

## SOLVED EXAMPLES

**Ex. 1** From the following data at 25°C

Reaction	$\Delta_r H^\circ / \text{KJ mol}^{-1}$
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g})$	42.09
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	-241.84
$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	435.88
$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$	495.04

Calculate  $\Delta_r H^\circ$  for the following reactions

- (a)  $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$   
 (b)  $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$   
 (c)  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g})$

**Sol.** (a) The desired equation is  
 $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$

We are to develop the desired equation by using the four given equations

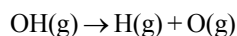
(i)  $\frac{1}{2} \text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$   $\Delta_r H^\circ = \frac{435.88}{2}$

(ii)  $\text{OH}(\text{g}) \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$   $\Delta_r H^\circ = -42.09$

(iii)  $\frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$   $\Delta_r H^\circ = \frac{495.04}{2}$

By adding equation (i), (ii) & (iii),

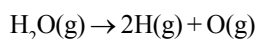
we get



$$\Delta_r H^\circ \rightarrow \frac{435.88}{2} - 42.09 + \frac{495.04}{2}$$

or  $\Delta_r H^\circ = 423.37 \text{ kJ/mol}$ . **Ans.**

(b) The desired equation is



(i)  $\frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$   $\Delta_r H^\circ = \frac{495.04}{2}$

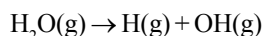
(ii)  $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$   $\Delta_r H^\circ = 435.88$

(iii)  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$   $\Delta_r H^\circ = 241.88$

The net equation is,



(c) The desired equation is



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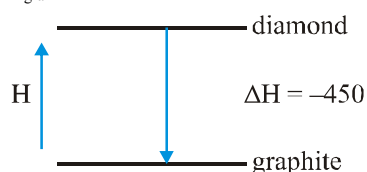
By adding eq<sup>n</sup> (i) and (ii)



**Ex. 2** From the given data prove that graphite is more stable allotrope of carbon than diamond from the given data



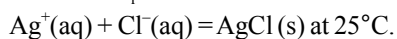
on subtraction



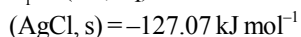
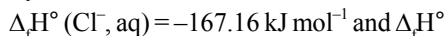
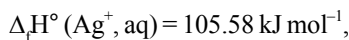
since heat content of diamond > graphite

Therefore diamond is less stable than graphite.

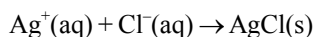
**Ex. 3** Calculate  $\Delta_f H^\circ$  for the reaction



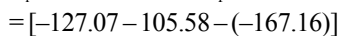
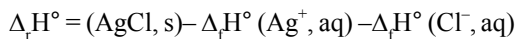
Given :



**Sol.** For the reaction



We have



**Ex. 4** Using bond enthalpy data given below, estimate enthalpy of formation of acetic acid.

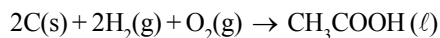
Bond	Bond enthalpies
C - H	$413.38 \text{ kJ mol}^{-1}$
C - C	$347.69 \text{ kJ mol}^{-1}$
C = O	$728.02 \text{ kJ mol}^{-1}$
C - O	$351.46 \text{ kJ mol}^{-1}$
O - H	$462.75 \text{ kJ mol}^{-1}$

**Enthalpy of atomization**

C	$718.39 \text{ kJ atom}^{-1}$
H	$217.94 \text{ kJ atom}^{-1}$
O	$247.52 \text{ kJ atom}^{-1}$

The observed  $\Delta_f H^\circ$  for acetic acid is  $-438.15 \text{ kJ mol}^{-1}$ . Compute the resonance energy of acetic acid.

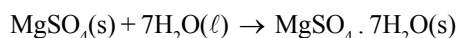
**Sol.** The desired reaction for the formation of  $\text{CH}_3\text{COOH}$  is



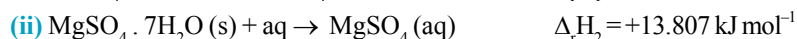
$$\begin{aligned} \Delta_f H^\circ &= -3 \times 413.38 - 1 \times 347.69 - 728.02 - 351.46 - 462.75 + 2 \times 718.39 + 4 \times 217.94 + 2 \times 247.52 \\ &= -326.48 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Resonance energy} &= \Delta H^\circ_{\text{obs}} - \Delta H^\circ \\ &= -438.15 + 326.48 \\ &= -111.67 \text{ kJ mol}^{-1} \end{aligned}$$

**Ex. 5** At  $25^\circ\text{C}$ , 1 mole  $\text{MgSO}_4$  was dissolved in water. The heat evolved was found to be  $91.211 \text{ kJ}$ . One mole of  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  on dissolution gives a solution of the same composition accompanied by an absorption of  $13.807 \text{ kJ}$ . Find the enthalpy of hydration, i.e.,  $\Delta H$  for the reaction



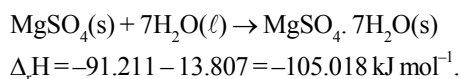
Given that



Equation **(i)** can be written as follows :

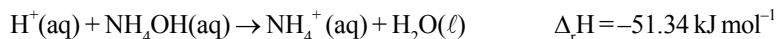


eqn **(iii)** – **(ii)** will give



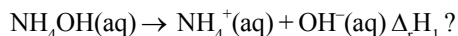
**Ex. 6** Enthalpy of neutralization of  $\text{HCl}$  by  $\text{NaOH}$  is  $-57.32 \text{ kJ mol}^{-1}$  and by  $\text{NH}_4\text{OH}$  is  $-51.34 \text{ kJ mol}^{-1}$ . Calculate the enthalpy of dissociation of  $\text{NH}_4\text{OH}$ .

**Sol.** Given that



we may consider neutralization in two steps :

**(i)** ionization



**(ii)** neutralization



Thus,  $\Delta_f H = \Delta_f H_1 + \Delta_f H_2$

Therefore,

$$\begin{aligned} \Delta_f H_1 &= \Delta_f H - \Delta_f H_2 \\ &= -51.34 + 57.32 = 5.98 \text{ kJ/mol}^{-1} \end{aligned}$$

**Ex. 7** The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are  $-2839.2$ ,  $-2275.2$  and  $-5536 \text{ kJ mol}^{-1}$  respectively. Calculate the resonance energy of benzene, compared with Kekule structure. The bond enthalpy of  $\text{C} - \text{H}$  bond is given as equal to  $410.87 \text{ kJ mol}^{-1}$ .

**Sol.** Bond enthalpy of  $\text{C} - \text{C}$  bond

$$\begin{aligned} &= \text{Enthalpy required to break } \text{C}_2\text{H}_6 \text{ into gaseous atoms} - 6 \times \text{bond enthalpy of } \text{C} - \text{H} \text{ bond} \\ &= 2839.2 \text{ kJ mol}^{-1} - 6 \times 410.87 \text{ kJ mol}^{-1} \\ &= 373.98 \text{ kJ mol}^{-1} \end{aligned}$$

Bond enthalpy of  $\text{C} = \text{C}$  bond = Enthalpy required to break  $\text{C}_2\text{H}_4$  into gaseous atoms  $-4 \times$  bond enthalpy of  $\text{C} - \text{H}$  bond

$$= 2275.2 \text{ kJ mol}^{-1} - 4 \times 410.87 \text{ kJ mol}^{-1}$$

$$= 631.72 \text{ kJ mol}^{-1}$$

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

$$[3(-373.98) + 3(-631.72) + 6(-410.87)]$$

$$= -5482.32 \text{ kJ mol}^{-1}$$

But the given value of  $\Delta_f H$  is

$$\Delta_f H (\text{actual}) = -5536 \text{ kJ mol}^{-1}$$

Hence resonance energy compared to Kekule structure

$$= \Delta_f H (\text{actual}) - \Delta_f H (\text{Kekule structure})$$

$$= (-5536 + 5482.32)$$

$$= -53.68 \text{ kJ mol}^{-1}$$

**Ex. 8** The specific heats of iodine vapour and solid are 0.031 and 0.055 cal/g respectively. If heats of sublimation of iodine is 24 cal/g at 200°C, what is its value at 250°C ?

**Sol.** Given



$$\Delta C_{p(\text{cal/g})} = C_p \text{ of product} - C_p \text{ of reactant}$$

$$= 0.031 - 0.055$$

$$= -0.024 \text{ cal/g}$$

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

$$\Delta H_2 - 24 = -0.024 \times (523 - 473)$$

$$\therefore \Delta H_2 = 24 - 1.2 = 22.8 \text{ cal/g.}$$

**Ex. 9** When 2 mole of  $C_2H_{6(g)}$  are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of  $C_2H_{6(g)}$ .  $\Delta_f H$  for  $CO_{2(g)}$  and  $H_2O_{(l)}$  are  $-395$  and  $-286 \text{ kJ mol}^{-1}$  respectively.

