole ratio of  $\text{O}_2$  & steam being passed over coke at 1273 K, so that temperature remains constant is :

(A) 0.6 : 1

(B) 1.67 : 1

(C) 0.3 : 1

(D) 0.4 : 1

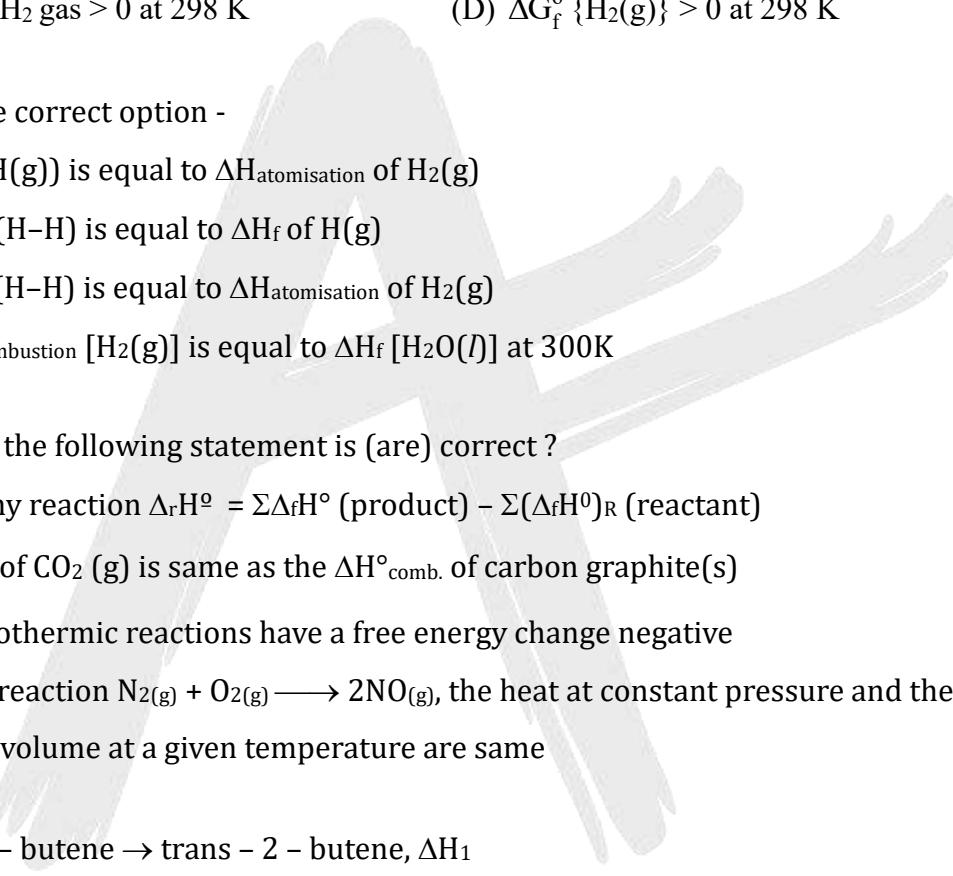


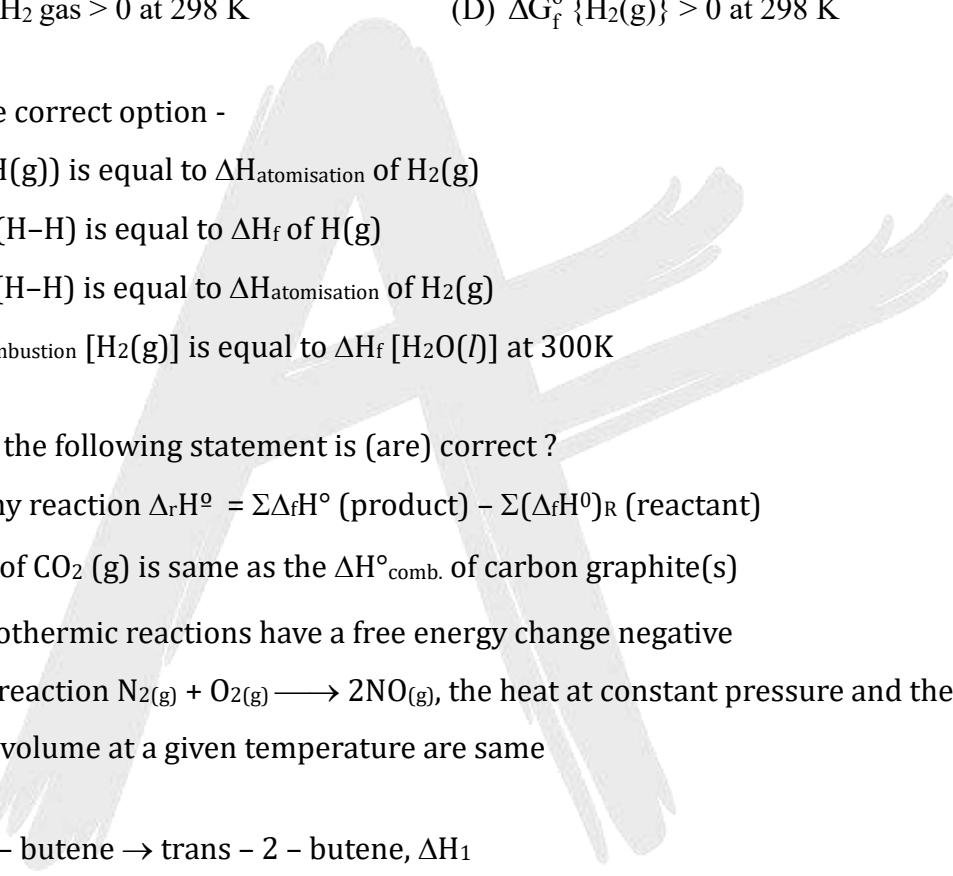
## EXERCISE # O-II

1. Which of the following do(es) not represent  $\Delta H$  formation of the product.
 

(A) $\frac{1}{2} \text{H}_2(\text{g}) + (\text{aq}) \longrightarrow \text{H}^+(\text{aq}) + \text{e}^-$	(B) $\frac{1}{2} \text{O}_3(\text{g}) \longrightarrow \text{O}_2(\text{g})$
(C) $\text{NH}_4^+ + \text{Cl}^-(\text{g}) \longrightarrow \text{NH}_4\text{Cl}(\text{s})$	(D) $\text{P}_4(\text{black}) + 5\text{O}_2(\text{g}) \longrightarrow \text{P}_4\text{O}_{10}(\text{s})$
  
2. Pick out the incorrect statement(s) among the following.
 

(A) $\Delta S_f^\circ \{\text{He}(\text{g})\} > 0$ at 298 K	(B) $\Delta S_f^\circ \{\text{H}_2\text{O}(\text{g})\} > 0$ at 298 K
(C) $S^\circ$ of $\text{H}_2$ gas > 0 at 298 K	(D) $\Delta G_f^\circ \{\text{H}_2(\text{g})\} > 0$ at 298 K
  
3. Select the correct option -
 

(A) $\Delta H_f(\text{H}(\text{g}))$ is equal to $\Delta H_{\text{atomisation}}$ of $\text{H}_2(\text{g})$	
(B) $\Delta H_{\text{BE}}(\text{H}-\text{H})$ is equal to $\Delta H_f$ of $\text{H}(\text{g})$	
(C) $\Delta H_{\text{BE}}(\text{H}-\text{H})$ is equal to $\Delta H_{\text{atomisation}}$ of $\text{H}_2(\text{g})$	
(D) $\Delta H_{\text{combustion}} [\text{H}_2(\text{g})]$ is equal to $\Delta H_f [\text{H}_2\text{O}(\text{l})]$ at 300K	
  
4. Which of the following statement is (are) correct ?
 

(A) for any reaction $\Delta_r H^\circ = \sum \Delta_f H^\circ (\text{product}) - \sum (\Delta_f H^\circ)_R (\text{reactant})$	
(B) $\Delta H_f^\circ$ of $\text{CO}_2(\text{g})$ is same as the $\Delta H_{\text{comb.}}$ of carbon graphite(s)	
(C) all exothermic reactions have a free energy change negative	
(D) for a reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$ , the heat at constant pressure and the heat at constant volume at a given temperature are same	
  
5. (i) Cis-2 – butene  $\rightarrow$  trans – 2 – butene,  $\Delta H_1$   
 (ii) Cis – 2 – butene  $\rightarrow$  1 – butene,  $\Delta H_2$   
 (iii)  $9\Delta H_1 + 5 \Delta H_2 = 0$   
 (iv) Enthalpy of combustion of 1-butene,  $\Delta H = -649.8$  kcal/mol  
 (v) Enthalpy of combustion of trans 2 – butene,  $\Delta H = -647.0$  kcal/mol.  
 The value of  $\Delta H_1$  &  $\Delta H_2$  in Kcal/mole are  

(A) $\Delta H_1 = -1.0$	(B) $\Delta H_2 = 1.8$
(C) $\Delta H_1 = -2.0$	(D) $\Delta H_2 = 2.8$



6. From the following data at 25°C

Reaction	$\Delta_r H^\circ \text{ kJ/mol}$
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g})$	-242
$\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g})$	436
$\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g})$	495

Which of the following statement(s) is/are correct:

- (A)  $\Delta_r H^\circ$  for the reaction  $\text{H}_2\text{O}(\text{g}) \longrightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$  is 925.5 kJ/mol
- (B)  $\Delta_r H^\circ$  for the reaction  $\text{OH}(\text{g}) \longrightarrow \text{H}(\text{g}) + \text{O}(\text{g})$  is 502 kJ/mol
- (C) Enthalpy of formation of  $\text{H}(\text{g})$  is 218 kJ/mol
- (D) Enthalpy of formation of  $\text{OH}(\text{g})$  is -121 kJ/mol

7. Which of the following mixture of strong acid & strong base will give same temperature change for solution (Assume density & specific heat same for all solutions)-
- (A) 50 ml 0.1 M HCl + 50 ml 0.1 M NaOH
  - (B) 30 ml 0.1 M HCl + 30 ml 0.1 M NaOH
  - (C) 25 ml 0.1 M  $\text{H}_2\text{SO}_4$  + 50 ml 0.1 M KOH
  - (D) 50 ml 0.1 M  $\text{H}_2\text{SO}_4$  + 50 ml 0.1 M NaOH

#### Paragraph for Q.8 to Q.9

Bond dissociation enthalpy of the first H-S bond in hydrogen sulphide is 376 kJ/mole.

The enthalpies of formation of  $\text{H}_2\text{S}(\text{g})$  and  $\text{S}(\text{g})$  are -20.0 and 277.0 kJ/mole respectively.

The enthalpy of formation of gaseous hydrogen atom is 218 kJ/mole. Using above information, answer following questions :

8. The enthalpy of formation of free radical HS is
- (A) 138 kJ/mole
  - (B) -138 kJ/mole
  - (C) -10 kJ/mole
  - (D) 357 kJ/mole
9. The bond dissociation enthalpy of the free radical HS is
- (A) 138 kJ/mole
  - (B) 276 kJ/mole
  - (C) 357 kJ/mole
  - (D) 376 kJ/mole



## Paragraph for Q.10 to Q.11

Amount of heat evolved during complete combustion of liquid benzene can be calculated from the following data.

(i) 18 gm of graphite on complete combustion evolve 591 kJ heat

(ii)  $\Delta H_f^\circ (H_2O, l) = -286 \text{ kJ/mol}$

(iii) The heat of formation of liquid benzene is 50 kJ /mole

- 10.** Heat of formation of  $CO_2(g)$  from following data is-

(A) -286 kJ/mole    (B) -590 kJ/mole    (C) -394 kJ/mole    (D) -3268 kJ/mole

- 11.** Find heat evolved from combustion of 78 gm benzene

(A) 3272 kJ    (B) 6345 kJ    (C) 4536 kJ    (D) 5364 kJ

## Match the column :

**12. Column-I**

- |   |  |
|---|--|
| (A) $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$                 | (P) $\Delta H_{\text{formation}}^0$      |
| (B) $C(\text{graphite}) \longrightarrow C(\text{gas})$                | (Q) $\Delta H_{\text{combustion}}^0$     |
| (C) $CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$ | (R) $\Delta H_{\text{atomization}}^0$    |
| (D) $CH_4(g) \longrightarrow C(g) + 4H(g)$                            | (S) $\Delta H_{\text{neutralization}}^0$ |

**Column-II****13. List-I**

- |               |                                     |                                 |
|---------------|-------------------------------------|---------------------------------|
| (P) $O_2(g)$  | (A) $\Delta_f H^\circ = +\text{ve}$ | $\Delta_f S^\circ = +\text{ve}$ |
| (Q) $O_3(g)$  | (B) $\Delta_f H^\circ = -\text{ve}$ | $\Delta_f S^\circ = -\text{ve}$ |
| (R) $Br_2(g)$ | (C) $\Delta_f H^\circ = +\text{ve}$ | $\Delta_f S^\circ = -\text{ve}$ |
| (S) $H_2(l)$  | (D) $\Delta_f H^\circ = 0$          | $\Delta_f S^\circ = 0$          |

## Match list

**List-II**

## Code :

	P	Q	R	S
(A)	4	3	1	2
(B)	2	4	1	3
(C)	3	4	1	2
(D)	2	3	1	4



14. Match the enthalpy change ( $\Delta H$ ) mentioned in list-II for 16 gm O<sub>2</sub> with the various reaction in list-I.

**List-I**

- (P)  $2\text{C}_2\text{H}_2 + 5\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}), -2601 \text{ kJ}$   
(Q)  $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}), -285.8 \text{ kJ}$   
(R)  $3\text{FeO}(\text{s}) + 1/2\text{O}_2(\text{g}) \longrightarrow \text{Fe}_3\text{O}_4(\text{s}), -302.4 \text{ kJ}$   
(S)  $\text{C}_{\text{graphite}} + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}), -393.5 \text{ kJ}$

**List-II ( $\Delta H$  in kJ)**

- (A) -285.8  
(B) -196.75  
(C) -260.1  
(D) -302.4

**Code :**

	P	Q	R	S
(A)	4	1	3	2
(B)	3	1	4	2
(C)	3	4	1	2
(D)	2	3	1	4



## EXERCISE # S-II

- An stoichiometric mixture of ferric oxide & Al is used as solid rocket fuel . Calculate the fuel value per gm & fuel value per CC of the mixture. Enthalpies of formation & densities are :  
 $\Delta H_f^0 (\text{Al}_2\text{O}_3) = -399 \text{ k Cal/mole}$  ;  $\Delta H_f^0 (\text{Fe}_2\text{O}_3) = -199 \text{ kCal / mole}$ ,  
density of  $\text{Fe}_2\text{O}_3 = 5.2 \text{ g/cc}$  ; density of Al =  $2.7 \text{ g/cc}$ .
- The enthalpy of formation of  $\text{C}_2\text{H}_5\text{OH}(l)$  is  $-66 \text{ k Cal/mol}$ . The enthalpy of combustion of  $\text{CH}_3-\text{O}-\text{CH}_3$  is  $-348 \text{ k Cal/mol}$ . Given that the enthalpies of formation of  $\text{CO}_2(g)$  and  $\text{H}_2\text{O}(l)$  are  $-94 \text{ k Cal/mol}$  &  $-68 \text{ k Cal/mol}$  respectively, calculate  $\Delta H$  for the isomerisation of ethanol to methoxymethane. All data are at  $25^\circ \text{C}$ .
- The enthalpy of combustion of acetylene is  $-312 \text{ kcal per mole}$ . If enthalpy of formation of  $\text{CO}_2$  &  $\text{H}_2\text{O}$  are  $-94$  &  $-68 \text{ kcal per mole}$  respectively, calculate C ≡ C bond enthalpy.  
Given that enthalpy of atomisation of C is  $150 \text{ kcal per mole}$  and H – H bond enthalpy and C – H bond enthalpy is  $103 \text{ kcal per mole}$  and  $93 \text{ kcal per mole}$  respectively.
- Calculate the mass of mercury which can be liberated from  $\text{HgO}$  at  $25^\circ \text{C}$  by the treatment of excess  $\text{HgO}$  with  $41.84 \text{ kJ}$  of heat at
  - constant pressure
  - constant volume
Given :  $\Delta H_f^0 (\text{HgO}, s) = -90.8 \text{ kJ mol}^{-1}$       &      M (Hg) =  $200.6 \text{ g mol}^{-1}$ .
- Find the bond enthalpy (in  $\text{kJ/mol}$ ) of one "three centre two electron bond" in  $\text{B}_2\text{H}_6 \{\text{B}-\text{H}-\text{B} \rightarrow 2\text{B}(g) + \text{H}(g)\}$  from the given data  
 $\Delta H_f^0 [\text{BH}_3(g)] = 100 \text{ kJ/mol}$        $\Delta H_f^0 [\text{B}_2\text{H}_6(g)] = 36 \text{ kJ/mol}$   
 $\Delta H_{\text{atm}2}[\text{B}(s)] = 565 \text{ kJ/mol}$        $\Delta H_{\text{atm}}[\text{H}_2(g)] = 436 \text{ kJ/mol}$
- Calculate the bond enthalpy of the O–H bond in water at  $298\text{K}$  using the information given below :-  
(A)  $\Delta_f H^0[\text{H}(g)] = 218 \text{ kJ/mol}$   
(B)  $\Delta_f H^0[\text{O}(g)] = 249.2 \text{ kJ/mol}$   
(C)  $\Delta_f H^0[\text{H}_2\text{O}(g)] = -241.8 \text{ kJ/mol}$   
Also, determine the  $\Delta U$  of the O–H bond in water at  $298\text{K}$ . Assume ideal gas behaviour.



7. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are  $-2840$ ,  $-2275$  and  $-5530 \text{ kJ mol}^{-1}$  respectively. Calculate the resonance energy of benzene. The bond enthalpy of C-H bond is given as equal to  $+410 \text{ kJ/mol}$ .

8. Calculate the enthalpy of combustion of methyl alcohol at  $298 \text{ K}$  from the following data

Bond	C-H	C-O	O-H	O = O	C = O
Bond Enthalpy( $\text{kJ mol}^{-1}$ )	414	351.5	464.5	494	711

Resonance energy of  $\text{CO}_2 = -143 \text{ kJ mol}^{-1}$

Latent heat of vaporisation of methyl alcohol =  $35.5 \text{ kJ mol}^{-1}$ .

Latent heat of vaporisation of water =  $40.6 \text{ kJ mol}^{-1}$ .

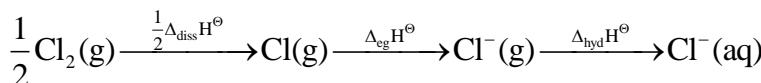


## EXERCISE # (JEE-MAIN)

1. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol<sup>-1</sup>, the value of enthalpy change for the reaction : [AIEEE-2003]  
 $\text{H}_2\text{C} = \text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{H}_3\text{C}-\text{CH}_3(\text{g})$  at 298 K  
 will be :-  
 (A) +125 kJ      (B) -125 kJ      (C) +250 kJ      (D) -250 kJ
2. The enthalpies of combustion of carbon and carbon monoxide are -393.5 and -283 kJ mol<sup>-1</sup> respectively. The enthalpy of formation of carbon monoxide per mole : [AIEEE-2004]  
 (A) 110.5 kJ      (B) 676.5 kJ      (C) -676.5 kJ      (D) -110.5 kJ
3. If the bond dissociation energies of XY, X<sub>2</sub> and Y<sub>2</sub> (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and  $\Delta_fH$  for the formation of XY is -200 kJ mol<sup>-1</sup>. The bond dissociation energy of X<sub>2</sub> will be : [AIEEE-2005]  
 (A) 200 kJ mol<sup>-1</sup>      (B) 100 kJ mol<sup>-1</sup>      (C) 800 kJ mol<sup>-1</sup>      (D) 300 kJ mol<sup>-1</sup>
4. The enthalpy changes for the following processes are listed below : [AIEEE-2006]  
 $\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl}(\text{g}), \quad 242.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{g}) \longrightarrow 2\text{I}(\text{g}), \quad 151.0 \text{ kJ mol}^{-1}$   
 $\text{ICl}(\text{g}) \longrightarrow \text{I}(\text{g}) + \text{Cl}(\text{g}), \quad 211.3 \text{ kJ mol}^{-1}$   
 $\text{I}_2(\text{s}) \longrightarrow \text{I}_2(\text{g}), \quad 62.76 \text{ kJ mol}^{-1}$   
 Given that the standard states for iodine and chlorine are I<sub>2</sub>(s) and Cl<sub>2</sub>(g), the standard enthalpy of formation for ICl(g) is :-  
 (A) -16.8 kJ mol<sup>-1</sup>      (B) +16.8 kJ mol<sup>-1</sup>      (C) +244.8 kJ mol<sup>-1</sup>      (D) -14.6 kJ mol<sup>-1</sup>
5. The standard enthalpy of formation ( $\Delta_fH^\circ$ ) at 298K for methane, CH<sub>4</sub>(g), is -74.8 kJ mol<sup>-1</sup>. The additional information required to determine the average energy for C–H bond formation would be:- [AIEEE-2006]  
 (A) Latent heat of vapourization of methane  
 (B) The first four ionization energies of carbon and electron gain enthalpy of hydrogen  
 (C) The dissociation energy of hydrogen molecule H<sub>2</sub>  
 (D) The dissociation energy of H<sub>2</sub> and enthalpy of sublimation of carbon



6. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below:



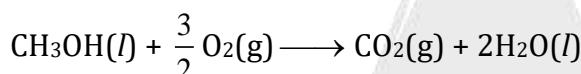
[AIEEE-2008]

The energy involved in the conversion of  $\frac{1}{2} \text{Cl}_2(\text{g})$  to  $\text{Cl}^-(\text{aq})$

(using the data  $\Delta_{\text{diss}}\text{H}^\ominus \text{Cl}_2 = 240 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{eg}}\text{H}^\ominus \text{Cl} = -349 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{hyd}}\text{H}^\ominus \text{Cl}^- = -381 \text{ kJ mol}^{-1}$ ) will be:-

- (A)  $-610 \text{ kJ mol}^{-1}$     (B)  $-850 \text{ kJ mol}^{-1}$     (C)  $+120 \text{ kJ mol}^{-1}$     (D)  $+152 \text{ kJ mol}^{-1}$

7. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is

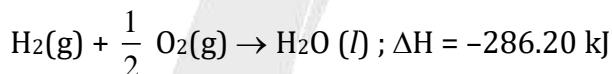


At 298 K standard Gibb's energies of formation for  $\text{CH}_3\text{OH}(\text{l})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$  are  $-166.2$ ,  $-237.2$  and  $-394.4 \text{ kJ mol}^{-1}$  respectively. If standard enthalpy of combustion of methanol is  $-726 \text{ kJ mol}^{-1}$ , efficiency of the fuel cell will be

[AIEEE-2009]

- (A) 90%    (B) 97%    (C) 80%    (D) 87%

8. On the basis of the following thermochemical data :  $(\Delta G_f^0 \text{H}_{(\text{aq})}^+ = 0)$



The value of enthalpy of formation of  $\text{OH}^-$  ion at  $25^\circ\text{C}$  is :-

[AIEEE-2009]

- (A)  $+228.88 \text{ kJ}$     (B)  $-343.52 \text{ kJ}$     (C)  $-22.88 \text{ kJ}$     (D)  $-228.88 \text{ kJ}$

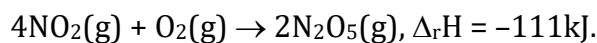
9. The standard enthalpy of formation of  $\text{NH}_3$  is  $-46.0 \text{ kJ mol}^{-1}$ . If the enthalpy of formation of  $\text{H}_2$  from its atoms is  $-436 \text{ kJ mol}^{-1}$  and that of  $\text{N}_2$  is  $-712 \text{ kJ mol}^{-1}$ , the average bond enthalpy of N-H bond in  $\text{NH}_3$  is :-

[AIEEE-2010]

- (A)  $-1102 \text{ kJ mol}^{-1}$     (B)  $-964 \text{ kJ mol}^{-1}$     (C)  $+352 \text{ kJ mol}^{-1}$     (D)  $+1056 \text{ kJ mol}^{-1}$

10. Consider the reaction :

[AIEEE-2011]



If  $\text{N}_2\text{O}_5(\text{s})$  is formed instead of  $\text{N}_2\text{O}_5(\text{g})$  in the above reaction, the  $\Delta_r\text{H}$  value will be :-

(given,  $\Delta\text{H}$  of sublimation for  $\text{N}_2\text{O}_5$  is  $54 \text{ kJ mol}^{-1}$ )

- (A)  $-165 \text{ kJ}$     (B)  $+54 \text{ kJ}$     (C)  $+219 \text{ kJ}$     (D)  $-219 \text{ kJ}$



11. The enthalpy of neutralisation of  $\text{NH}_4\text{OH}$  with  $\text{HCl}$  is  $-51.46 \text{ kJ mol}^{-1}$  and the enthalpy of neutralisation of  $\text{NaOH}$  with  $\text{HCl}$  is  $-55.90 \text{ kJ mol}^{-1}$ . The enthalpy of ionisation of  $\text{NH}_4\text{OH}$  is:

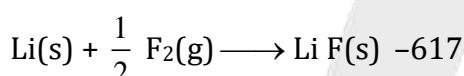
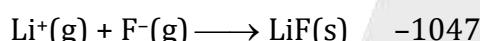
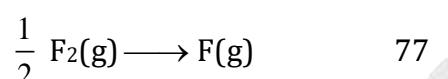
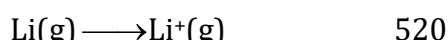
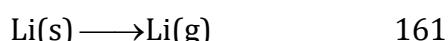
[JEE-MAINS (online) 2012]

- (A)  $+107.36 \text{ kJ mol}^{-1}$  (B)  $-4.44 \text{ kJ mol}^{-1}$  (C)  $-107.36 \text{ kJ mol}^{-1}$  (D)  $+4.44 \text{ kJ mol}^{-1}$

12. Given

[JEE-MAINS (OnLine) 2013]

Reaction	Energy Change (in kJ)
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Based on data provided, the value of electron gain enthalpy of fluorine would be :

- (A)  $-300 \text{ kJ mol}^{-1}$  (B)  $-328 \text{ kJ mol}^{-1}$  (C)  $-350 \text{ kJ mol}^{-1}$  (D)  $-228 \text{ kJ mol}^{-1}$

13. Given :

[JEE-MAINS (online) 2013]



The molar enthalpy of vapourisation of water will be :-

- (A)  $241.8 \text{ kJ mol}^{-1}$  (B)  $527.7 \text{ kJ mol}^{-1}$  (C)  $44.1 \text{ kJ mol}^{-1}$  (D)  $22.0 \text{ kJ mol}^{-1}$

14. The standard enthalpy of formation ( $\Delta_f H^\ominus_{298}$ ) for methane,  $\text{CH}_4$  is  $-74.9 \text{ kJ mol}^{-1}$ .

In order to calculate the average energy given out in the formation of a C-H bond from this it is necessary to know which one of the following?

[JEE-MAINS(online) 2014]

- (A) the dissociation energy of the hydrogen molecule,  $\text{H}_2$ .
- (B) the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon (graphite).
- (C) the first four ionisation energies of carbon and electron affinity of hydrogen.
- (D) the first four ionisation energies of carbon.



15. For complete combustion of ethanol,  $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ , the amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ .