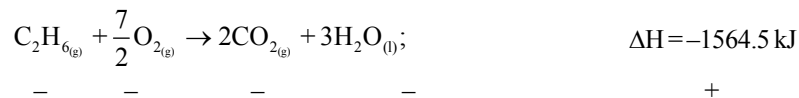
**Sol.** We have to find



Multiplying Eq. (2) by 2 and Eq. (3) by 3, then adding



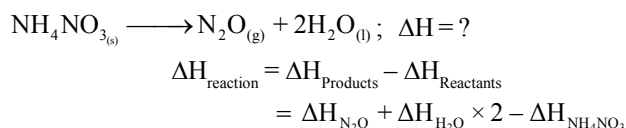
Subtracting Eq. (4) from Eq. (5)



$$\therefore \Delta_f H \text{ of } C_2H_6 = -83.5 \text{ kJ}$$

**Ex. 10** The molar heat of formation of  $\text{NH}_4\text{NO}_3$  is  $-367.54 \text{ kJ}$  and those of  $\text{N}_2\text{O}_{(g)}$ ,  $\text{H}_2\text{O}_{(l)}$  are  $81.46$  and  $-285.8 \text{ kJ}$  respectively at  $25^\circ\text{C}$  and 1 atmosphere pressure. Calculate  $\Delta H$  and  $\Delta E$  of the reaction  $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O}_{(g)} + 2\text{H}_2\text{O}_{(l)}$

**Sol.** We have to find  $\Delta H$  for



Given,  $\Delta H_{\text{N}_2\text{O}} = +81.46 \text{ kJ}$ ,  $\Delta H_{\text{H}_2\text{O}} = -285.8 \text{ kJ}$ ,  $\Delta H_{\text{NH}_4\text{NO}_3} = -367.54 \text{ kJ}$

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

$$\Delta H = -122.6 \text{ kJ}$$

Further  $\Delta H = \Delta E + \Delta nRT$  ( $\Delta n = 1 - 0 = 1$ ,  $R = 8.314 \text{ J}$ ,  $T = 298 \text{ K}$ )

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

$$\therefore \Delta E = -125077 \text{ joule}$$

$$= 125.077 \text{ kJ}$$

**Ex. 11**  $\Delta H$  for combustion of ethane and ethyne are  $-341.1$  and  $-310.0 \text{ kcal}$  respectively. Which is better gas welder and why?

**Sol.** A better gas welder is one which possesses high calorific value, i.e., heat produced by 1 g of fuel.

$\Delta H_{\text{combustion}}$  for  $\text{C}_2\text{H}_6 = -341.1 \text{ kcal}$

$$\therefore \text{Calorific value} = \frac{-341.1}{30} \text{ kcal/g} = -11.37 \text{ kcal/g}$$

$\Delta H_{\text{combustion}}$  for  $\text{C}_2\text{H}_2 = -310.0 \text{ kcal}$

$$\therefore \text{Calorific value} = \frac{-310.0}{26} \text{ kcal/g} = -11.92 \text{ kcal/g}$$

$\therefore \text{C}_2\text{H}_2$  is better gas welder.

**Ex. 12** The heats of combustion of  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{H}_2$  are  $-1409.5$ ,  $-1558.3$  and  $-285.6 \text{ kJ}$  respectively. Calculate heat of hydrogenation of ethylene.

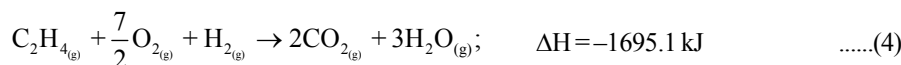
**Sol.** We have to find



Given,  $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}; \Delta H = -1409.5 \text{ kJ} \dots(1)$



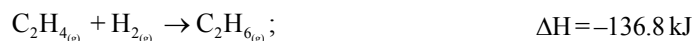
Adding Eqs. (1) and (3)



Subtracting Eq. (2) from (4)



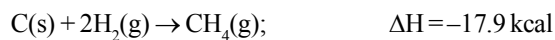
-                    -                    -                    -                    +



$\therefore$  Heat of hydrogenation of  $\text{C}_2\text{H}_4 = 136.8 \text{ kJ}$

**Ex. 13** The heat of formation of methane is  $-17.9$  kcal. If the heats of atomisation of carbon and hydrogen are  $170.9$  and  $52.1$  kcal per mole, calculate the C–H bond energy in methane.

**Sol.** Given that



Energy change in reactants :

Heat of atomisation of 1 mole of C =  $170.9$  kcal

Heat of atomisation of 4 moles of H =  $4 \times 52.1$  kcal

Energy change in product :

Heat of formation of 4 moles of C–H bonds =  $4 \times x$  kcal.

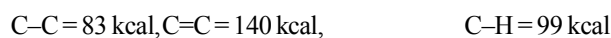
(where  $x$  is the energy of formation of C–H bonds in kcal/mole).

Since the algebraic sum of all the heat changes is equal to the heat of formation of the above given equation, we have

$$170.9 + 4 \times 52.1 + 4x = -17.9; x = -99.3 \text{ kcal}$$

Thus the bond energy =  $+99.3$  kcal/mole

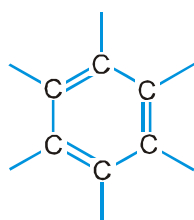
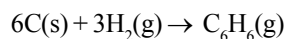
**Ex. 14** Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :



Heat of atomisation of C =  $170.9$  kcal

Heat of atomisation of H =  $52.1$  kcal

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



$\Delta\text{H} = ?$

For reactants :

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

Heat of atomisation of 6 moles of H =  $6 \times 52.1$  kcal

For products :

Heat of formation of 6 moles of C–H bonds =  $-6 \times 99$

Heat of formation of 3 moles of C–C bonds =  $-3 \times 83$

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

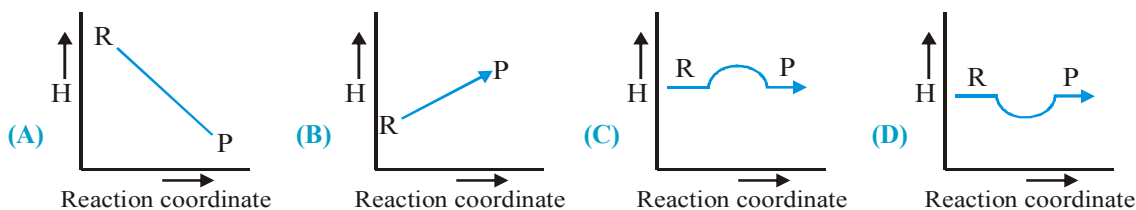
On adding, we get heat of formation of  $\text{C}_6\text{H}_6$ , i.e.,

$$\Delta\text{H} = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = 75.0 \text{ kcal.}$$

## Exercise # 1

[Single Correct Choice Type Questions]

1. For which of the following change  $\Delta H \neq \Delta E$  ?  
 (A)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}(\text{g})$  (B)  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \longrightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 (C)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  (D)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{NH}_3(\text{g})$
2. If  $\Delta H$  is the change in enthalpy and  $\Delta E$  the change in internal energy accompanying a gaseous reaction  
 (A)  $\Delta H$  is always greater than  $\Delta E$   
 (B)  $\Delta H < \Delta E$  only if the number of moles of the products is greater than the number of the reactants  
 (C)  $\Delta H$  is always less than  $\Delta E$   
 (D)  $\Delta H < \Delta E$  only if the number of moles of the products is less than the number of moles of the reactants
3. Which plot represent an exothermic reaction ?



4.  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \quad \Delta H = -94.3 \text{ kcal/mol}$   
 $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \quad \Delta H = -67.4 \text{ kcal/mol}$   
 $\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g}); \quad \Delta H = 117.4 \text{ kcal/mol}$   
 $\text{CO}(\text{g}) \longrightarrow \text{C}(\text{g}) + \text{O}(\text{g}); \quad \Delta H = 230.6 \text{ kcal/mol}$   
 Calculate  $\Delta H$  for  $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})$  in kcal/mol.  
 (A) 171 (B) 154 (C) 117 (D) 145
5.  $2\text{C} + \text{O}_2 \rightarrow 2\text{CO}; \Delta H = -220 \text{ kJ}$  Which of the following statement is correct for this reaction  
 (A) Heat of combustion of carbon is 110 kJ (B) Reaction is exothermic  
 (C) Reaction needs no initiation (D) All of these are correct
6. Given,  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \longrightarrow 2\text{HBr}(\text{g}), \Delta H^0_1$  and standard enthalpy of condensation of bromine is  $\Delta H^0_2$ , standard enthalpy of formation of HBr at  $25^\circ\text{C}$  is  
 (A)  $\Delta H^0_1/2$  (B)  $\Delta H^0_1/2 + \Delta H^0_2$  (C)  $\Delta H^0_1/2 - \Delta H^0_2$  (D)  $(\Delta H^0_1 - \Delta H^0_2)/2$
7. For the following reaction,  $\text{C}(\text{diamond}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g}); \Delta H = -94.3 \text{ kcal}$   
 $\text{C}(\text{graphite}) + \text{O}_2 \longrightarrow \text{CO}_2(\text{g}); \Delta H = -97.6 \text{ kcal}$   
 The heat required to change 1 g of C (diamond)  $\longrightarrow$  C (graphite) is  
 (A) 1.59 kcal (B) 0.1375 kcal (C) 0.55 kcal (D) 0.275 kcal
8. In the reaction,  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}); \quad \Delta H = 2.8 \text{ kJ}$ ,  $\Delta H$  represents  
 (A) heat of reaction (B) heat of combustion (C) heat of formation (D) heat of solution
9. The heat of combustion of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) is 1350 kcal. How much of heat will be liberated when 17.1 g of sucrose is burnt ?  
 (A) 67.5 kcal (B) 13.5 kcal (C) 40.5 kcal (D) 25.5 kcal