Assuming ideality the Enthalpy of combustion,  $\Delta_c H$ , for the reaction will be :-

$$(R = 8.314 \text{ kJ mol}^{-1})$$

[JEE-MAINS 2014]

$$(A) -1460.50 \text{ kJ mol}^{-1}$$

$$(B) -1350.50 \text{ kJ mol}^{-1}$$

$$(C) -1366.95 \text{ kJ mol}^{-1}$$

$$(D) -1361.95 \text{ kJ mol}^{-1}$$

16. The heat of atomisation of methane and ethane are  $360 \text{ kJ/mol}$  and  $620 \text{ kJ/mol}$ , respectively.

The longest wavelength of light capable of breaking the C-C bond is :

$$(\text{Avogadro number} = 6.02 \times 10^{23}, h = 6.62 \times 10^{-34} \text{ J s})$$

[JEE-MAINS (Online) 2015]

$$(A) 2.48 \times 10^3 \text{ nm} \quad (B) 1.49 \times 10^3 \text{ nm} \quad (C) 2.49 \times 10^4 \text{ nm} \quad (D) 2.48 \times 10^4 \text{ nm}$$

17. The heats of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is :

[JEE-MAINS 2016]

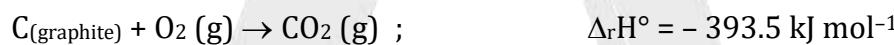
$$(A) 676.5$$

$$(B) -676.5$$

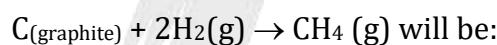
$$(C) -110.5$$

$$(D) 110.5$$

18. Given



Based on the above thermochemical equations, the value of  $\Delta_r H^\circ$  at  $298 \text{ K}$  for the reaction



[JEE-MAINS 2017]

$$(A) +74.8 \text{ kJ mol}^{-1} \quad (B) +144.0 \text{ kJ mol}^{-1} \quad (C) -74.8 \text{ kJ mol}^{-1} \quad (D) -144.0 \text{ kJ mol}^{-1}$$

19. The combustion of benzene (*l*) gives  $CO_2(g)$  and  $H_2O(l)$ . Given that heat of combustion of benzene at constant volume is  $-3263.9 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ ; heat of combustion (in  $\text{kJ mol}^{-1}$ ) of benzene at constant pressure will be : ( $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ )

[JEE-MAINS 2018]

$$(A) -3267.6$$

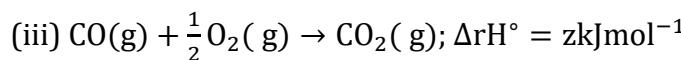
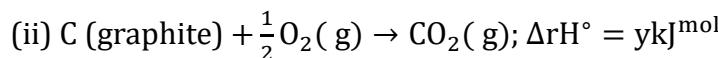
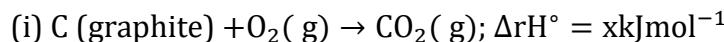
$$(B) 4152.6$$

$$(C) -452.6$$

$$(D) 3260$$



20. Given:



Based on the above thermochemical equations, find out which one of the following algebraic relationships is correct ?

[JEE-MAINS 2019 (Jan.)]

- (A) x = y - z      (B) y = 2z - x      (C) z = x + z      (D) x = y + z

21. Enthalpy of sublimation of iodine is 24 cal g<sup>-1</sup> at 200°C. If specific heat of I<sub>2</sub>(s) and I<sub>2</sub>(vap) are 0.055 and 0.031 cal g<sup>-1</sup> K<sup>-1</sup> respectively, then enthalpy of sublimation of iodine at 250°C in cal g<sup>-1</sup> is:

[JEE-MAINS 2019 (Apr.)]

- (A) 2.85      (B) 22.8      (C) 11.4      (D) 5.7

22. The internal energy change (in J) when 90 g of water undergoes complete evaporation at 100°C is (Given : ΔH<sub>vap</sub> for water at 373 K = 41 kJ/mol, R = 8.314 JK<sup>-1</sup> mol<sup>-1</sup>)

[JEE-MAINS 2020]

23. Lattice enthalpy and enthalpy of solution of NaCl are 788 kJ mol<sup>-1</sup> and 4 kJ mol J m<sup>-1</sup>, respectively.

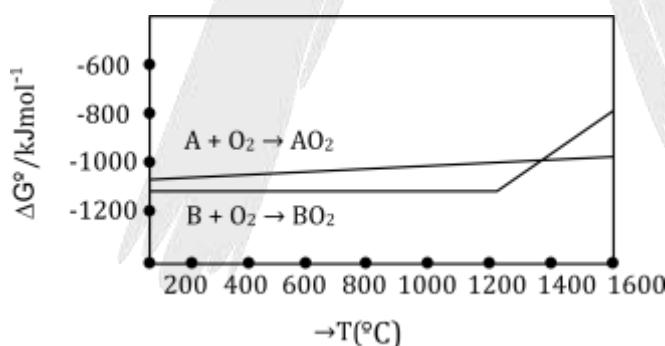
The hydration enthalpy of NaCl is

[JEE-MAINS 2020]

- (A) 784 kJ mol<sup>-1</sup>      (B) -780 kJ mol<sup>-1</sup>      (C) 780 kJ mol<sup>-1</sup>      (D) -784 kJ mol<sup>-1</sup>

24. According to the following diagram, A reduces CO<sub>2</sub> when the temperature is :

[JEE-MAINS 2020]



- (A) > 1400°C      (B) < 1400°C

- (C) > 1200°C but < 1400°C      (D) < 1200°C

25. The first and second ionisation enthalpies of a metal are 496 and 4560 kJ mol<sup>-1</sup>, respectively.

How many moles of HCl and H<sub>2</sub>SO<sub>4</sub>, respectively, will be needed to react completely with 1 mole of the metal hydroxide?

[JEE-MAINS 2020]

- (A) 1 and 0.5      (B) 2 and 0.5      (C) 1 and 2      (D) 1 and 1



26. For the reaction



the reaction enthalpy  $\Delta_r H = \text{_____ kJ mol}^{-1}$ .

(Round off to the Nearest Integer).

[Given : Bond enthalpies in  $\text{kJ mol}^{-1}$  : C–C : 347, C=C : 611; C–H : 414, H–H : 436]

[JEE Main, March 2021]

27. The Born-Haber cycle for KCl is evaluated with the following data:

[JEE Main, August 2021]

$$\Delta_f H^\circ \text{ for KCl} = -436.7 \text{ kJ mol}^{-1};$$

$$\Delta_{\text{sub}} H^\circ \text{ for K} = 89.2 \text{ kJ mol}^{-1};$$

$$\Delta_{\text{ionization}} H^\circ \text{ for K} = 419.0 \text{ kJ mol}^{-1};$$

$$\Delta_{\text{electron gain}} H^\circ \text{ for Cl(g)} = -348.6 \text{ kJ mol}^{-1};$$

$$\Delta_{\text{bond}} H^\circ \text{ for Cl}_2 = 243.0 \text{ kJ mol}^{-1};$$

The magnitude of lattice enthalpy of KCl in  $\text{kJ mol}^{-1}$  is  $\text{_____}$  (Nearest integer)

28. At  $25^\circ\text{C}$  and 1 atm pressure, the enthalpy of combustion of benzene (A) and acetylene (g) are  $-3268 \text{ kJ mol}^{-1}$  and  $-1300 \text{ kJ mol}^{-1}$ , respectively. The change in enthalpy for the reaction  $3\text{C}_2\text{H}_2(\text{g}) \rightarrow \text{C}_6\text{H}_6(\text{l})$ , is

[JEE Main, June 2022]

(A)  $+324 \text{ kJ mol}^{-1}$

(B)  $+632 \text{ kJ mol}^{-1}$

(C)  $-632 \text{ kJ mol}^{-1}$

(D)  $-732 \text{ kJ mol}^{-1}$

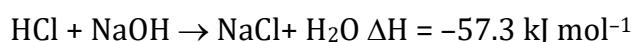
29. 2.4 g coal is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atm pressure.

The temperature of the calorimeter rises from 298 K to 300 K. The enthalpy change during the combustion of coal is  $-x \text{ kJ mol}^{-1}$ . The value of  $x$  is  $\text{_____}$ . (Nearest integer)

(Given : Heat capacity of bomb calorimeter  $20.0 \text{ kJ K}^{-1}$ . Assume coal to be pure carbon)

[JEE Main, July 2022]

30. While performing a thermodynamics experiment, a student made the following observations,



The enthalpy of ionization of  $\text{CH}_3\text{COOH}$  as calculated by the student is  $\text{_____ kJ mol}^{-1}$ .

(Nearest integer)

[JEE Main, July 2022]



31. When 600 mL of 0.2 M HNO<sub>3</sub> is mixed with 400 mL of 0.1M NaOH solution in a flask, the rise in temperature of the flask is \_\_\_\_\_  $\times 10^{-2}$  °C.

(Enthalpy of neutralization = 57 kJ mol<sup>-1</sup> and specific heat of water = 4.2 JK<sup>-1</sup> g<sup>-1</sup>)

(Neglect heat capacity of flask)

[JEE Main, July 2022]





## **EXERCISE # (JEE-ADVANCE)**

- 1.** Estimate the average S-F bond enthalpy in SF<sub>6</sub>. The  $\Delta H_f^\circ$  values of SF<sub>6</sub> (g), S(g), and F (g) are – 1100, 275 and 80 kJ/mol respectively. [JEE 1999]

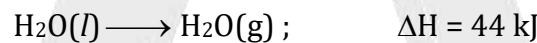
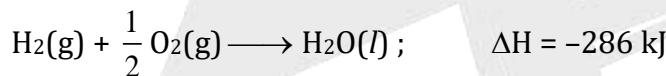
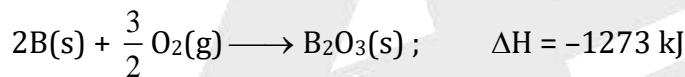
2. Which of the following is not an endothermic reaction? [JEE 1999]

  - (A) Combustion of methane
  - (B) Decomposition of water
  - (C) Dehydrogenation of ethene to acetylene
  - (D) Conversion of graphite to diamond

3. Diborane is a potential rocket fuel which undergoes combustion according to the reaction,  
 $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$

From the following data, calculate the enthalpy change for the combustion of diborane :

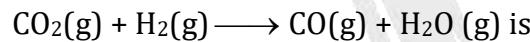
[JEE 2000]



4.  $\Delta H^\circ_f$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-393.5$ ,  $-110.5$  and  $-241.8 \text{ kJ mo}^{-1}$  respectively

The standard enthalpy change (in kJ) for the reaction

[JEE 2000]



- (A) 524.1      (B) 41.2      (C) -262.5      (D) -41.2

5. Which of the following reactions defines  $\Delta H_f^\circ$ ?

- (A)  $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g)$       (B)  $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \rightarrow HF(g)$   
 (C)  $N_2(g) + 3H_2(g) \rightarrow 2NH_3$       (D)  $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$  [JEE 2003]

6. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K<sup>-1</sup>, the numerical value for the enthalpy of combustion of the gas in kJ mol<sup>-1</sup> is

[JEE 2009]



7. Using the data provided, calculate the multiple bond energy ( $\text{kJ mol}^{-1}$ ) of a  $\text{C} \equiv \text{C}$  bond in  $\text{C}_2\text{H}_2$ . That energy is (take the bond energy of a C-H bond as  $350 \text{ kJ mol}^{-1}$ ). [JEE 2012]



- (A) 1165      (B) 837      (C) 865      (D) 815

8. The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O(l)}$  and glucose(s) at  $25^\circ\text{C}$  are  $-400 \text{ kJ/mol}$ ,  $-300 \text{ kJ/mol}$  and  $-1300 \text{ kJ/mol}$ , respectively. The standard enthalpy of combustion per gram of glucose at  $25^\circ\text{C}$  is [JEE (Advance) 2013]

- (A)  $+2900 \text{ kJ}$       (B)  $-2900 \text{ kJ}$       (C)  $-16.11 \text{ kJ}$       (D)  $+16.11 \text{ kJ}$

9. Choose the reaction(s) from the following options, for which the standard enthalpy of reaction is equal to the standard enthalpy of formation. [JEE (Advance) 2019]



10. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place. At  $298 \text{ K}$ :  $\Delta_f H^0(\text{SnO}_2(\text{s})) = -581.0 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^0(\text{CO}_2(\text{g})) = -394.0 \text{ kJ mol}^{-1}$ ,  $S^0(\text{SnO}_2(\text{s})) = 56.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^0(\text{Sn(s)}) = 52.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^0(\text{C(s)}) = 6.0 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^0(\text{CO}_2(\text{g})) = 210.0 \text{ J K}^{-1} \text{ mol}^{-1}$ .

Assume that the enthalpies and the entropies are temperature independent.

[JEE (Advance) 2020]

11. 2 mol of  $\text{Hg(g)}$  is combusted in a fixed volume bomb calorimeter with excess of  $\text{O}_2$  at  $298 \text{ K}$  and  $1 \text{ atm}$  into  $\text{HgO(s)}$ . During the reaction, temperature increases from  $298.0 \text{ K}$  to  $312.8 \text{ K}$ . If heat capacity of the bomb calorimeter and enthalpy of formation of  $\text{Hg(g)}$  are  $20.00 \text{ kJ K}^{-1}$  and  $61.32 \text{ kJ mol}^{-1}$  at  $298 \text{ K}$ , respectively, the calculated standard molar enthalpy of formation of  $\text{HgO(s)}$  at  $298 \text{ K}$  is  $X \text{ kJ mol}^{-1}$ . The value of  $|X|$  is \_\_\_\_\_. [JEE (Advance) 2022]

[Given: Gas constant  $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$  ]



## ANSWER KEY

## EXERCISE O-I

1. (B)    2. (D)    3. (C)    4. (D)    5. (D)    6. (A)  
 7. (B)    8. (D)    9. (D)    10. (D)    11. (A)    12. (C)  
 13. (B)    14. (C)    15. (B)    16. (C)    17. (D)    18. (B)  
 19. (B)    20. (B)    21. (B)    22. (B)    23. (A)    24. (D)  
 25. (D)    26. (A)    27. (B)    28. (A)    29. (C)    30. (B)  
 31. (C)    32. (B)    33. (C)

## EXERCISE S-I

1. (-266 kJ/mol and -825 kJ/mol)  
 2. (- 88 kJ/mol)    3. (129 kJ)    4. (-1560.1 kJ mol<sup>-1</sup>)  
 5. (25.66 days)  
 6. ((i) - 3201 kJ/mol (ii) - 3199.75 kJ/mol)  
 7. ((i) - 885 kJ/mol (ii) - 889.95 kJ/mol)    8. (3.69 mol % CH<sub>4</sub>)  
 9. (132.5 kJ/mol)    10. (400 kJ/mole)  
 11. (- 119 kJ/mol)    12. (+20.6 k Cal)    13. (-266 kJ mol<sup>-1</sup>)  
 14. (213 kJ / mol)    15. (275 kJ/mol)    16. (- 72 kJ mol<sup>-1</sup>)  
 17. (292 kcal/mol)    18. (-392 kJ mol<sup>-1</sup>)    19. (- 90.75 kcal mol<sup>-1</sup>)  
 20. (for Cl<sup>-</sup> -384 kJ mol<sup>-1</sup>, for I<sup>-</sup> -307 kJ mol<sup>-1</sup>)  
 21. (-19 kCal/mole)  
 22. (- 80 kJ/mole)    23. (-255 kJ/mol)    24. (84)  
 25. (-2669)    26. (- 1410 Cal)  
 27. (480 J)    28. (-31.5 kJ/mole)    29. (2 kcal)  
 30. ( $\Delta H = - 41.192 \text{ kJ}$ )    31. (-8070 cal)  
 32. ((i) - 11 kCal/mole; (ii) - 8 kCal/mole, (iii) - 10.067 Cal / K mole, (iv) -11 kCal/mole,  
     (v) + 45.067Cal/ K mole)  
 33. (200 J/K mole)  
 34. (A)