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10. The standard heat of combustion of solid boron is equal to :  
 (A)  $\Delta H_f^\circ(\text{B}_2\text{O}_3)$  (B)  $1/2 \Delta H_f^\circ(\text{B}_2\text{O}_3)$  (C)  $2\Delta H_f^\circ(\text{B}_2\text{O}_3)$  (D)  $1/2 \Delta H_f^\circ(\text{B}_2\text{O}_3)$
11. The following is (are) endothermic reaction(s) :  
 (A) Combustion of methane. (B) Rusting of iron  
 (C) Dehydrogenation of ethane to ethylene. (D) Making ice cubes
12. In the reaction  $\text{CS}_2(\ell) + 3\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g})$   $\Delta H = -265$  kcal  
 The enthalpies of formation of  $\text{CO}_2$  and  $\text{SO}_2$  are both negative and are in the ratio 4 : 3. The enthalpy of formation of  $\text{CS}_2$  is +26 kcal/mol. Calculate the enthalpy of formation of  $\text{SO}_2$ .  
 (A) -90 kcal/mol (B) -52 kcal/mol (C) -78 kcal/mol (D) -71.7 kcal/mol
13. If  $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2, \Delta H = -298.2$  kJ mole<sup>-1</sup>  
 $\text{SO}_2 + 1/2 \text{O}_2 \longrightarrow \text{SO}_3, \Delta H = -98.7$  kJ mole<sup>-1</sup>  
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4, \Delta H = -130.2$  kJ mole<sup>-1</sup>  
 $\text{H}_2 + 1/2 \text{O}_2 \longrightarrow \text{H}_2\text{O}, \Delta H = -287.3$  kJ mole<sup>-1</sup>  
 the enthalpy of formation of  $\text{H}_2\text{SO}_4$  at 298 K will be -  
 (A) -814.4 kJ mol<sup>-1</sup> (B) +814.4 kJ mole<sup>-1</sup> (C) -650.3 kJ mole<sup>-1</sup> (D) -433.7 kJ mole<sup>-1</sup>
14. When a certain amount of ethylene was combusted, 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of  $\text{O}_2$  (at NTP) that entered into the reaction is :  
 (A) 296.5 ml (B) 296.3 L (C)  $6226 \times 22.4$  L (D) 22.4 L
15. One mole of anhydrous  $\text{MgCl}_2$  dissolves in water and liberates 25 cal/mol of heat.  $\Delta H_{\text{hydration}}$  of  $\text{MgCl}_2 = -30$  cal/mol. Heat of dissolution of  $\text{MgCl}_2 \cdot \text{H}_2\text{O}$  is  
 (A) +5 cal/mol (B) -5 cal/mol (C) 55 cal/mol (D) -55 cal/mol
16. If heat of dissociation of  $\text{CHCl}_2\text{COOH}$  is 0.7 kcal/mole then  $\Delta H$  for the reaction :  
 $\text{CHCl}_2\text{COOH} + \text{KOH} \longrightarrow \text{CHCl}_2\text{COOK} + \text{H}_2\text{O}$   
 (A) -13 kcal (B) +13 kcal (C) -14.4 kcal (D) -13.7 kcal
17. Enthalpy of neutralization of  $\text{H}_3\text{PO}_3$  acid is -106.68 kJ/mol using NaOH. If enthalpy of neutralization of HCl by NaOH is -55.84 kJ/mol. Calculate  $\Delta H_{\text{ionization}}$  of  $\text{H}_3\text{PO}_3$  into its ions :  
 (A) 50.84 kJ/mol (B) 5 kJ/mol (C) 2.5 kJ/mol (D) None of these
18. If  $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} + q_1$   
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + q_2$   
 then the enthalpy change for the reaction  
 $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+$  is equal to  
 (A)  $(q_1 + q_2)$  (B)  $(q_1 - q_2)$  (C)  $(q_2 - q_1)$  (D)  $-(q_1 + q_2)$
19. Heat of hydrogenation of ethene is  $x_1$  and that of benzene is  $x_2$ . Hence, resonance energy is :  
 (A)  $x_1 - x_2$  (B)  $x_1 + x_2$  (C)  $3x_1 - x_2$  (D)  $x_1 - 3x_2$
20. AB,  $\text{A}_2$  and  $\text{B}_2$  are diatomic molecules. If the bond enthalpies of  $\text{A}_2$ , AB &  $\text{B}_2$  are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from  $\text{A}_2$  and  $\text{B}_2$  is -100 kJ/mol<sup>-1</sup>. What is the bond enthalpy of  $\text{A}_2$ .  
 (A) 400 kJ/mol (B) 200 kJ/mol (C) 100 kJ/mol (D) 300 kJ/mol
21. The bond dissociation energy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and HCl are 104, 58 and 103 kcal mol<sup>-1</sup> respectively. The enthalpy of formation for HCl gas will be  
 (A) -44.0 kcal (B) -22.0 kcal (C) 22.0 kcal (D) 44.0 kcal



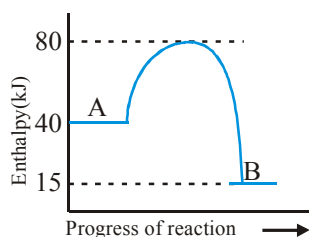
22. In Haber's process of manufacturing of ammonia :



Molecule	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$C_p \text{ JK}^{-1} \text{ mol}^{-1}$	29.1	28.8	35.1

If  $C_p$  is independent of temperature, then reaction at  $100^\circ\text{C}$  as compared to that of  $25^\circ\text{C}$  will be :

- (A) More endothermic    (B) Less endothermic    (C) More exothermic    (D) Less exothermic
23. From the following data of  $\Delta H$ , of the following reactions,
- $$\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{CO}(\text{g}) \quad \Delta H = -110 \text{ kJ}$$
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \longrightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}) \quad \Delta H = 132 \text{ kJ}$$
- What is the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, to maintain constant temperature :
- (A) 0.5 : 1                      (B) 1 : 0.6                      (C) 0.8 : 1                      (D) 1 : 1
24. When 12.0 g of carbon reacted with limited quantity of oxygen, 57.5 kcal of heat was produced, Calculate the number of moles of CO produced ( $\Delta_f H(\text{CO}_2) = -94.05 \text{ kcal}$ ,  $\Delta_f H(\text{CO}) = -21.41 \text{ kcal}$ ).
- (A) 0.54 mol                      (B) 0.46 mol                      (C) 0.64 mol                      (D) 0.74 mol
25. The standard enthalpy of formation of 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 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 thermal energy will be released per mole of the initial mixture ?
- (A) 13.4 kcal/mole                      (B) 14.6 kcal/mole                      (C) 15.7 kcal/mole                      (D) 16.8 kcal/mole
26. In the reaction  $\text{AB}_2(\ell) + 3\text{X}_2(\text{g}) \rightleftharpoons \text{AX}_2(\text{g}) + 2\text{BX}_2(\text{g})$   $\Delta H = -270 \text{ kcal per mol. of } \text{AB}_2(\ell)$ , the enthalpies of formation of  $\text{AX}_2(\text{g})$  &  $\text{BX}_2(\text{g})$  are in the ratio of 4 : 3 and have opposite sign. The value of  $\Delta_f H^0(\text{AB}_2(\ell)) = +30 \text{ kcal/mol}$ . Then
- (A)  $\Delta_f H^0(\text{AX}_2) = -96 \text{ kcal/mol}$                       (B)  $\Delta_f H^0(\text{BX}_2) = +480 \text{ kcal/mol}$   
 (C)  $K_p = K_c$  &  $\Delta_f H^0(\text{AX}_2) = +480 \text{ kcal/mol}$                       (D)  $K_p = K_c RT$  &  $\Delta_f H^0(\text{AX}_2) + \Delta_f H^0(\text{BX}_2) = -240 \text{ kcal/mol}$
27. Look at the following diagram :