## EXERCISE O-II

1. (A,B,C,D)    2. (A,B,D)    3. (C,D)    4. (A,B,D)    5. (A,B)  
 6. (A,C)    7. (A,B,D)    8. (A)    9. (C)    10. (C)  
 11. (A)    12. A → P, Q ; B → P, R ; C → S, D → R    13. (A)  
 14. (B)



## EXERCISE S-II

1.  $(0.9345 \text{ kCal g}^{-1}, 3.94 \text{ kCal cm}^{-3})$     2.  $(22 \text{ kCal mol}^{-1})$
3.  $(EC \equiv C = 161 \text{ kcal/mol})$     4.  $((\text{a}) 92.435 \text{ g } (\text{b}) 93.715 \text{ g})$
5.  $(E_{B-H-B} = 455 \text{ kJ/mole})$
6.  $(\Delta H(\text{O-H}) = 463.5 \text{ kJ/mol } \Delta U = 461 \text{ kJ/mol})$
7.  $(-25 \text{ kJ/mol})$     8.  $(-669.7 \text{ kJ mol}^{-1})$

## JEE MAIN

1. (B)    2. (C)    3. (C)    4. (A)    5. (D)    6. (A)  
 7. (B)    8. (D)    9. (C)    10. (D)    11. (D)    12. (B)  
 13. (C)    14. (B)    15. (C)    16. (B)    17. (C)    18. (C)  
 19. (A)    20. (D)    21. (B)    22. (189494)    23. (D)  
 24. (A)    25. (A)    26. (128)    27. (718)    28. (C)    29. (200)  
 30. (B)    31. (54)

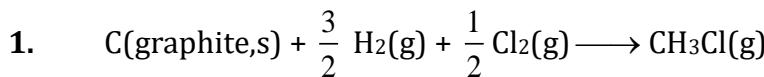
## JEE ADVANCED

1.  $(309.16 \text{ kJ/mol})$     2. (A)    3.  $(-2035 \text{ kJ mol}^{-1})$     4. (B)  
 5. (B)    6. (9)    7. (D)    8. (C)    9. (C,D)  
 10. (935)    11. (90.39)



## SOLUTION

## EXERCISE O-I



2.  $\Delta rH = -944.7 - 4 \times 92.3 + 763.2 + 2 \times 241.8 = -67.1 \text{ kJ}$

3.  $-890.4 = -393.5 - 2 \times 285.9 - \Delta H_f + CH_4(g)$   
 $\Delta H_f CH_4(g) = -74.9 \text{ kJ}$

4.  $-40 = 2\Delta H_f NH_3 - \Delta H_f N_2H_4(g)$   
 $-40 = 2 \Delta H_f NH_3(g) + 120$

$2\Delta H_f NH_3(g) = -160 \Rightarrow \Delta H_f NH_3(g) = -80 \text{ kJ}$

5.  $-2601 = -4 \times 394 - 2 \times 285.8 - 2 \Delta H_f C_2H_2$   
 $2\Delta H_f C_2H_2 = 453.4$   
 $\Delta H_f C_2H_2 = 226.7 \text{ kJ}$

6.  $\Delta H_f HCl(g) = \frac{\Delta H_3}{2}$

$\Delta H_f NH_3(g) = \frac{\Delta H_2}{2}$

$-\Delta H_1 = \Delta H_f NCl_3(g) + 3\Delta H_f HCl(g) - \Delta H_f NH_3(g)$

$-\Delta H_1 = \Delta H_f NI_3(g) + \frac{3}{2} \Delta H_3 - \frac{\Delta H_2}{2}$

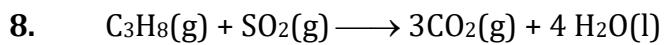
$\Delta H_f NCl_3(g) = \frac{\Delta H_2}{2} - \frac{3}{2} \Delta H_3 - \Delta H_1$

7.  $A \longrightarrow B \quad \Delta H = + 100 \text{ Kcal}$   
 $\Delta H_f B > \Delta H_f A$

$B \longrightarrow C \quad \Delta H = -80 \text{ Kcal}$   
 $\Delta H_f B > \Delta H_f C$

$A \longrightarrow C \quad \Delta H = + 20 \text{ Kcal}$   
 $\Delta H_f C > \Delta H_f A$

$\Rightarrow \Delta H_f B > \Delta H_f C > \Delta H_f A$

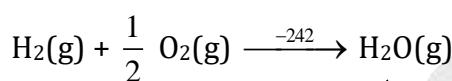
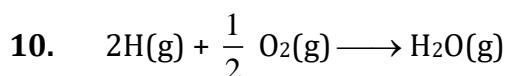


$$-2221.6 = -3 \times 394 - 4 \times 285.8 - \Delta H_f \text{ C}_3\text{H}_8(\text{g})$$

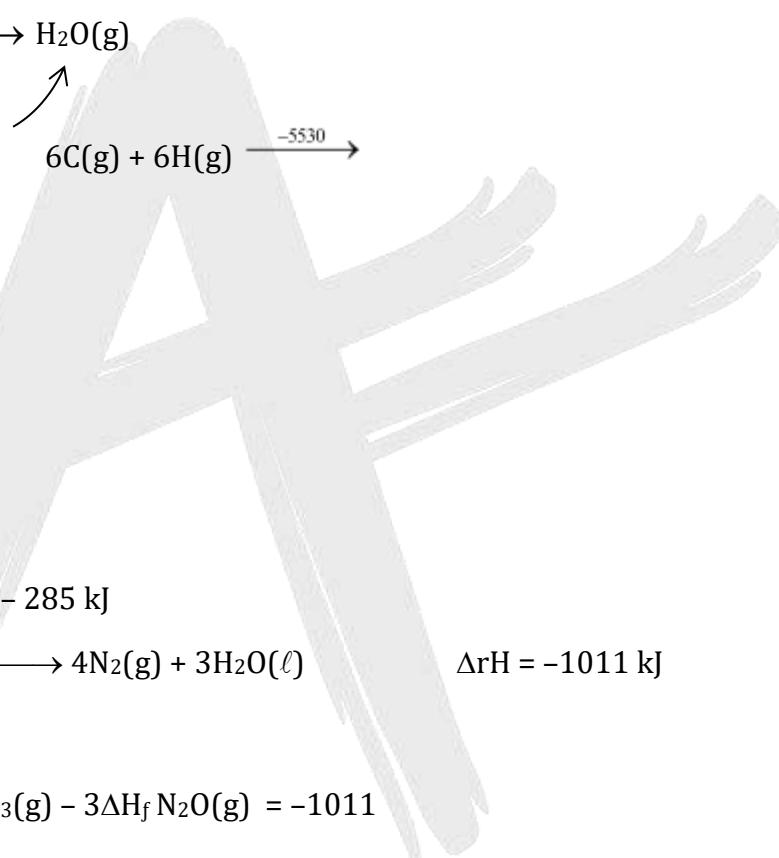
$$\Delta H_f \text{ C}_3\text{H}_8(\text{g}) = 103.6 \text{ kJ}$$

$$\Delta U_f^0 \text{ NO}_2(\text{g}) = -\frac{0.5 \times 2 \times 1000}{1000} = +8 \text{ Kcal mol}^{-1}$$

9.  $\Delta H = -\frac{1939.1}{40} \times 12 = -1939.1 \times 0.3 \text{ kJ} = -581.73 \text{ kJ}$



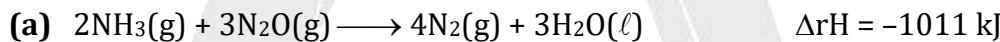
Resonating  
R.H.  
Structure



$$= -242$$

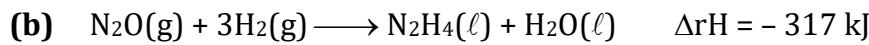
$$\Delta rH_1 = -678 \text{ kJ}$$

$$\frac{\Delta rH_1}{\Delta rH_2} = \frac{678}{242} = 2.8$$



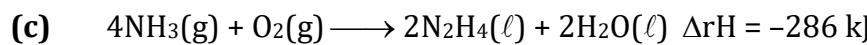
$$3\Delta H_f \text{ H}_2\text{O}(\ell) - 2\Delta H_f \text{ NH}_3(\text{g}) - 3\Delta H_f \text{ N}_2\text{O}(\text{g}) = -1011$$

$$2\Delta H_f \text{ NH}_3(\text{g}) + 3\Delta H_f \text{ N}_2\text{O}(\text{g}) = -3 \times 285 + 1011 = 156 \quad (\text{i})$$



$$\Delta H_f \text{ N}_2\text{H}_4(\ell) - \Delta H_f \text{ N}_2\text{O}(\text{g}) + \Delta H_f \text{ H}_2\text{O}(\ell) = -317 \text{ kJ}$$

$$\Delta H_f \text{ N}_2\text{H}_4(\ell) - \Delta H_f \text{ N}_2\text{O}(\text{g}) = -32 \quad (\text{ii})$$



$$2\Delta H_f \text{ N}_2\text{H}_4(\ell) + 2\Delta H_f \text{ H}_2\text{O}(\ell) - 4\Delta H_f \text{ NH}_3(\text{g}) = -286 \text{ kJ}$$

$$2\Delta H_f \text{ N}_2\text{H}_4(\ell) - 4\Delta H_f \text{ NH}_3(\text{g}) = 284 \quad (\text{iii})$$

from (i), (iii) and (iii)

$$\Delta H_f \text{ N}_2\text{H}_4(\ell) = 50.5 \text{ kJ/mol}$$

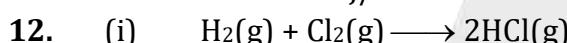
$$\Delta H_f \text{ N}_2\text{O}(\text{g}) = 82.5 \text{ kJ/mol}$$

$$\Delta H_f \text{ NH}_3(\text{g}) = -45.75 \text{ kJ/mol}$$

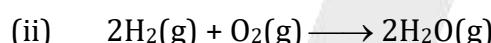
$$\Delta rH = 3\Delta H_f \text{ H}_2\text{O}(\ell) - \Delta H_f \text{ N}_2\text{H}_4(\ell)$$

$$= -3 \times 285 - 50.5$$

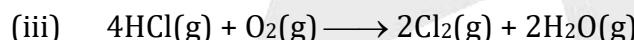
$$= -620.5 \text{ kJ/mol}$$



$$\Delta rH_{300\text{K}} = -184.5$$



$$\Delta rH_{300\text{K}} = -483 \text{ kJ/mol}$$



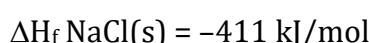
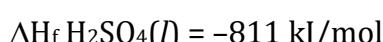
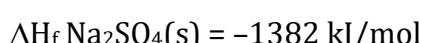
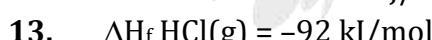
$$(\text{iii}) = (\text{ii}) - 2 \times (\text{i})$$

$$\Delta rH_3 = \Delta rH_2 - 2 \times \Delta rH_1 = -483 + 2 \times 184.5 = -114 \text{ kJ/mol}$$

$$\Delta H = \Delta U + \Delta n g RT$$

$$-114 = \Delta U + \frac{-1 \times 8.3 \times 300}{1000}$$

$$\Delta U = -111.5 \text{ kJ/mol}$$



$$\Delta rH = -2 \times 92 - 1382 + 811 + 2 \times 411 = 67 \text{ kJ/mol}$$

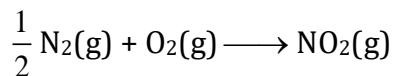
$$\Delta H = \Delta U + \Delta n g RT$$

$$67 = \Delta U + \frac{2 \times 8.3 \times 300}{1000} \Rightarrow \Delta U = 62.02 \text{ kJ/mol}$$

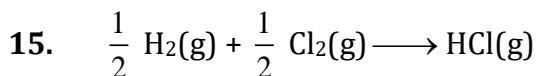


14.  $-16 = 2 - 2 \Delta U_f^0 \text{ NO}_2(\text{g})$

$$\Delta U_f^0 \text{ NO}_2(\text{g}) = 9 \text{ Kcal mol}^{-1}$$



$$\Delta n_g = -0.5$$

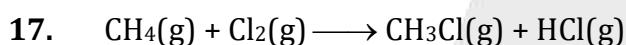


$$\Delta rH = \frac{1}{2} \times 104 + \frac{1}{2} \times 58 - 103 = -22.0 \text{ Kcal}$$



$$\Delta rH = 3 \epsilon_{\text{Cl-F}} = 513 \text{ kJ}$$

$$\epsilon_{\text{Cl-F}} = 171 \text{ kJ}$$



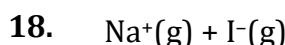
$$\Delta rH = 4 \times \epsilon_{\text{C-H}} + \epsilon_{\text{Cl-Cl}} - 3 \times \epsilon_{\text{C-H}} - 3 \times \epsilon_{\text{C-H}} - \epsilon_{\text{C-Cl}} - \epsilon_{\text{H-Cl}}$$

$$-25 = x + y - 84 - 103$$

$$x + y = 162 \text{ and } \frac{x}{y} = \frac{9}{5}$$

$$2.8y = 162 \quad x = 1.8y$$

$$\epsilon_{\text{Cl-Cl}} = y = 57.75$$



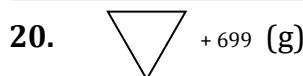
$$\Delta rH_2 = x_1 + \frac{x_2}{2} - 2x_3$$

$$\Delta rH_1 = x_1 + \frac{x_2}{2} - 2x_3 - x_4$$



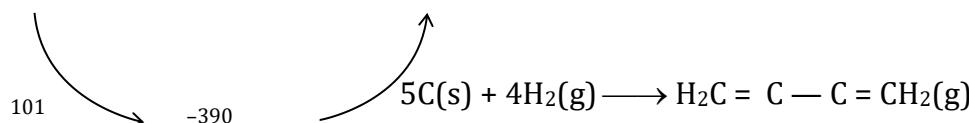
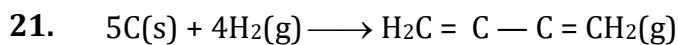
$$2\epsilon_{\text{O-H}} = 498 + 428$$

$$\epsilon_{\text{O-H}} = 463 \text{ kJ/mol}$$



$$\Delta rH = 3 \in_{C-C} - \in_{C-C} - \in_{C=C}$$

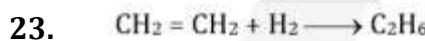
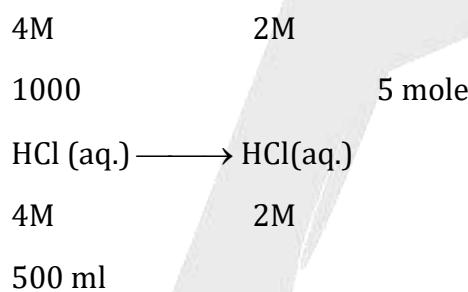
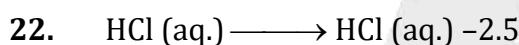
$$= 2 \in_{C-C} - \in_{C=C} = 2 \times 348 - 615 = + 81 \text{ kJ/mol}$$



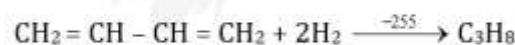
$$2 = 772 + \Delta H_{hyd} \text{ Na}^+(\text{g}) + \Delta H_{hyd} \text{ Cl}^-(\text{g})$$

$$-770 = \Delta H_{hyd} \text{ Cl}^-(\text{g}) + \frac{3}{2.5} \Delta H_{hyd} \text{ Cl}^-(\text{g})$$

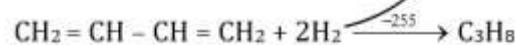
$$\Delta H_{hyd} \text{ Cl}^-(\text{g}) = \frac{-770 \times 2.5}{5.5} = -350 \text{ kJ/mol}$$



$$\Delta rH = -132 \text{ kJ/mol}$$



$$\Delta rH = -132 \text{ kJ/mol}$$



R.H.

-RE

1.3 Butadiene

R.S

$$\Delta rH = -140 - 115 = -255$$

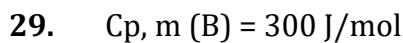


$$-255 = -RE - 264 \Rightarrow RE = 255 - 264 = -9 \text{ kJ}$$



$$-57.3 = -285.8 - \Delta H_f^\circ \text{ OH}^-(\text{aq})$$

$$\Delta H_f^\circ \text{ OH}^-(\text{aq}) = -285.8 + 57.3 = -228.5 \text{ kJ/mol}$$



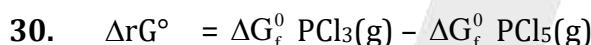
$$C_p, m(C) = 200 \text{ J/mol}$$

$$C_p, m(A) = 150 \text{ J/mol}$$

$$(\Delta C_p)_r = 3 \times 200 - 150 - 2 \times 300 = -150 \text{ J/mol}$$

$$\Delta rH_{310K} + 10 = -\frac{150 \times 10}{1000}$$

$$\Delta rH_{310K} = -10 - 1.5 = -11.5 \text{ kJ/mol}$$



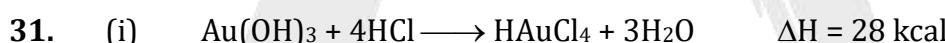
$$= -60 + 74 = +14 \text{ Kcal/mol}$$

$$\Delta rG^\circ = -RT \ln k$$

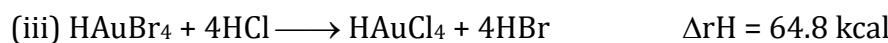
$$14 = -\frac{2 \times 1000}{1000} \ln k$$

$$-7 = \ln k$$

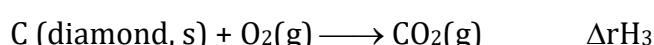
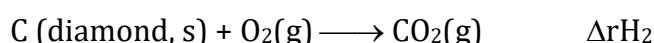
$$-10 \ln 2 = \ln k \Rightarrow k = 2^{-10}$$



$$(i) - (ii) = (iii)$$



$$\% \text{ conversion of } \text{HAuBr}_4 = \frac{0.44}{64.8} \times 100 = 0.6 \%$$

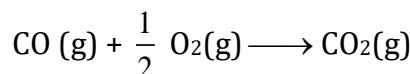






## EXERCISE S-I

1. From reaction (D)



$$\Delta H = -282 \text{ kJ}$$

$$-282 = \Delta H_f \text{CO}_2(\text{g}) - \Delta H_f \text{CO(g)}$$

From reaction (C)

$$\Delta H_f \text{CO}_2(\text{g}) = -393 \text{ kJ}$$

$$-282 = -393 - \Delta H_f \text{CO(g)}$$

$$\Delta H_f \text{CO(g)} = -393 + 282 = -111 \text{ kJ/mol}$$

From reaction (B)

$$155 = \Delta H_f \text{CO(g)} - \Delta H_f \text{FeO(s)}$$

$$\Delta H_f \text{FeO(s)} = -111 - 155 = -266 \text{ kJ/mol}$$

$$492 = -3 \times 111 - \Delta H_f \text{Fe}_2\text{O}_3(\text{s})$$

$$\Delta H_f \text{Fe}_2\text{O}_3(\text{s}) = -333 - 492 = -825 \text{ kJ}$$

2.  $\text{C}_2\text{H}_6(\text{g}) + 3.5 \text{O}_2(\text{g}) \longrightarrow 2 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O(l)}$

$$\Delta H = -\frac{3120}{2} = -1560 \text{ kJ}$$

$$-1560 = -2 \times 395 - 3 \times 286 - \Delta H_f \text{C}_2\text{H}_6(\text{g})$$

$$\Delta H_f \text{C}_2\text{H}_6(\text{g}) = -2 \times 395 - 3 \times 395 - 3 \times 286 + 1560$$

$$\Delta H_f \text{C}_2\text{H}_6(\text{g}) = -88 \text{ kJ}$$

3.  $\text{CS}_2(\text{l}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2 \text{SO}_2(\text{g})$

$$\Delta H_c \text{C(graphite, s)} = \Delta H_f \text{CO}_2(\text{g})$$

$$\Delta H_c \text{S(rhombic, s)} = \Delta H_f \text{SO}_2(\text{g})$$

$$-1108 = \Delta H_f \text{CO}_2(\text{g}) + 2 \Delta H_f \text{SO}_2(\text{g}) - \Delta H_f \text{CS}_2(\text{l})$$

$$-1108 = -393 - 2 \times 293 - \Delta H_f \text{CS}_2(\text{l})$$

$$\Delta H_f \text{CS}_2(\text{l}) = -393 - 2 \times 293 + 1108 = 129 \text{ kJ mol}^{-1}$$

4.  $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$

$$-55.7 = \Delta H_c \text{C}_3\text{H}_8(\text{g}) + \Delta H_c \text{H}_2(\text{g}) - \Delta H_c \text{C}_2\text{H}_6(\text{g}) + \Delta H_c \text{H}_2(\text{g})$$

$$-55.7 = -2220 + 285.5 - \Delta H_c \text{C}_2\text{H}_6 + 890$$

$$\Delta H_c \text{C}_2\text{H}_6 = -2220 + 285.5 + 890 + 55.7 = -1560.1 \text{ kJ/mol}$$



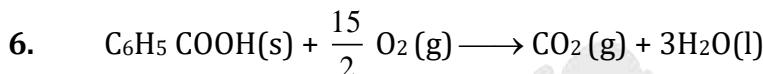
5.  $q = +2658 \text{ kJ/mol}$

$$\text{moles of butane} = \frac{11.2 \times 10^3}{58}$$

$$\text{total heat released} = \frac{11.2 \times 10^3}{58} \times 2658 \text{ kJ}$$

$$20,000 \times n = \frac{11.2 \times 10^3}{58} \times 2658$$

$$n = \frac{11.2 \times 2658}{20 \times 58} = 25.66$$



$$\Delta rH = 7\Delta H_f \text{CO}_2(g) + 3\Delta H_f \text{H}_2\text{O}(l) - \Delta H_f \text{C}_6\text{H}_5\text{COOH}(s)$$

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

$$q_p = \Delta H = -3201 \text{ kJ/mol}$$

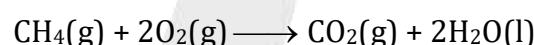
$$q_v = \Delta U$$

$$\Delta H = \Delta U + \Delta n gRT - 3201 = \Delta U - \frac{0.5 \times 8.314 \times 300}{1000}$$

$$\Delta U = -3201 + \frac{0.5 \times 8.314 \times 300}{1000} = -3199.75 \text{ kJ/mol}$$

7.  $q = 0.5 \times 17.7 \text{ kJ}$

$$\Delta H = \frac{-0.5 \times 17.7}{0.16} \times 16 = -885 \text{ kJ mol}^{-1}$$



$$\Delta H = -885 - \frac{2 \times 8.314 \times 300}{1000} = -889.95 \text{ kJ/mol}$$

8.  $q = 1200 \times 0.25 = 300 \text{ cal}$

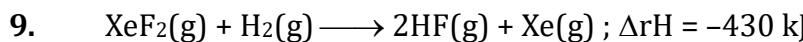
$$q = 200 \text{ Kcal mol}^{-1}$$

$$n_{\text{CH}_4} = \frac{300}{200 \times 10^3} = 1.5 \times 10^{-3}$$

$$n_T = 1 \times 1 = 0.0406$$

$$0.0821 \times 300 = 0.406 \times 10^{-3}$$

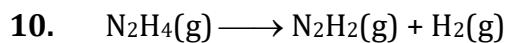
$$\text{mole \% of CH}_4 = \frac{1.5 \times 10^{-3}}{0.406 \times 10^{-3}} \times 100 = \frac{15}{4.06} = 3.69 \%$$



$$\Delta rH = 2 \times \epsilon_{\text{Xe-F}} + \epsilon_{\text{H-H}} - (2 \times \epsilon_{\text{H-F}})$$

$$-430 = 2 \times \epsilon_{\text{Xe-F}} + 435 - 2 \times 265$$

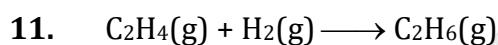
$$\epsilon_{\text{Xe-F}} = +132.5 \text{ kJ/mol}$$



$$\Delta rH = 4 \epsilon_{\text{N-H}} + \epsilon_{\text{N-N}} - \epsilon_{\text{N=N}} - 2 \times \epsilon_{\text{N-H}} - \epsilon_{\text{H-H}}$$

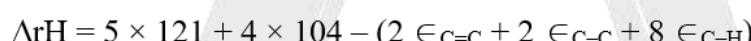
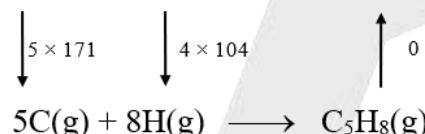
$$109 = 2 \times 391 + 163 - \epsilon_{\text{N=N}} - 436$$

$$\epsilon_{\text{N=N}} = 2 \times 391 + 163 - 436 - 109 = +400 \text{ kJ/mol}$$

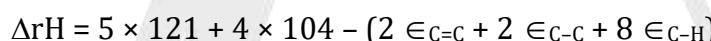
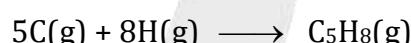


$$\Delta rH = 4 \times \epsilon_{\text{C-H}} + \epsilon_{\text{C=C}} + \epsilon_{\text{H-H}} - [\epsilon_{\text{C-C}} + 6 \epsilon_{\text{C-H}}]$$

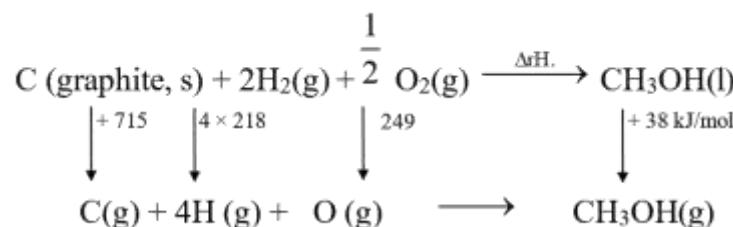
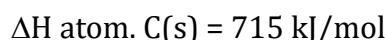
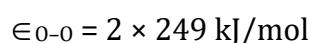
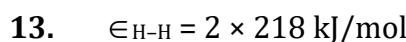
$$= 606 + 431 - 336 - 2 \times 410 = -119 \text{ kJ/mol}$$



$$= 5 \times 171 + 4 \times 104 - (2 \times 147 + 2 \times 83 + 8 \times 98.8) = 20.6 \text{ Kcal}$$



$$= 5 \times 171 + 4 \times 104 - (2 \times 147 + 2 \times 83 + 8 \times 98.8) = 20.6 \text{ Kcal}$$

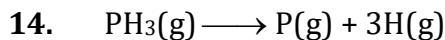


$$\Delta rH_1 + 38 = 715 + 4 \times 218 + 249 - (3 \times \epsilon_{\text{C-H}} + \epsilon_{\text{C-O}} + \epsilon_{\text{O-H}})$$