The enthalpy change for the reaction  $\text{A} \rightarrow \text{B}$  will be

- (A)  $-25 \text{ kJ}$                       (B)  $-40 \text{ kJ}$                       (C)  $+25 \text{ kJ}$                       (D)  $-65 \text{ kJ}$
28. The difference between  $\Delta H$  and  $\Delta E$  (on a molar basis) for the combustion of n-octane ( $\ell$ ) at  $25^\circ\text{C}$  would be :
- (A)  $-13.6 \text{ kJ}$                       (B)  $-1.14 \text{ kJ}$                       (C)  $-11.15 \text{ kJ}$                       (D)  $+11.15 \text{ kJ}$

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29. The heat of formation of HCl at 348 K from the following data, will be  
 $0.5 \text{ H}_2(\text{g}) + 0.5 \text{ Cl}_2(\text{g}) \longrightarrow \text{HCl} \quad \Delta H^\circ_{298} = -22060 \text{ cal}$   
 The mean heat capacities over this temperature range are,  
 $\text{H}_2(\text{g}), C_p = 6.82 \text{ cal mol}^{-1} \text{ K}^{-1}$ ;  $\text{Cl}_2(\text{g}), C_p = 7.71 \text{ cal mol}^{-1} \text{ K}^{-1}$ ;  $\text{HCl}(\text{g}), C_p = 6.81 \text{ cal mol}^{-1} \text{ K}^{-1}$   
**(A)** -20095 cal      **(B)** -32758 cal      **(C)** -37725 cal      **(D)** -22083 cal
30. The enthalpy of neutralization of 40.0 g of NaOH by 60.0 g of  $\text{CH}_3\text{COOH}$  will be :  
**(A)** 57.1 kJ equiv<sup>-1</sup>      **(B)** less than 57.1 kJ equiv<sup>-1</sup>  
**(C)** more than 57.1 kJ equiv<sup>-1</sup>      **(D)** 13.7 kJ equiv<sup>-1</sup>
31. Given  $\Delta_{\text{ioniz}} H^\circ(\text{HCN}) = 45.2 \text{ kJ mol}^{-1}$  and  $\Delta_{\text{ioniz}} H^\circ(\text{CH}_3\text{COOH}) = 2.1 \text{ kJ mol}^{-1}$ . Which one of the following facts is true ?  
**(A)**  $\text{pK}_a(\text{HCN}) = \text{pK}_a(\text{CH}_3\text{COOH})$   
**(B)**  $\text{pK}_a(\text{HCN}) > \text{pK}_a(\text{CH}_3\text{COOH})$   
**(C)**  $\text{pK}_a(\text{HCN}) < \text{pK}_a(\text{CH}_3\text{COOH})$   
**(D)**  $\text{pK}_a(\text{HCN}) = (45.17/2.07) \text{pK}_a(\text{CH}_3\text{COOH})$
32. A solution is 500 ml of 2 M KOH is added to 500 ml of 2 M HCl and the mixture is well shaken. The rise in temperature  $T_1$  is noted. The experiment is then repeated using 250 ml of each solution and rise in temperature  $T_2$  is again noted. Assume all heat is taken by the solution  
**(A)**  $T_1 = T_2$   
**(B)**  $T_1$  is 2 times as large as  $T_2$   
**(C)**  $T_2$  is twice of  $T_1$   
**(D)**  $T_1$  is 4 times as large as  $T_2$
33. 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.  
**(A)**  $-2.5 \times 10^2 \text{ kJ/mole}$       **(B)**  $-1.3 \times 10^2 \text{ kJ/mole}$       **(C)**  $-8.4 \times 10^1 \text{ kJ/mole}$       **(D)**  $-6.3 \times 10^1 \text{ kJ/mole}$
34. The average O-H bond energy in  $\text{H}_2\text{O}$  with the help of following data.  
 (1)  $\text{H}_2\text{O}(\ell) \longrightarrow \text{H}_2\text{O}(\text{g}); \Delta H = +40.6 \text{ KJ mol}^{-1}$   
 (2)  $2\text{H}(\text{g}) \longrightarrow \text{H}_2(\text{g}); \Delta H = -435.0 \text{ KJ mol}^{-1}$   
 (3)  $\text{O}_2(\text{g}) \longrightarrow 2\text{O}(\text{g}); \Delta H = +489.6 \text{ KJ mol}^{-1}$   
 (4)  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\ell); \Delta H = -571.6 \text{ KJ mol}^{-1}$   
**(A)** 584.9 KJ mol<sup>-1</sup>      **(B)** 279.8 KJ mol<sup>-1</sup>      **(C)** 462.5 KJ mol<sup>-1</sup>      **(D)** 925 KJ mol<sup>-1</sup>
35. Reactions involving gold have been of particular interest to alchemists. Consider the following reactions,  
 $\text{Au}(\text{OH})_3 + 4 \text{ HCl} \longrightarrow \text{HAuCl}_4 + 3 \text{ H}_2\text{O}, \quad \Delta H = -28 \text{ kcal}$   
 $\text{Au}(\text{OH})_3 + 4 \text{ HBr} \longrightarrow \text{HAuBr}_4 + 3 \text{ H}_2\text{O}, \quad \Delta H = -36.8 \text{ kcal}$   
 In an experiment, there was an absorption of 0.44 kcal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of HCl. Then, the fraction of  $\text{HAuBr}_4$  converted into  $\text{HAuCl}_4$  (percentage conversion)  
**(A)** 5%      **(B)** 6%      **(C)** 7%      **(D)** 8%

36. The heat of formation of  $C_2H_5OH(l)$  is  $-66$  kcal/mole. The heat of combustion of  $CH_3OCH_3(g)$  is  $-348$  kcal/mole.  $\Delta H_f$  for  $H_2O$  and  $CO_2$  are  $-68$  kcal/mole and  $-94$  kcal/mole respectively. Then, the  $\Delta H$  for the isomerisation reaction  $C_2H_5OH(l) \longrightarrow CH_3OCH_3(g)$ , and  $\Delta E$  for the same are at  $T = 25^\circ C$
- (A)  $\Delta H = 18$  kcal/mole,  $\Delta E = 17.301$  kcal/mole  
 (B)  $\Delta H = 22$  kcal/mole,  $\Delta E = 21.408$  kcal/mole  
 (C)  $\Delta H = 26$  kcal/mole,  $\Delta E = 25.709$  kcal/mole  
 (D)  $\Delta H = 30$  kcal/mole,  $\Delta E = 28.522$  kcal/mole
37. The average Xe-F bond energy is  $34$  kcal/mol, first I.E. of Xe is  $279$  kcal/mol, electron affinity of F is  $85$  kcal/mol & bond dissociation energy of  $F_2$  is  $38$  kcal/mol. Then, the enthalpy change for the reaction
- $$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$$
- will be
- (A)  $367$  kcal/mole                      (B)  $425$  kcal/mole                      (C)  $292$  kcal/mole                      (D)  $392$  kcal/mole
38. Caesium chlorides is formed according to the following equation  $Cs(s) + 0.5 Cl_2(g) \rightarrow CsCl(s)$ . The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs and electron affinity of chlorine are  $81.2$ ,  $243.0$ ,  $375.7$  and  $-348.3$   $kJ\ mol^{-1}$ . The energy change involved in the formation of  $CsCl$  is  $-388.6$   $kJ\ mol^{-1}$ . Calculate the lattice energy of  $CsCl$ .
- (A)  $618.7$   $kJ\ mol^{-1}$                       (B)  $1237.4$   $kJ\ mol^{-1}$                       (C)  $-1237.4$   $kJ\ mol^{-1}$                       (D)  $-618.7$   $kJ\ mol^{-1}$
39. The enthalpies of neutralization of a weak base AOH and a strong base BOH by HCl are  $-12250$  cal/ mol and  $-13000$  cal/ mol respectively. When one mole of HCl is added to a solution containing 1 mole of AOH and 1 mole of BOH, the enthalpy change was  $-12500$  cal/ mol. In what ratio the acid is distributed between AOH and BOH?
- (A) 2 : 1                                      (B) 2 : 3                                      (C) 1 : 2                                      (D) None of these
40. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true ?
- (A)  $x = y$                                       (B)  $x = \frac{1}{2}y$                                       (C)  $x = 2y$                                       (D) None of these
41. Enthalpy of polymerisation of ethylene, as represented by the reaction,  $nCH_2=CH_2 \longrightarrow (-CH_2-CH_2-)_n$  is  $-100$  kJ per mole of ethylene. Given bond enthalpy of C=C bond is  $600$   $kJ\ mol^{-1}$ , enthalpy of C-C bond (in kJ mol) will be :
- (A) 116.7                                      (B) 350                                      (C) 700                                      (D) indeterminate
42. The average energy required to break a P - P bond in  $P_4(s)$  into gaseous atoms is  $53.2$   $kcal\ mol^{-1}$ . The bond dissociation energy of  $H_2(g)$  is  $104.2$   $kcal\ mol^{-1}$ ;  $\Delta H_f^0$  of  $PH_3(g)$  from  $P_4(s)$  is  $5.5$   $kcal\ mol^{-1}$ . The P-H bond energy in  $kcal\ mol^{-1}$  is [Neglect presence of Van der Waals forces in  $P_4(s)$ ]
- (A) 85.2                                      (B) 57.6                                      (C) 76.9                                      (D) 63.3