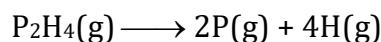
$$\Delta rH_1 + 38 = 715 + 4 \times 218 + 249 - (3 \times 415 + 356 + 463)$$

$$\Delta rH_1 = -266 \text{ kJ/mol}$$



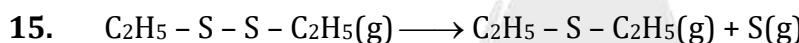
$$\Delta H \text{ atom. } \text{PH}_3(\text{g}) = 3 \in_{\text{P-H}} = 95.4$$

$$\in_{\text{P-H}} = \frac{954}{3} = 318 \text{ kJ/mol}$$



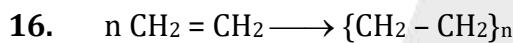
$$\Delta H \text{ atom. } \text{P}_2\text{H}_4(\text{g}) = \in_{\text{P-P}} + 4 \in_{\text{P-H}} = 1485$$

$$\in_{\text{P-P}} = 1485 - 4 \times 318 = +213 \text{ kJ mol}^{-1}$$

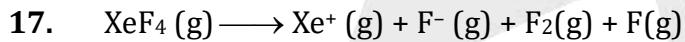


$$\Delta rH = -150 + 225 + 200 = +275 \text{ kJ/mol}$$

$$\Delta rH = \in_{\text{S-S}} = +275 \text{ kJ/mol}$$

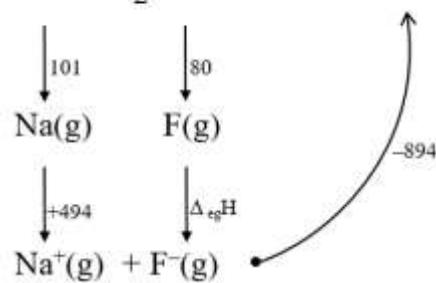
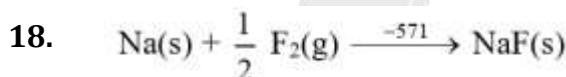


$$\Delta rH = \in_{\text{C=C}} - 2 \in_{\text{C-C}} = 590 - 2 \times 331 = -72 \text{ kJ/mol}$$



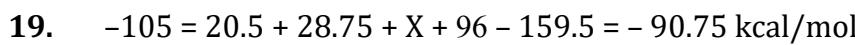
$$\Delta rH = 4 \times \in_{\text{Xe-F}} + \text{I.E. Xe(g)} - \Delta egH \text{ F(g)} - \in_{\text{F-F}}$$

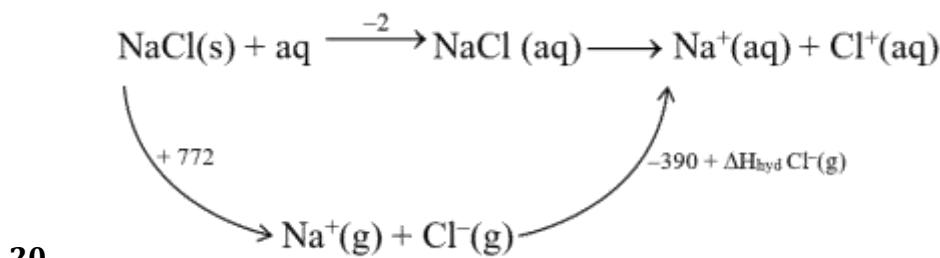
$$= 4 \times 34 + 279 - 85 - 38 = +292 \text{ Kcal / mol}$$



$$-571 = 101 + 494 + 80 + \Delta_{egH} \text{ F(g)} - 894$$

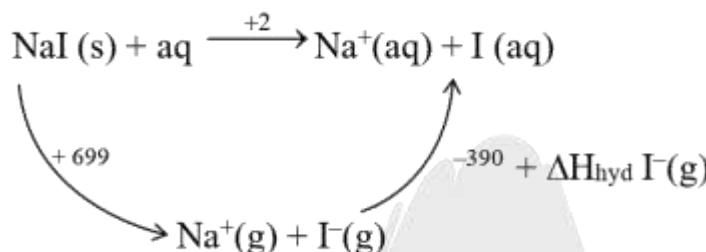
$$\Delta_{egH} \text{ F(g)} = -392 \text{ kJ/mol}$$





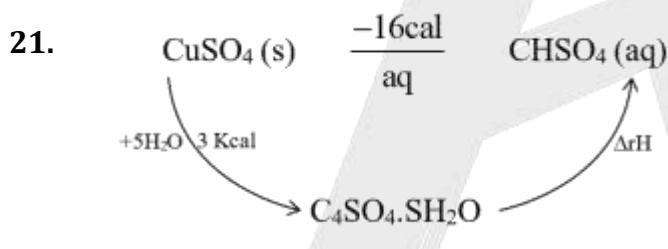
$$-2 = +772 - 390 + \Delta H_{\text{hyd}} \text{ Cl}^-(\text{g})$$

$$\Delta H_{\text{hyd}} \text{ Cl}^-(g) = -2 + 390 - 172 = -384 \text{ kJ/mol}$$



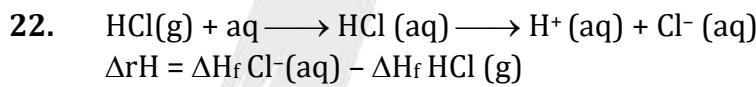
$$+2 = 699 - 390 + \Delta H_{\text{hyd}} I^-(g)$$

$$\Delta H_{\text{hyd}} \text{ I}^-(g) = -307 \text{ kJ/mol}$$

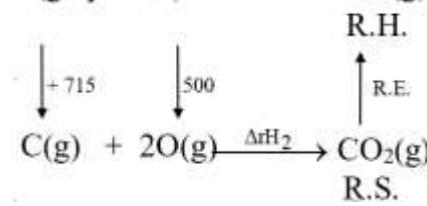


$$-16 = 3 + \Delta rH$$

$$\Delta rH = -19 \text{ Kcal}$$



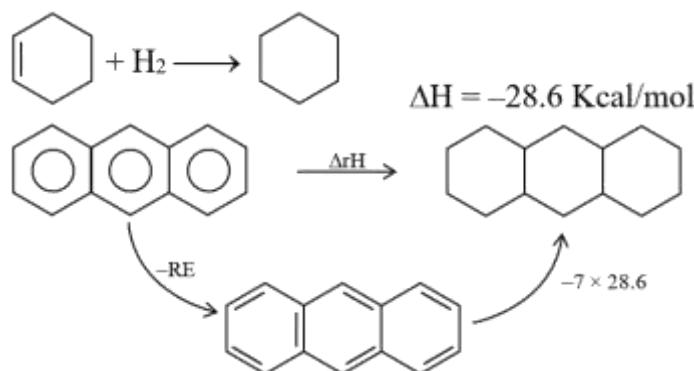
$$= -170 + 90 = -80 \text{ kJ/mol}$$



$$-390 = 715 + 500 - 2 \times 875 + RE$$

$$RE = -390 + 2 \times 675 - 715 - 500 = -255 \text{ kJ/mol}$$

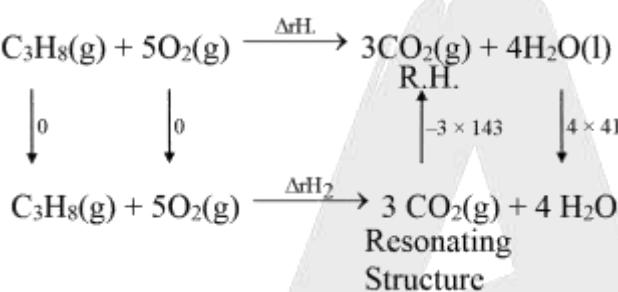
24.



$$-116.2 = -RE - 7 \times 28.6$$

$$RE = -7 \times 28.6 + 116.2 = -84 \text{ Kcal mol}^{-1}$$

25.



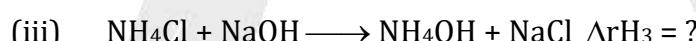
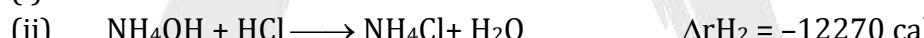
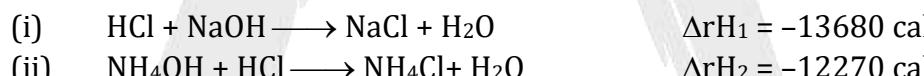
$$\Delta rH_1 + 4 \times 41 = \Delta rH_2 - 3 \times 143$$

$$\Delta rH_2 = 2 \in_{C-C} + 8 \in_{C-H} + 5 \in_{O=O} - 3 \times 2 \times \in_{C=O} - 4 \times 2 \times \in_{O-H}$$

$$\Delta rH_2 = 2 \times 345 + 8 \times 410 + 5 \times 498 - 6 \times 804 - 8 \times 464 = -2076$$

$$\Delta rH_1 + 4 \times 41 = -2076 - 3 \times 143 = -2669 \text{ kJ/mol}$$

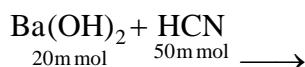
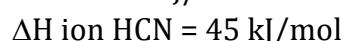
26.



$$(iii) = (ii) - (i)$$

$$\Delta rH_3 = \Delta rH_2 - \Delta rH_1 = -12270 + 13680 = +1410 \text{ cal}$$

27.



$$\text{m mol of } H^+ = 50; \text{ m mol } OH^- = 40$$

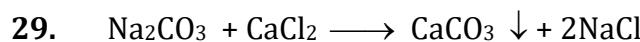


$$\Delta H_{\text{neut}} = -57 \times 0.04 + 45 \times 0.04 = -12 \times 0.04 \text{ kJ} = -480 \text{ J}$$

28.  $q = \frac{500 \times 2.1 \times 1.2}{1000} \text{ kJ}$  (for 80 m mole)

$$q = \frac{500 \times 2.1 \times 1.2}{1000 \times 0.08} \text{ (for 1 mole)}$$

$$= + 31.5 \text{ kJ mol}^{-1}$$



$$\Delta rH = \Delta H_f^\circ \text{ CaCO}_3 - \Delta H_f^\circ \text{ Ca}^{2+} - \Delta H_f^\circ \text{ CO}_3^{2-}$$

$$= -288 + 129 + 161 = + 2 \text{ kcal/mol}$$

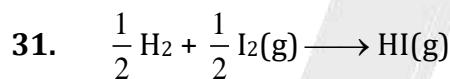
30.  $\Delta H_{500K} - \Delta H_{298K} = (\Delta C_p)r (500 - 298)$

$$(\Delta C_p)_r = 37 + 29 - 33 - 29 = 4 \text{ J/mol K}$$

$$\Delta rH = -393 + 241 + 110 = 351 - 393 = -42 \text{ kJ/mol}$$

$$\Delta H_{500K} - (-42) = \frac{4 \times 302}{1000}$$

$$\Delta H_{500K} = -42 + \frac{4 \times 202}{1000} = -41.192 \text{ kJ/mol}$$



$$(\Delta C_p)r = -2 \times 10^{-3}T$$

$$\Delta rH \text{ } 400K - \Delta rH \text{ } 300K = \int_{300}^{400} CpdT$$

$$\Delta rH \text{ } 400K - (-8000) = -2 \times 10^{-3} \int_{300}^{400} TdT$$

$$\Delta rH \text{ } 400K = -8000 - 70 = -8070 \text{ cal}$$

32. (i)  $\Delta rH^\circ = \Delta H_f^\circ \text{ CO}_2(g) - \Delta H_f^\circ \text{ H}_2\text{O}(g) - \Delta H_f^\circ \text{ CO}(g)$   
 $= -94 + 57 + 26 = -11 \text{ Kcal mol}^{-1}$

(ii)  $\Delta rG^\circ \text{ } 298K = -94 + 32 + 54 = -8 \text{ Kcal/mol}$

(iii)  $\Delta rS^\circ \text{ } 298K$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$-8 = -11 - 298 \times \Delta S^\circ$$

$$298 \times \Delta S^\circ = -3$$



$$\Delta S^\circ = -\frac{3}{298} \times 1000 = -10.067 \text{ Cal K}^{-1} \text{ mol}^{-1}$$

$$-10.067 = 31 + S^\circ_{\text{H}_2\text{O}} - 47.51$$

$$S^\circ_{\text{H}_2\text{O}} = 56.933 \text{ Cal K}^{-1} \text{ mol}^{-1}$$

(iv)  $\Delta H = \Delta U + \Delta n g RT$

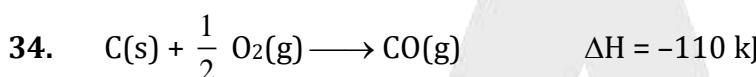
$$\Delta U = -11 \text{ Kcal/mol}$$

33.  $\Delta rH^\circ = -75 - 392 + 484 = +17 \text{ kJ/mol}$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

for a process to be spontaneous

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} = \frac{17 \times 1000}{85} = 200 \text{ J mol}^{-1} \text{ K}^{-1}$$

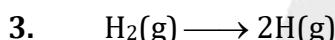


To keep the temp of reaction constant

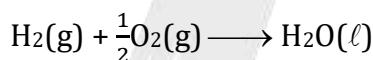
$$220x = 130y$$

$$x/y = 0.6$$

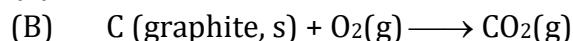
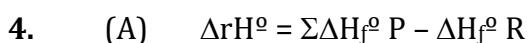
### EXERCISE O-II



$$\Delta rH = \Delta H_{\text{atom.}} H_2(g) = 2 \Delta H_f^o H(g) = E_{H-H}$$

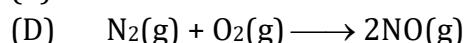


$$\Delta rH = \Delta H_f^o N_2O(l) = \Delta H_c^o H_2(g)$$



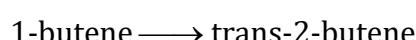
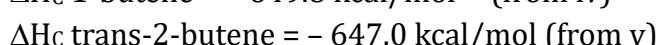
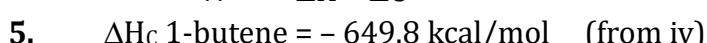
$$\Delta rH^\circ = \Delta H_f^\circ CO_2(g) = \Delta H_c^\circ C(\text{graphite, } s)$$

(C)  $\Delta G = \Delta H - T\Delta S$

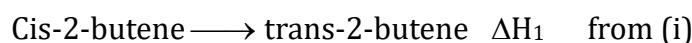


$$\therefore \Delta n g = 0$$

$$\therefore \Delta H = \Delta U$$



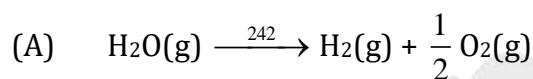
$$\Delta rH = -2.8 \text{ kcal/mol}$$



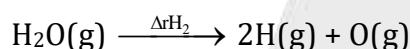
$$\Delta H_1 = -1.0 \text{ kcal/mol}$$

$$\Delta H_2 = 1.8 \text{ kcal/mol}$$

6.  $\epsilon_{H-H} = 436 \text{ kJ/mol}$  and  $\epsilon_{O=O} = 495 \text{ kJ/mol}$



$$\downarrow 0 \quad \downarrow 436 \quad \downarrow 495/2$$

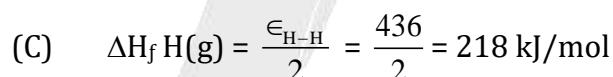


$$\Delta rH_2 = 242 + 436 + \frac{495}{2}$$

$$2 \epsilon_{O-H} = 925.5 \text{ kJ/mol}$$



$$\Delta rH = \epsilon_{O-H} = 462.75 \text{ kJ/mol}$$



8.  $H_2S(g) \longrightarrow H(g) + HS(g)$

$$\Delta rH = \Delta H_f HS(g) + \Delta H_f H(g) - \Delta H_f H_2S(g)$$

$$376 = \Delta H_f HS(g) + 218 + 20$$

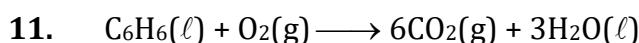
$$\Delta H_f HS(g) = 138 \text{ kJ/mol}$$

9.  $HS(g) \longrightarrow H(g) + S(g)$

$$\Delta rH = \epsilon_{S-H} = 218 + 277 - 138 = 357 \text{ kJ/mol}$$

10. C (graphite, s) +  $O_2(g) \longrightarrow CO_2(g)$

$$\Delta rH = \frac{-591}{18} \times 12 = -394 \text{ kJ}$$



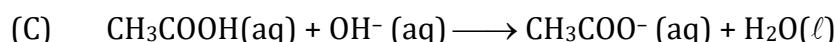
$$\Delta rH = - 6 \times 394 - 3 \times 286 - 50 = - 3272 \text{ kJ}$$



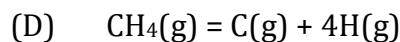
$$\Delta rH^\ominus = \Delta H_f^\ominus \text{CO}_2(\text{g}) = \Delta H_c^\ominus \text{C} (\text{graphite, s})$$



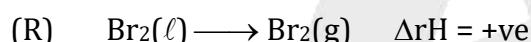
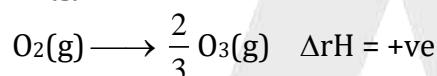
$$\Delta rH^\ominus = \Delta H^\ominus \text{ atom.} = \Delta H^\ominus \text{ sub.}$$



$$\Delta rH^\ominus = \Delta H^\ominus \text{ neat.}$$



$$\Delta rH^\ominus = \Delta H^\ominus \text{ atom.} \text{CH}_4(\text{g}) = 4 \in_{\text{C-H}}$$



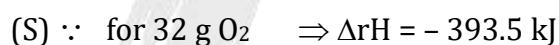
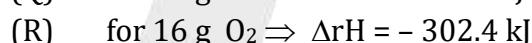
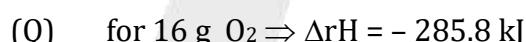
$$\Delta fS^\ominus = + \text{ve}$$



$$\Delta fS^\ominus = - \text{ve}$$



$$\text{for } 16 \text{ g O}_2 \Rightarrow \Delta H = - \frac{-285.8}{5 \times 32} \times 16 = - 260.1 \text{ kJ}$$



$$\therefore \text{for } 16 \text{ g O}_2 \Rightarrow \Delta rH = \frac{-393.5}{2} = - 196.75 \text{ kJ}$$



## EXERCISE S-II



$$\Delta rH^\circ = \Delta H_f^\circ \text{Al}_2\text{O}_3 - \Delta H_f^\circ \text{Fe}_2\text{O}_3 = -399 + 199 = -200 \text{ kcal/mol}$$

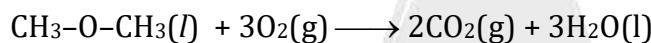
if  $\text{Fe}_2\text{O}_3$  and Al are taken in stoichiometric ratio then 1 mol of  $\text{Fe}_2\text{O}_3$  react with 2 moles of Al

$\therefore$  160 g of  $\text{Fe}_2\text{O}_3$  + 54 g  $\text{Al}_2\text{O}_3$  react to produce = 200 kcal heat

$$\therefore \text{heat produced per gram} = \frac{200}{204} = 0.9345 \text{ Kcal g}^{-1}$$

$$\text{Total vol.} = \frac{160}{5.2} + \frac{54}{2.7} = 50.77 \text{ mL}$$

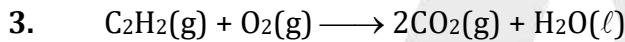
$$\text{Heat produced per mL} = \frac{200}{50.77} = 3.94 \text{ Kcal mL}^{-1}$$



$$-348 = 2\Delta H_f \text{CO}_2(g) + 3\Delta H_f \text{H}_2\text{O}(l) - \Delta H_f \text{CH}_3-\text{O}-\text{CH}_3$$

$$\Delta H_f \text{CH}_3-\text{O}-\text{CH}_3 = -2 \times 94 - 3 \times 68 + 348 = -44 \text{ Kcal mol}^{-1}$$

$$\Delta rH = -44 + 66 = 22 \text{ kcal mol}^{-1}$$



$$-312 = 2\Delta H_f \text{CO}_2(g) + \Delta H_f \text{H}_2\text{O}(l) - \Delta H_f \text{C}_2\text{H}_2(g)$$

$$\Delta H_f \text{C}_2\text{H}_2(g) = -2 \times 94 - 68 + 312 = 56 \text{ kcal}$$



$$\downarrow 2 \times 150 \quad \downarrow 103 \quad \uparrow 0$$



$$56 = 2 \times 150 + 103 - 2 \times 93 - \epsilon_{\text{C=C}}$$

$$\epsilon_{\text{C=C}} = 161 \text{ kJ/mol}$$



$$\Delta rH^\circ = -\Delta H_f^0 \text{HgO(s)} = +90.8$$

$$q_p = +90.8 \text{ kJ/mol}^{-1}$$

$$\Delta rH^\circ = \Delta rU^\circ + \Delta n g RT$$

$$90.8 = \Delta U + \frac{0.5 \times 8.314 \times 298}{1000}$$

$$q_v = \Delta rU^\circ = +89.56 \text{ kJ/mol}$$

at const p

$$\text{Moles of HgO(s) reacted} = \frac{41.84}{90.8} = 0.46$$

$$\text{Moles of Hg(l) formed} = 0.46$$

$$\text{mass of Hg(l) formed} = 0.46 \times 200.6 = 92.435 \text{ g}$$

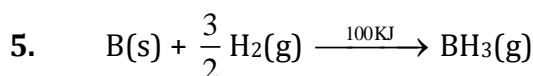


at const. vol.

$$\text{Moles of HgO(s) reacted} = \frac{41.84}{89.56}$$

$$\text{Moles of Hg(l) formed} = \frac{41.84}{89.56}$$

$$\text{Mass of Hg(l) formed} = \frac{41.84}{89.56} \times 200.6 = 93.715\text{g}$$



$$\downarrow 565 \quad \downarrow 1.5 \times 436 \quad \uparrow 0$$

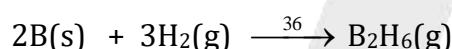


$$\Delta rH^\ominus = \Delta H_f^\ominus \text{ BH}_3(\text{g}) = 100 \text{ kJ}$$

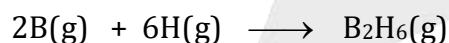
$$100 = 565 + 1.5 \times 436 - 3 \times \epsilon_{\text{B-H}}$$

$$3 \times \epsilon_{\text{B-H}} = 565 + 1.5 \times 436 - 100$$

$$\epsilon_{\text{B-H}} = 373 \text{ kJ/mol}$$



$$\downarrow 2 \times 565 \quad \downarrow 3 \times 436 \quad \uparrow 0$$

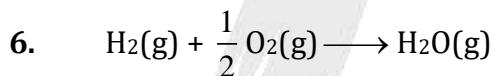


$$\Delta rH^\ominus = \Delta H_f^\ominus \text{ B}_2\text{H}_6(\text{g}) = 36 \text{ kJ/mol}$$

$$36 = 2 \times 565 + 3 \times 436 - 4 \times 373 - 2 \epsilon_{\text{B-H-B}}$$

$$2 \epsilon_{\text{B-H-B}} = 910 \text{ kJ}$$

$$\epsilon_{\text{B-H-B}} = 455 \text{ kJ/mol}$$



$$\Delta rH = \Delta H_f^\ominus \text{ H}_2\text{O}(\text{g}) = -241.8$$

$$-241.8 = 2 \times 218 + 249.2 - 2 \epsilon_{\text{O-H}}$$

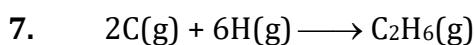
$$\epsilon_{\text{O-H}} = 463.5 \text{ kJ/mol}$$

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

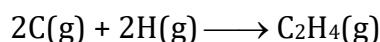
$$2 \times 463.5 = \Delta U + \frac{2 \times 8.314 \times 298}{1000}$$

$$\Delta U = 922 \text{ (for 2 O-H bond)}$$

$$= \frac{922}{2} \text{ (for 1 O-H bond)} = 461 \text{ kJ/mol}$$



$$2840 = \epsilon_{\text{C-C}} + 6 \epsilon_{\text{C-H}}$$

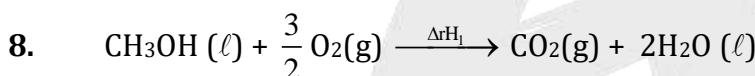
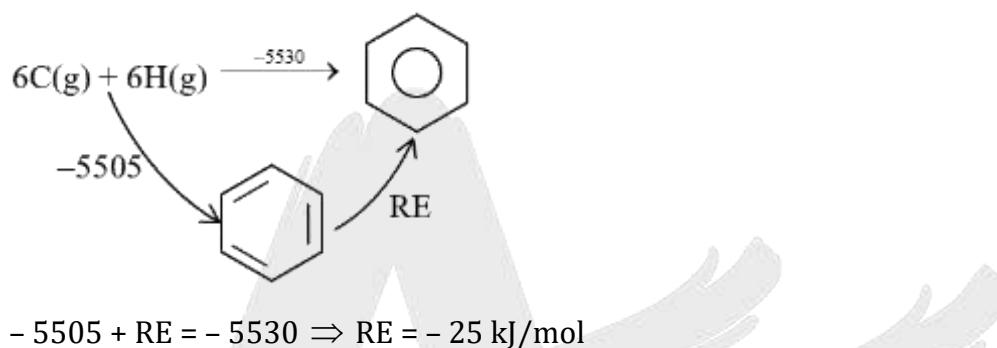


$$2275 = \epsilon_{\text{C=C}} + 4 \epsilon_{\text{C-H}}$$

if  $\epsilon_{\text{C-H}} = 410 \text{ kJ/mol}$

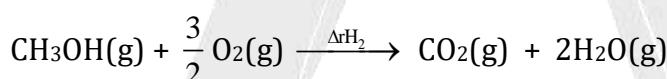
then  $\epsilon_{\text{C-C}} = 380 \text{ kJ/mol}$

$$\epsilon_{\text{C=C}} = 635 \text{ kJ/mol}$$



R.H.

$$\downarrow 35.5 \quad \downarrow 0 \quad \uparrow -143 \quad \downarrow 2 \times 40.6$$



$$\Delta rH_1 + 2 \times 40.6 = \Delta rH_2 + 35.5 - 143$$

$$\Delta rH_2 = 3 \epsilon_{\text{C-H}} + \epsilon_{\text{C-O}} + \epsilon_{\text{O-H}} + \frac{3}{2} \epsilon_{\text{O=O}} - 2 \epsilon_{\text{C=O}} - 4 \epsilon_{\text{O-H}}$$

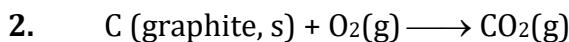
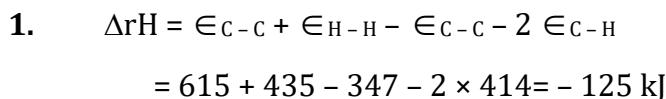
$$= 3 \times 414 + 351.5 + \frac{3}{2} \times 494 - 2 \times 7.11 - 3 \times 464.5 = -481$$

$$\Delta rH_1 + 2 \times 40.6 = -481 + 35.5 - 143$$

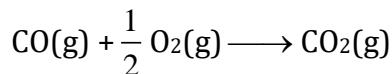
$$\Delta rH_1 = -669.7 \text{ kJ/mol}$$



## EXERCISE JEE-MAIN



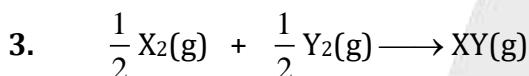
$$\Delta rH = - 393.5$$



$$\Delta rH = - 283 \text{ kJ}$$

$$- 283 = - 393.5 - \Delta H_f CO(g)$$

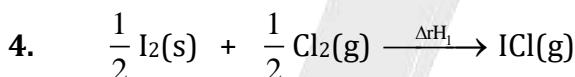
$$\Delta H_f CO(g) = - 110.5 \text{ kJ}$$



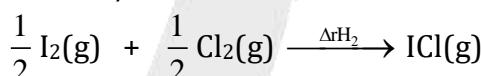
$$\Delta rH = \frac{1}{2} \in_{X-X} + \frac{1}{2} \in_{Y-Y} - \in_{X-Y}$$

$$- 200 = \frac{1}{2} \times a + \frac{1}{2} \times 0.5a - a$$

$$A = \in_{X-X} = 800$$



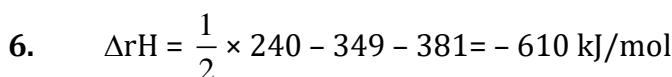
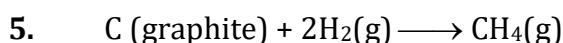
$$\downarrow 62.76/2 \quad \downarrow 0 \quad \downarrow 0$$



$$\Delta rH_2 + \frac{62.76}{2} = \Delta rH_1$$

$$\Delta rH_2 = \frac{1}{2} \times 151 + \frac{1}{2} \times 242.3 - 211.3 = 196.65 - 211.3 = - 14.65$$

$$\Delta rH_1 = - 14.65 + \frac{62.76}{2} = 16.73 \text{ kJ/mol}$$





7.  $\Delta rG^\ominus = -394.4 - 2 \times 237.2 + 166.2$   
 $= -702.6 \text{ kJ/mol}$