Exercise # 2

Part # I

[Multiple Correct Choice Type Questions]

- Use the given standard enthalpies of formation to determine the heat of reaction of the following reaction :  
 $2\text{LiOH(s)} + \text{CO}_2\text{(g)} \rightarrow \text{Li}_2\text{CO}_3\text{(s)} + \text{H}_2\text{O(l)}$   
 $\Delta H_f^\circ \text{LiOH(s)} = -487.23 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{Li}_2\text{CO}_3\text{(s)} = -1215.6 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{H}_2\text{O(l)} = -285.85 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{CO}_2\text{(g)} = -393.5 \text{ kJ/mole}$   
 (A) +303.4 (B) -133.5 (C) -198.6 (D) +198.6
- $\text{NH}_3\text{(g)} + 3\text{Cl}_2\text{(g)} \rightleftharpoons \text{NCl}_3\text{(g)} + 3\text{HCl(g)} ; -\Delta H_1$   
 $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)} ; \Delta H_2$   
 $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{HCl(g)} ; \Delta H_3$   
 The heat of formation of  $\text{NCl}_3\text{(g)}$  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
- Determine  $\Delta H^\circ$  of the following reaction using the listed heats of formation :  
 $4\text{HNO}_3\text{(l)} + \text{P}_4\text{O}_{10}\text{(s)} \rightarrow 2\text{N}_2\text{O}_5\text{(s)} + 4\text{HPO}_3\text{(s)}$   
 $\Delta H_f^\circ \text{HNO}_3\text{(l)} = -174.1 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{N}_2\text{O}_5\text{(s)} = -43.1 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{P}_4\text{O}_{10}\text{(s)} = -2984.0 \text{ kJ/mole}$   
 $\Delta H_f^\circ \text{HPO}_3\text{(s)} = -948.5 \text{ kJ/mole}$   
 (A) -176.3 (B) -199.8 (C) +276.2 (D) -242.4
- 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 hydrogen.  
 (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)  $2x_1 - x_1 - \frac{x_2}{2} - x_4$
- Use the given bond enthalpy data to estimate the  $\Delta H^\circ$  (kJ) for the following reaction.  
 (C-H = 414 kJ, H-Cl = 431 kJ, Cl-Cl = 243 kJ, C-Cl = 331 kJ).  
 $\text{CH}_4\text{(g)} + 4\text{Cl}_2\text{(g)} \rightarrow \text{CCl}_4\text{(g)} + 4\text{HCl(g)}$   
 (A) 620 (B) 330 (C) 420 (D) 105
- For which of the following change  $\Delta H \neq \Delta E$  ?  
 (A)  $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$  (B)  $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$   
 (C)  $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$  (D)  $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightarrow 2\text{NH}_3\text{(g)}$
- $\Delta H_f$  of which of the following reactions is zero ?  
 (A)  $\text{H}_2\text{(g)} \rightarrow 2\text{H}^+\text{(aq)} + 2\text{e}^-$  (B)  $2\text{H(g)} + \text{aq} \rightarrow 2\text{H}^+\text{(aq)} + 2\text{e}^-$   
 (C)  $2\text{H(g)} \rightarrow 2\text{H}^+\text{(g)} + 2\text{e}^-$  (D)  $\text{H}_2\text{(g)} + \text{aq} \rightarrow 2\text{H}^+\text{(aq)} + 2\text{e}^-$

8.  $\Delta H_f^\circ$  of water is  $-285.8 \text{ kJ mol}^{-1}$ . If enthalpy of neutralisation of monoacid strong base is  $-57.3 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ$  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)  $-114.25 \text{ kJ mol}^{-1}$
9. 4 grams of sodium hydroxide pellets were dissolved in  $100 \text{ cm}^3$  of water. The temperature before adding the sodium hydroxide pellets was  $25^\circ\text{C}$ , and after adding the pellets it was  $35^\circ\text{C}$ . Calculate the enthalpy change in  $\text{kJ/mole}$  of the reaction (Specific heat capacity of water =  $4.2 \text{ J/K/g}$ )  
 (A)  $42 \text{ kJ/mole}$       (B)  $4.2 \text{ kJ/mole}$       (C)  $4200 \text{ kJ/mole}$       (D) none
10.  $50.0 \text{ mL}$  of  $0.10 \text{ M HCl}$  is mixed with  $50.0 \text{ mL}$  of  $0.10 \text{ M NaOH}$ . The solution temperature rises by  $3.0^\circ\text{C}$ . Calculate the enthalpy of neutralization per mol of  $\text{HCl}$ .  
 (A)  $-2.5 \times 10^2 \text{ kJ}$       (B)  $-1.3 \times 10^2 \text{ kJ}$       (C)  $-8.4 \times 10^1 \text{ kJ}$       (D)  $-6.3 \times 10^1 \text{ kJ}$
11. Which of the following statements is (are) correct ?  
 (A) the reaction between the strong acid and strong base takes place with the evolution of heat  
 (B)  $\Delta H_{\text{neut.}}$  of weak acid/strong base is less than the  $\Delta H_{\text{neut.}}$  of strong acid/strong base  
 (C)  $\Delta H_{\text{neut.}}$  of strong acid/strong base is equal to the  $\Delta H$  of formation of  $\text{H}_2\text{O}(\text{l})$  from its ions in the aqueous medium  
 (D)  $\Delta H_{\text{neut. (weak acid/strong base)}} - \Delta H_{\text{neut. (strong acid/strong base)}} = \Delta H_{\text{ioni (weak acid)}}$
12. The standard enthalpies of formation of  $\text{CO}_{2(\text{g})}$  and  $\text{HCOOH}(\text{l})$  are  $-393.7 \text{ kJ/mol}$  and  $-409.2 \text{ kJ/mol}$  respectively :-  
 (A)  $-393.7 \text{ kJ/mol}$  is the enthalpy change for the reaction  $\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$   
 (B) the enthalpy change for the reaction  $\text{CO}_{2(\text{g})} + \text{H}_{2(\text{g})} \rightarrow \text{HCOOH}_{(\text{l})}$  would be  $-15.5 \text{ kJ/mol}$   
 (C) the enthalpy change for the reaction  

$$\text{H}_2\text{O} + \text{CO} \rightarrow \text{HCOOH} \text{ is } -409.2 \text{ kJ/mol}$$
  
 (D) the enthalpy change for the reaction  

$$\text{H}_{2(\text{g})} + \text{CO}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{CO}_{(\text{g})} \text{ is } -409.2 \text{ kJ/mol}$$
13. Ethanol can undergoes decomposition to form two sets of products ?  

$$\text{C}_2\text{H}_5\text{OH}(\text{g}) \longrightarrow \begin{cases} 1 \text{ } \text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) & \Delta H^\circ = 45.54 \text{ kJ} \\ 2 \text{ } \text{CH}_3\text{CHO}(\text{g}) + \text{H}_2(\text{g}) & \Delta H^\circ = 68.91 \text{ kJ} \end{cases}$$
  
 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 energy 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)  $57.22 \text{ kJ}$
14. Reactions involving gold have been of particular interest to a chemist. Consider the following reactions,  

$$\text{Au}(\text{OH})_3 + 4 \text{HCl} \longrightarrow \text{HAuCl}_4 + 3 \text{H}_2\text{O}, \quad \Delta H = -28 \text{ kcal}$$

$$\text{Au}(\text{OH})_3 + 4 \text{HBr} \longrightarrow \text{HAuBr}_4 + 3 \text{H}_2\text{O}, \quad \Delta H = -36.8 \text{ kcal}$$
  
 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)  $50\%$

## CHEMISTRY FOR JEE MAIN & ADVANCED

15. Which of the following statement is (are) correct ?
- (A) for an exothermic reactions,  $\sum \Delta H_f^\circ$  (products) <  $\sum \Delta H_f^\circ$  (reactants)
- (B)  $\sum \Delta H_f^\circ$  of  $\text{CO}_2(\text{g})$  is same as the  $\Delta H_{\text{comb.}}^\circ$  of carbon graphite
- (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
16. Which of the reaction defines molar  $\Delta H_f^\circ$ ?
- (A)  $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \longrightarrow \text{CaCO}_3(\text{s})$
- (B)  $\frac{1}{2} \text{Br}_2(\ell) + \frac{1}{2} \text{H}_2(\text{g}) \longrightarrow \text{HBr}(\text{g})$
- (C)  $\text{N}_2(\text{g}) + 2\text{H}_2(\text{g}) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{NH}_4\text{NO}_3(\text{s})$
- (D)  $\frac{1}{2} \text{I}_2(\text{s}) + \frac{1}{2} \text{H}_2(\text{g}) \longrightarrow \text{HI}(\text{g})$
17. Consider the reactions
- (i)  $\text{S}(\text{rhombic}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}), \Delta H_1$
- (ii)  $\text{S}(\text{monoclinic}) + 3/2 \text{O}_2(\text{g}) \longrightarrow \text{SO}_3(\text{g}), \Delta H_2$
- (iii)  $\text{S}(\text{rhombic}) + \text{O}_3(\text{g}) \longrightarrow \text{SO}_3(\text{g}), \Delta H_3$
- (iv)  $\text{S}(\text{monoclinic}) + \text{O}_3(\text{g}) \longrightarrow \text{SO}_3(\text{g}), \Delta H_4$
- (A)  $\Delta H_1 < \Delta H_2 < \Delta H_4$  (magnitude only)
- (B)  $\Delta H_1 < \Delta H_3 < \Delta H_4$  (magnitude only)
- (C)  $\Delta H_1 < \Delta H_2 = \Delta H_3 < \Delta H_4$  (magnitude only)
- (D)  $\Delta H_1 + \Delta H_4 = \Delta H_2 + \Delta H_3$