$= W_{\text{non}} - PV$

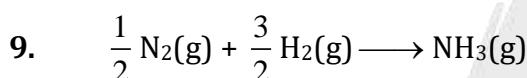
$\Delta H = -726 \text{ kJ/mol} = q$

$$\eta = \frac{465.4}{726} \times 100 \approx 97\%$$

8.  $57.32 = \Delta H_f \text{ OH}^- (\text{aq}) - \Delta H_f \text{ H}_2\text{O}(\ell)$

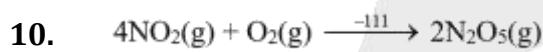
$57.32 = \Delta H_f \text{ OH}^- (\text{aq}) + 286.2$

$\Delta H_f \text{ OH}^- (\text{aq}) = -228.88 \text{ kJ}$



$$-46 = \frac{3}{2} \times 436 + \frac{1}{2} \times 712 - 3 \in_{\text{N-H}}$$

$3 \in_{\text{N-H}} = 1056 \Rightarrow \in_{\text{N-H}} = 352 \text{ kJ mol}^{-1}$

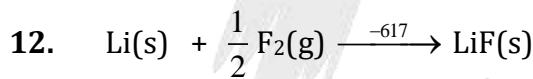


$$\Delta rH \quad 2\text{N}_2\text{O}_5(\text{s}) \quad 2 \times 54$$

$\Delta rH + 2 \times 54 = -111 \Delta rH = -219 \text{ kJ}$

11.  $-51.46 = -55.90 + \Delta H_{\text{ion}}$

$\Delta H_{\text{ion.}} = +4.44 \text{ kJ mol}^{-1}$



$\downarrow 161 \quad \downarrow 77$

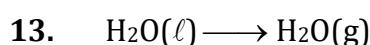
$\text{Li}(\text{g}) \quad \text{F}(\text{g})$

$\downarrow 520 \quad \downarrow \Delta egH$

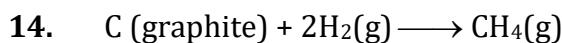
$\text{Li}^+(\text{g}) + \text{F}^-(\text{g})$

$161 + 520 + 77 + \Delta egH \text{ F}(\text{g}) - 1047 = -617$

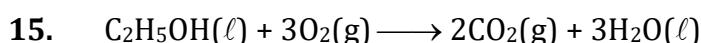
$\Delta egH \text{ F}(\text{g}) = -328 \text{ kJ/mol}$



$\Delta rH = b - a = -241.8 + 285.9 = +44.1 \text{ kJ}$



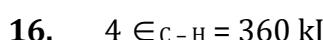
$$\Delta rH = \Delta H \text{ sub. } \text{C}(\text{graphite}) + 2 \in_{\text{H-H}} - 4 \in_{\text{C-H}}$$



$$\Delta U = -1364.47 \text{ kJ/mol}$$

$$\Delta H = \Delta U + \Delta n g RT$$

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000} = -1366.95 \text{ kJ/mol}$$



$$\in_{\text{C-H}} = 90 \text{ kJ/mol}$$

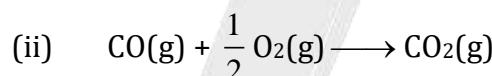
$$\in_{\text{C-C}} + \in_{\text{C-H}} = 620$$

$$\in_{\text{C-C}} = 80 \text{ kJ/mol} = \frac{80}{96.5} \text{ ev / bond}$$

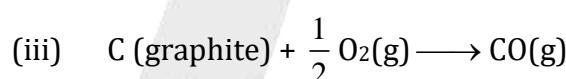
$$\lambda = \frac{1240}{80} \times 96.5 \text{ nm} = 1.493 \times 10^3 \text{ nm}$$



$$\Delta H = -393.5 \text{ kJ mol}^{-1}$$

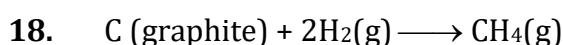


$$\Delta H = -283.5 \text{ kJ/mol}$$



$$(iii) = (i) - (ii)$$

$$\Delta rH = -393.5 + 283.5 = -110.0 \text{ kJ/mol}$$

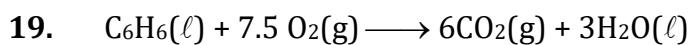


$$\Delta rH = \Delta H_f \text{CH}_4(\text{g})$$

$$890.3 = \Delta H_f \text{CH}_4(\text{g}) - \Delta H_f \text{CO}_2(\text{g}) - 2 \Delta H_f \text{H}_2\text{O}(\ell)$$

$$890.3 = \Delta H_f \text{CH}_4(\text{g}) + 393.5 + 2 \times 285.8$$

$$\Delta rH = \Delta H_f \text{CH}_4(\text{g}) = -74.8 \text{ kJ/mol}$$



$$\Delta ng = -1.5$$

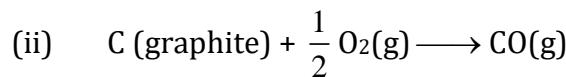


$$\Delta H = \Delta U + \Delta n g RT$$

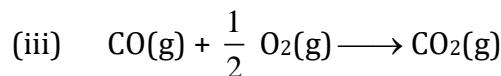
$$\Delta H = -3263.9 - \frac{1.5 \times 8.314 \times 298}{1000} = -3267.6 \text{ kJ}$$



$$\Delta rH^\ominus = x \text{ kJ/mol}$$

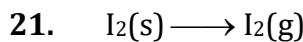


$$\Delta rH^\ominus = y \text{ kJ/mol}$$



$$\Delta rH^\ominus = 2 \text{ kJ/mol}$$

$$(i) = (ii) + (iii) x = y + z$$

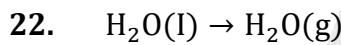


$$(\Delta C_p)_r = 0.031 - 0.055 = -0.024 \text{ cal g}^{-1} \text{ K}^{-1}$$

$$\Delta rH \text{ } 523 \text{ K} - \Delta rH \text{ } 473 \text{ K} = -0.024 \times (523 - 473)$$

$$\Delta rH \text{ } 523 \text{ K} - 24 = -0.024 \times 50$$

$$\Delta rH \text{ } 523 \text{ K} = 22.8 \text{ cal g}^{-1}$$



$$\Delta H_{\text{vap}} = \Delta U + \Delta n_g RT$$

$$\Delta U = \Delta H_{\text{vap}} - RT$$

$$= 41,000 - 8.314 \times 373 \text{ J mol}^{-1}$$

$$= 37898.878$$

$$\text{For 5 moles, } \Delta U = 37898.878 \times 5 \text{ J} = 189494 \text{ J}$$



$$4 = 788 + \Delta_{\text{Hyd.}}H^\ominus$$

$$\Delta_{\text{Hyd}}H^\ominus = -784 \text{ kJ/mol}$$



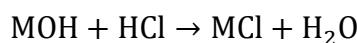
$$\Delta G = -\nu e$$



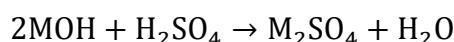
Only above 1400°C

25. According to the given data of I.E,

This element must belong to group 1 and thus is monovalent and form hydroxide of the type  $M(OH)$ .



1 mole 1 mole



1 mole 1/2 mole

$$27. \Delta_f H_{KCl}^\Theta = \Delta_{\text{sub}} H_{(K)}^\Theta + \Delta_{\text{ionization}} H_{(K)}^\Theta + \frac{1}{2} \Delta_{\text{bond}} H_{(Cl_2)}^\Theta + \Delta_{\text{electron gain}} H_{(Cl)}^\Theta + \Delta_{\text{lattice}} H_{(KCl)}^\Theta$$

$$\Rightarrow -436.7 = 89.2 + 419.0 + \frac{1}{2}(243.0) + \{-348.6\} + \Delta_{\text{lattice}} H_{(KCl)}^\Theta$$

$$\Rightarrow \Delta_{\text{lattice}} H_{(KCl)}^\Theta = -717.8 \text{ kJ mol}^{-1}$$

The magnitude of lattice enthalpy of KCl in  $\text{kJ mol}^{-1}$  is 718 (Nearest integer).

$$28. \Delta H = \sum \Delta H_{\text{Combustion}} (\text{Reactant}) - \sum \Delta H_{\text{Combustion}}$$

(Product)

$$= 3 \times (-1300) - [-3268]$$

$$= -632 \text{ kJ mol}^{-1}$$

$$29. C(s) + O_2(g) \rightarrow CO_2(g); \Delta H = -x \text{ kJ/mole}$$

$$Q = C\Delta T = 20 \text{ kJ} \times 2$$

40 kJ heat is released for 2.4 g of C

$$\text{For 1 mole 'C': } Q = \frac{40}{2.4} \times 12$$

$$= \frac{400}{24} \times 12 = 200 \text{ kJ/mole}$$

$$Q = \Delta E = \Delta H = 200 \text{ kJ} (\because \Delta n_g = 0)$$

$$x = 200$$

$$30. \Delta H_{\text{ionisation}} \text{ of CH}_3\text{COOH} = |-57.3 - (-55.3)|$$

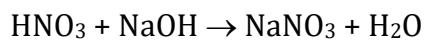
$$= 2 \text{ kJ/mol}$$

$$31. \text{HNO}_3 \quad \text{NaOH}$$



$$600 \text{ mL} \times 0.2 \text{ M} \quad 400 \text{ mL} \times 0.1 \text{ M}$$

$$= 120 \text{ m mol} \quad = 40 \text{ m mol}$$



$$\text{Bef.} \quad 120 \quad 40$$

$$\text{Aft.} \quad 80 \quad 0 \quad 40 \text{ m mol}$$

$$\Delta_r H = 40 \text{ mmol} \times (57 \times 10^3) \frac{\text{J}}{\text{mol}}$$

$$= 40 \times 10^{-3} \text{ mol} \times 57 \times 10^3 \frac{\text{J}}{\text{mol}}$$

$$= 2280 \text{ J}$$

$$mS\Delta T = 2280$$

$$\Rightarrow 1000 \text{ mL} \times \frac{1 \text{ gm}}{\text{mL}} \times 4,2 \times \Delta T = 2280$$

$$\Delta T = \frac{2280}{4.2} \times 10^{-3}$$

$$= \frac{22800}{42} \times 10^{-3} = 542.86 \times 10^{-3}$$

$$\Delta T = 54.286 \times 10^{-2} \text{ K}$$

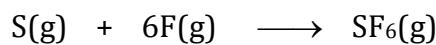
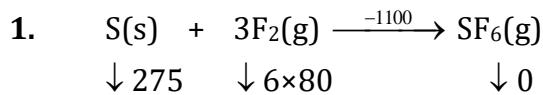
$$\Delta T = 54.286 \times 10^{-20} \text{ C}$$

Ans. 54.286

Answer mentioned as 54 (Closest integer)



## EXERCISE JEE-ADVANCE

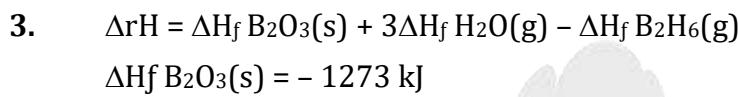


$-1100 = 275 + 6 \times 80 - 6 \in_{S-F}$

$6 \in_{S-F} = 275 - 6 \times 80 + 1100$

$\in_{S-F} = 309.16 \text{ kJ/mol}$

2. Combination is exothermic reaction

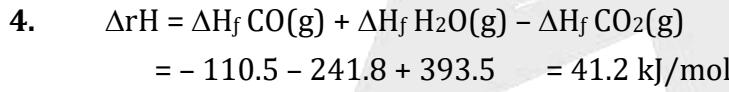


$44 = \Delta H_f H_2O(g) + 286$

$\Delta H_f H_2O(g) = -242 \text{ kJ}$

$\Delta H_f B_2H_6 = 36 \text{ kJ}$

$\Delta rH = -1273 - 3 \times 242 - 36 = -2035 \text{ kJ/mol}$

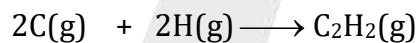


6.  $9 = 2.5 \times 0.45 \text{ kJ}$

$\Delta H = -\frac{2.5 \times 0.45}{3.5} \times 28 = -9 \text{ kJ/mol}$



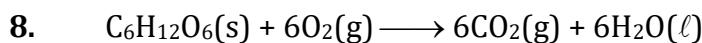
$\downarrow 1410 \quad \downarrow 330 \quad \downarrow 0$



$225 = 1410 + 330 - 2 \times \in_{C-H} - \in_{C=C}$

$225 = 1740 - 2 \times 350 - \in_{C=C}$

$\in_{C=C} = 1740 - 700 - 225 = +815 \text{ kJ}$



$\Delta rH = -6 \times 400 - 6 \times 30 + 1300$

$= -2700 \text{ kJ/mol}$

$= -\frac{2900}{180} \text{ kJ (per gram)} = -16.11 \text{ kJ}$



$$\Delta H = (\Delta_f H)_P - (\Delta_f H)_R$$

$$= -394 + 581$$

$$= +187 \text{ kJ/mol}$$

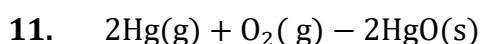
$$\Delta S = (\Delta S)_P - (\Delta S)_R$$

$$= 210 + 52 - 56 - 6$$

$$= 200 \text{ J/kmol}$$

$$\Delta G = 187 \times 1000 - 200 \times T$$

$$T = [187 \times 1000]/200 = 935 \text{ K}$$



$$\text{Heat capacity of calorimeter} = 20 \text{ kJ K}^{-1}$$

$$\text{Rise in temperature} = 14.8 \text{ K}$$

$$\text{Heat evolved} = 20 \times 14.8 = 296 \text{ kJ}$$

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

$$= -296 - 3 \times 8.3 \times 298 \times 10^{-3}$$

$$\approx -303.42 \text{ kJ}$$

$$\Delta H^\circ = \Delta H_f^\circ(\text{HgO(s)}) - \Delta H_f^\circ(\text{Hg(g)})$$

$$-303.42 = \Delta H_f^\circ(\text{HgO(s)}) - 2 \times 61.32$$

$$\Delta H_f^\circ(\text{HgO(s)}) = -303.42 + 122.64$$

$$= -180.78 \text{ kJ}$$

$$|\Delta H_f^\circ(\text{HgO(s)})| = 90.39 \text{ kJ mol}^{-1}$$