### Part # II

### [Assertion & Reason Type Questions]

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

- (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
- (B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1
- (C) Statement-1 is true, Statement-2 is false
- (D) Statement-1 is false, Statement-2 is true
- (E) Both Statements are false
1. **Statement-1** : Heat of neutralisation of perchloric acid,  $\text{HClO}_4$ , with  $\text{NaOH}$  is same as that of  $\text{HCl}$  with  $\text{NaOH}$ .  
**Statement-2** : Both  $\text{HCl}$  and  $\text{HClO}_4$  are strong acids.
2. **Statement-1** : In the following reaction :  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$ ;  $\Delta H = \Delta U - RT$   
**Statement-2** :  $\Delta H$  is related to  $\Delta U$  by the equation,  $\Delta H = \Delta U + \Delta n_g RT$
3. **Statement-I** : Heat of neutralisation of  $\text{HF}(\text{aq.})$ , a weak acid, with  $\text{NaOH}(\text{aq.})$  is more than 13.7 kcal, in an exothermic reaction.  
**Statement-II** : Some heat is lost in the ionisation of a weak acid.
4. **Statement-I**: Enthalpy changes are positive when  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and salts like  $\text{NaCl}$ ,  $\text{KCl}$ , etc., which do not form hydrates are dissolved in water. But enthalpy changes are negative when anhydrous salts capable of forming hydrates are dissolved in water.  
**Statement-II**: The difference in the behaviour is due to large differences in the molecular weight of hydrated and anhydrous salts. The substances with larger molecular weights usually show positive enthalpy changes on dissolution.

5. **Statement-I :** Enthalpy of neutralization of  $\text{CH}_3\text{COOH}$  by  $\text{NaOH}$  is less than that of  $\text{HCl}$  by  $\text{NaOH}$ .  
**Statement-II :** Enthalpy of neutralization of  $\text{CH}_3\text{COOH}$  is less because of the absorption of heat in the ionization process.
6. **Statement-I :** As temperature increases, heat of reaction also increases for exothermic as well as for endothermic reactions.  
**Statement-II :**  $\Delta H$  varies with temperature as given by  $\Delta H_2(\text{at } T_2) = \Delta H_1(\text{at } T_1) + \Delta C_p(T_2 - T_1)$
7. **Statement-I :** Heat of combustion is always negative.  
**Statement-II :** Heat of combustion is used to calculate of fuels.
8. **Statement-I :** Enthalpy of formation of  $\text{HCl}$  is equal to bond energy of  $\text{HCl}$ .  
**Statement-II :** Enthalpy of formation and bond energy both involve the formation of one mole of  $\text{HCl}$  from the elements.
9. **Statement-I :** Enthalpy of atomization is the heat of reaction  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$ .  
**Statement-II :** Gaseous molecules are far apart of each other due to less attraction.
10. **Statement-I :** The enthalpy of formation of  $\text{H}_2\text{O}(\text{l})$  is greater than that of  $\text{H}_2\text{O}(\text{g})$ .  
**Statement-II :** Enthalpy change is negative for the condensation reaction,  $\text{H}_2\text{O}(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$ .

Exercise # 3

Part # I

[Matrix Match Type Questions]

1. **Column-I**
- (A)  $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$
- (B)  $C(s, \text{graphite}) \longrightarrow C(g)$
- (C)  $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$
- (D)  $CH_4(g) \longrightarrow C(g) + 4H(g)$
- Column-II**
- (p)  $\Delta H^\circ_{\text{combustion}}$
- (q)  $\Delta H^\circ_{\text{formation}}$
- (r)  $\Delta H^\circ_{\text{atomization}}$
- (s)  $\Delta H^\circ_{\text{sublimation}}$
2. List equation/law (in Column I) with statement (in Column II) :
- Column-I**
- (A) Arrhenius equation
- (B) Kirchhoff equation
- (C) Second law of thermodynamics
- (D) Hess's law of constant heat summation
- Column-II**
- (p) Variation of enthalpy of a reaction with temperature
- (q) Variation of rate constant with temperature
- (r) Entropy of an isolated system tends to increase and reach a maximum value
- (s) Enthalpy change in a reaction is always constant and independent of the manner in which the reaction occurs.
3. Match the reaction (In Column I) with relation between  $\Delta H$  and  $\Delta E$  (in Column II) :
- Column-I**
- (A)  $C(s) + O_2(g) \longrightarrow CO_2(g)$
- (B)  $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
- (C)  $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g)$
- (D)  $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2$
- (E)  $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
- Column-II**
- (p)  $\Delta H = \Delta E + RT$
- (q)  $\Delta H = \Delta E$
- (r)  $\Delta H = \Delta E - 2RT$
- (s)  $\Delta H = \Delta E + 2RT$
- (t)  $\Delta H = \Delta E - RT$
4. **Column-I**
- (A)  $S(g) + O_2(g) \longrightarrow SO_2(g)$ ;  $\Delta H$
- (B)  $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$ ;  $\Delta H$
- (C)  $NaOH(s) + aq \longrightarrow NaOH(aq)$ ;  $\Delta H$
- (D)  $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$ ;  $\Delta H$
- Column-II**
- (p) Heat of solution
- (p) Heat of neutralisation
- (p) Heat of formation
- (s) Heat of combustion

Part # II

[Comprehension Type Questions]

Comprehension # 1

The commercial production of "Water gas" utilises the endothermic reaction  $C(s) + H_2O(g) \rightarrow H_2(g) + CO(g)$ . The heat required for this reaction is generated by combustion of coal to  $CO_2$  using stoichiometric amount of air. (79%  $N_2$  by volume and 21%  $O_2$  by volume). The superheated steam undergoes 75% conversion. Using the following data, answer the question that follows

$$\Delta H_f[CO(g)] = -110.53 \text{ kJ.mol}; \Delta H_f[H_2O(g)] = -241.81 \text{ kJ/mol}; \Delta H_f[CO_2(g)] = -314.0 \text{ kJ/mol}$$

1. The amount of heat liberated when one litre of product gases are burnt at 373 K and at 1 atm is
- (A)  $\cong 3.6 \text{ kJ}$                       (B)  $\cong 3.9 \text{ kJ}$                       (C)  $\cong 4.43 \text{ kJ}$                       (D)  $\cong 5.34 \text{ kJ}$



2. Match the gas and percentage of each gas in one litre product gases.

Gas	Percentage
(I) N <sub>2</sub>	(A) ≈ 23.1
(II) CO <sub>2</sub>	(B) ≈ 36.4
(III) H <sub>2</sub>	(C) ≈ 7.7
(IV) H <sub>2</sub> O	(D) ≈ 9.7
(A) (I-a), (II-b), (III-c), (IV-d)	(B) (I-b), (II-a), (III-d), (IV-c)
(C) (I-c), (II-d), (III-a), (IV-c)	(D) (I-b), (II-d), (III-a), (IV-c)

### Comprehension # 2

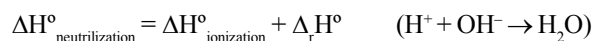
Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is



$\Delta H^\circ_{\text{ionization}}$  of aqueous solution of strong acid and strong base is zero.

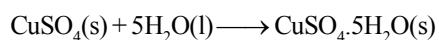
When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base



- If enthalpy of neutralization of CH<sub>3</sub>COOH by NaOH is -49.86 kJ/mol then enthalpy of ionization of CH<sub>3</sub>COOH is:  
 (A) 5.98 kJ/mol                      (B) -5.98 kJ/mol                      (C) 105.7 kJ/mol                      (D) None of these
- What is  $\Delta H^\circ$  for complete neutralization of strong diacidic base A(OH)<sub>2</sub> by HNO<sub>3</sub>?  
 (A) -55.84 kJ                      (B) -111.68 kJ                      (C) 55.84 kJ/mol                      (D) None of these
- Under the same condition how many mL of 0.1 M NaOH and 0.05 M H<sub>2</sub>A (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature :  
 (A) 25 : 75                      (B) 50 : 50                      (C) 75 : 25                      (D) 66.66 : 33.33

### Comprehension # 3

The hydration enthalpy of anhydrous copper (II) sulphate is defined as the heat absorbed or evolved when one mole of anhydrous solid is converted to one mole of crystalline hydrated solid.



It cannot be measured directly.

In an experiment to determine the hydration enthalpy indirectly, 4 g of the anhydrous solid were added to 50 g of water and the rise in temperature was 8 degrees. When 4 g of the hydrated solid was added to 50 g of water the fall in temperature was 1.3 degrees.

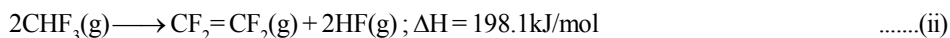
- What is the heat produced when 4 g of anhydrous solid is added to 50 g of water.  
 (A) 400 kJ                      (B) 1672 kJ                      (C) 200 kJ                      (D) 836 kJ
- What is the enthalpy of solution of anhydrous copper (II) sulphate in kJ/mol.  
 (A) 69.9472 kJ/mol                      (B) 4054.375 kJ/mol                      (C) 139.8948 kJ/mol                      (D) 8108.750 kJ/mol
- Given that the enthalpy of solution of the hydrated copper (II) sulphate is +11.3 kJ/mol, what is the enthalpy of hydration of the anhydrous solid.  
 (A) 97.321 kJ/mol                      (B) -97.321 kJ/mol                      (C) -77.971 kJ/mol                      (D) 77.971 kJ/mol

## Comprehension # 4

The industrial preparation of a polymer, PTFE, is based on the synthesis of the monomer  $\text{CF}_2 = \text{CF}_2$ , which is produced according to reaction (i) below :



The monomer  $\text{CF}_2 = \text{CF}_2$  is also obtained by reaction (ii) below :



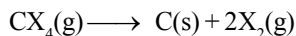
Consider the information below to answer the questions:

Compound	$\Delta H_f$	Molecule X-X	$\Delta(X-X)$
HCl(g)	-92.3	F-F	154.7
CHClF <sub>2</sub> (g)	-485.2	Cl-Cl	246.7
CF <sub>2</sub> =CF <sub>2</sub> (g)	-658.3		
CF <sub>4</sub>	-679.6		
CCl <sub>4</sub>	-106.6		

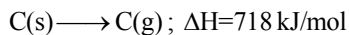
1. The enthalpy change for reaction (i).

(A) 100.23 kJ/mol    (B) 127.5 kJ/mol  
(C) -127.5 kJ/mol     (D) -100.23 kJ/mol

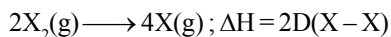
2. (i) Use the expressions



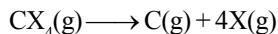
$$\Delta H = -\Delta H_f$$



and



where X = F, Cl, to the enthalpy change for the two processes



What is the average C-X bond energies for the species  $\text{CX}_4(\text{g})$  (where X = F, Cl).

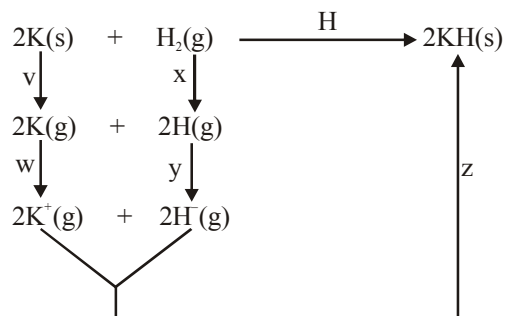
(A) 329.5 kJ/mol, 426.75 kJ/mol  
(B) 426.75 kJ/mol, 329.5 kJ/mol  
(C) -329.5 kJ/mol, -426.75 kJ/mol  
(D) -426.75 kJ/mol, -329.5 kJ/mol

- (ii) Given that the C-H bond energy is 416.1 kJ/mol, the order of relative chemical reactivities of C-H, C-F, and C-Cl bonds.

(A) C-H > C-Cl > C-F  
(B) C-F > C-Cl > C-H  
(C) C-Cl > C-H > C-F  
(D) C-Cl > C-F > C-H

## Comprehension # 5

The Born Haber cycle below represents the energy changes occurring at 298K when KH is formed from its elements



$$\Delta H_{\text{atomisation K}} = 90 \text{ kJ/mol}$$

$$\Delta H_{\text{ionisation K}} = 418 \text{ kJ/mol}$$

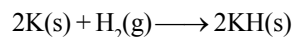
$$\Delta H_{\text{dissociation H}} = 436 \text{ kJ/mol}$$

$$\Delta H_{\text{electron affinity H}} = -78 \text{ kJ/mol}$$

$$\Delta H_{\text{lattice KH}} = -710 \text{ kJ/mol}$$

1. In terms of the letters v to z write down expressions for

(i)  $\Delta H$  for the reaction



(ii)  $\Delta H_f$  of K

(iii)  $\Delta H_{\text{electron affinity}}$  of H

(iv)  $\Delta H_{\text{lattice}}$  of KH(s)

2. Which of v to y is

(i) The most exothermic .....

(ii) The most endothermic .....

3. Calculate the value of  $\Delta H$  showing all your working.

4. Calculate the  $\Delta H_f$  of KH(s).

5. Write a balanced equation for the reaction of KH with water.

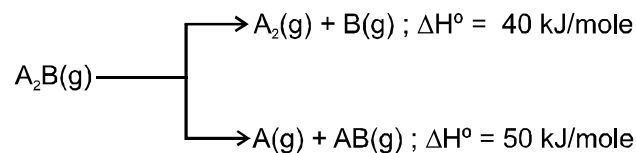
6. On complete reaction with water, 0.1 g of KH gave a solution requiring 25 cm<sup>3</sup> of 0.1M HCl for neutralisation. Calculate the relative atomic mass of potassium from this information.

## Exercise # 4

### [Subjective Type Questions]

- Why is the enthalpy of sublimation equal to the sum of enthalpy of fusion and enthalpy of vaporisation ?
- For a chemical reaction,  $\Delta C_p$  is negative ( $\Delta C_p < 0$ ).  
The heat required to increase temperature of reactants of this reaction by a certain amount =  $q_1$  and heat required to increase temperature of products of the same reaction by same amount =  $q_2$ , Relate  $q_1$  and  $q_2$
- The specific heats of iodine vapour and solid are  $0.031 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  and  $0.055 \text{ cal g}^{-1} \text{ }^\circ\text{C}^{-1}$  respectively. If heat of sublimation of iodine is  $24 \text{ cal/g}$  at  $200^\circ\text{C}$ , what is its value at  $250^\circ\text{C}$  ?
- Predict the standard reaction enthalpy of  $2 \text{ NO}_2(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g})$  at  $100^\circ\text{C}$ .  $\Delta H^\circ$  at  $25^\circ\text{C}$  is  $-57.2 \text{ kJ mol}^{-1}$   $C_p(\text{NO}_2) = 37.2 \text{ J mol}^{-1} \text{ K}^{-1}$   $C_p(\text{N}_2\text{O}_4) = 77.28 \text{ J mol}^{-1} \text{ K}^{-1}$ .
- Classify the following processes as exothermic or endothermic :  
(A) Burning of a match stick (B) Melting of ice  
(C) Molten metal solidifies (D) Reaction between Na and  $\text{H}_2\text{O}$   
(E) Rubbing alcohol evaporates.
- Diborane is a potential rocket fuel which undergoes combustion according to the reaction  
$$\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \longrightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g})$$
  
From the following data, calculate the enthalpy change for the combustion of diborane  
$$2\text{B}(\text{s}) + (3/2)\text{O}_2(\text{g}) \longrightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ mol}^{-1}$$
  
$$\text{H}_2(\text{g}) + (1/2)\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -286 \text{ kJ mol}^{-1}$$
  
$$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = 44 \text{ kJ mol}^{-1}$$
  
$$2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow \text{B}_2\text{H}_6(\text{g}) \quad \Delta H = 36 \text{ kJ mol}^{-1}$$
- Find out the heat evolved in combustion if 112 litres (at STP) of water gas (mixture of equal volume of  $\text{H}_2(\text{g})$  and  $\text{CO}(\text{g})$ ).  
$$\text{H}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = -241.8 \text{ kJ}$$
  
$$\text{CO}(\text{g}) + 1/2 \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) \quad \Delta H = -283 \text{ kJ}$$
- If  $\text{H}_2 + 1/2 \text{O}_2 \longrightarrow \text{H}_2\text{O}$ ,  $\Delta H = -68 \text{ kcal}$   
 $\text{K} + \text{H}_2\text{O} \longrightarrow \text{KOH}(\text{aq}) + 1/2 \text{H}_2$ ,  $\Delta H = -48 \text{ kcal}$   
 $\text{KOH} + \text{water} \longrightarrow \text{KOH}(\text{aq})$ ,  $\Delta H = -14 \text{ kcal}$   
Find the heat of formation of KOH.
- One litre sample of a mixture of  $\text{CH}_4$  and  $\text{O}_2$  measured at  $25^\circ\text{C}$  and 740 torr, was allowed to react at constant pressure in a calorimeter. The complete combustion of  $\text{CH}_4$  to  $\text{CO}_2$  and water caused a temperature rise in calorimeter of  $0.667 \text{ K}$ . Calculate mole % of  $\text{CH}_4$  in original mixture.  
[Given : Heat of combustion of  $\text{CH}_4$  is  $-210.8 \text{ Kcal/mol}$ . Total heat capacity of the calorimeter =  $1260 \text{ cal/K}$ ]
- The heat of combustion of ethyl alcohol is  $-300 \text{ kcal}$ . If the heats of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-94.3$  and  $-68.5 \text{ kcal}$  respectively, calculate the heat of formation of ethyl alcohol.
- 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  $\text{H}_3\text{NSO}_2$ .  $\Delta H_f^\circ(\text{NH}_3) = -46.11 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{SO}_2) = -296.83$
- When  $12.0 \text{ g}$  of carbon (graphite) reacted with oxygen to form  $\text{CO}$  and  $\text{CO}_2$  at  $25^\circ\text{C}$  and constant pressure,  $313.8 \text{ kJ}$  of heat was released and no carbon remained. If  $\Delta H_f^\circ(\text{CO}, \text{g}) = -110.5 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -393.5 \text{ kJ mol}^{-1}$ , calculate the mass of oxygen consumed.

13. Substance  $A_2B(g)$  can undergoes decomposition to form two set of products :



If the molar ratio of  $A_2(g)$  to  $A(g)$  is 5 : 3 in a set of product gases, calculate the energy involved in the decomposition of 1 mole of  $A_2B_2$ ,

14. Calculate the standard enthalpy of solution of  $\text{AgCl}(s)$  in water  $\Delta H_f^\circ(\text{AgCl}, s) = -127.07 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^\circ(\text{Ag}^+, \text{aq}) = 105.58$ ,  $\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = 167.16$
15. The  $\Delta H_f^\circ(\text{KF}, s)$  is  $-563 \text{ kJ mol}^{-1}$ . The ionization enthalpy of  $\text{K}(g)$  is  $419 \text{ kJ mol}^{-1}$ . and the enthalpy of sublimation of potassium is  $88 \text{ kJ mol}^{-1}$ . The electron affinity of  $\text{F}(g)$  is  $322 \text{ kJ mol}^{-1}$  and  $\text{F-F}$  bond enthalpy is  $158 \text{ kJ mol}^{-1}$ . Calculate the lattice enthalpy of  $\text{KF}(S)$ .  
The give data are as follows :
16. The heats of neutralization of  
(i)  $\text{CHCl}_2-\text{COOH}$  by  $\text{NaOH}$  is 12830 cal; (ii)  $\text{HCl}$  by  $\text{NaOH}$  is 13680 calories,  
(iii)  $\text{NH}_4\text{OH}$  by  $\text{HCl}$  is 12270 calories.  
What is the heat of neutralization of dichloro acetic acid by  $\text{NH}_4\text{OH}$  ? Calculate also the heats of ionization of dichloro acetic acid &  $\text{NH}_4\text{OH}$ .
17. Calculate the heat of neutralisation from the following data. 200 mL of 1M  $\text{HCl}$  is mixed with 400 mL of 0.5 M  $\text{NaOH}$ . The temperature rise in calorimeter was found to be  $4.4^\circ\text{C}$ . Water equivalent of calorimeter was found to be  $4.4^\circ\text{C}$ . Water equivalent of calorimeter is 12 g and specific heat is 1 cal/ml/degree for solution.
18. Calculate  $\Delta H_r^\circ$  for the reaction  $\text{CH}_2\text{Cl}_2(g) \longrightarrow \text{C}(g) + 2\text{H}(g) + 2\text{Cl}(g)$ . The average bond enthalpies of  $\text{C-H}$  and  $\text{C-Cl}$  bonds are  $414 \text{ kJ mol}^{-1}$  and  $330 \text{ kJ mol}^{-1}$ .
19. Calculate the enthalpy change ( $\Delta H$ ) of the following reaction  
 $2\text{C}_2\text{H}_2(g) + 5\text{O}_2(g) \longrightarrow 4\text{CO}_2(g) + 2\text{H}_2\text{O}(g)$  given average bond enthalpies of various bonds, i.e.,  $\text{C-H}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{O}=\text{O}$ ,  $\text{C}=\text{O}$ ,  $\text{O-H}$  as 414, 814, 499, 724 and 640  $\text{kJ mol}^{-1}$  respectively.
20. Estimate the average  $\text{S-F}$  bond enthalpy in  $\text{SF}_6$ . The values of standard enthalpy of formation of  $\text{SF}_6(g)$ ,  $\text{S}(g)$  and  $\text{F}(g)$  are :  $-1100$ , 275 and 80  $\text{kJ mol}^{-1}$  respectively.
21. Calculate the bond energy of  $\text{Cl-Cl}$  bond from the following data :  
 $\text{CH}_4(g) + \text{Cl}_2(g) \longrightarrow \text{CH}_3\text{Cl}(g) + \text{HCl}(g)$ ;  $\Delta H = -100.3 \text{ kJ}$ . Also the bond enthalpies of  $\text{C-H}$ ,  $\text{C-Cl}$ ,  $\text{H-Cl}$  bonds are 413, 326 and 431  $\text{kJ mol}^{-1}$  respectively.
22. Calculate free energy change for the reaction at  $27^\circ\text{C}$   
 $\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{H-Cl}(g)$   
by using the bond energy and energy data  
Bond energies of  $\text{H-H}$ ,  $\text{Cl-Cl}$  and  $\text{H-Cl}$  bonds are 435  $\text{kJ mol}^{-1}$ , 240  $\text{kJ mol}^{-1}$  and 430  $\text{kJ mol}^{-1}$  respectively. Standard entropies of  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 131, 223 and 187  $\text{JK}^{-1} \text{ mol}^{-1}$  respectively.
23. Find the standard enthalpy of combustion of hydrazine using the following thermochemical reactions.  
(i)  $2\text{NH}_3(g) + 3\text{N}_2\text{O}(g) \rightarrow 4\text{N}_2(g) + 3\text{H}_2\text{O}(l) + 1011 \text{ kJ}$   
(ii)  $\text{N}_2\text{O}(g) + 3\text{H}_2(g) \rightarrow \text{N}_2\text{H}_4(l) + \text{H}_2\text{O}(l) + 317 \text{ kJ}$   
(iii)  $4\text{NH}_3(g) + \text{O}_2(g) \rightarrow 2\text{N}_2\text{H}_4(l) + 2\text{H}_2\text{O}(l) + 286 \text{ kJ}$   
(iv)  $\text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l) + 286 \text{ kJ}$

Also find  $\Delta H_f^\circ(\text{N}_2\text{H}_4)$ . Is  $\text{N}_2\text{H}_4$  an endothermic compound?

## CHEMISTRY FOR JEE MAIN & ADVANCED

24. For reduction of ferric oxide by hydrogen,  $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{H}_2\text{O}(\ell)$  ;  
 $\Delta H_{300}^\circ = -35 \text{ kJ}$ . The reaction was found to be too exothermic. To be convenient, it is desirable that  $\Delta H^\circ$  should be at the most  $-26 \text{ kJ}$ . At what temperature is it possible ?  
 $C_p[\text{Fe}_2\text{O}_3] = 105$ ,  $C_p[\text{Fe}(\text{s})] = 25$ ,  $C_p[\text{H}_2\text{O}(\ell)] = 75$ ,  $C_p[\text{H}_2(\text{g})] = 29$  (all are in J/mol)
25. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.  
 (i) 18 gm of graphite on complete combustion evolve 590 KJ heat  
 (ii) 15889 KJ heat is required to dissociate all the molecules of 1 litre water into  $\text{H}_2$  and  $\text{O}_2$ .  
 (iii) The heat of formation of liquid benzene is 50 kJ/mol  
 (iv) Density of  $\text{C}_6\text{H}_6(\ell) = 0.87 \text{ gm/ml}$
26. Given the following reactions :  
 I :  $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ ,  $\Delta H_{\text{I}} = 16.18 \text{ kcal}$   
 II :  $\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{N}_2\text{O}_4(\text{g})$ ,  $\Delta H_{\text{II}} = 2.31 \text{ kcal}$   
 Which is more stable between  $\text{N}_2\text{O}_4$  &  $\text{NO}_2$  at low temperature
27. When 0.36g of glucose was burned in a bomb calorimeter (Heat capacity  $640 \text{ JK}^{-1}$ ) the temperature rise by 10 K. Calculate the standard molar enthalpy of combustion.
28. Use the equations  
 $(C_p)_C = 1.1 + 4.8 \times 10^{-3}T - 1.2 \times 10^{-6}T^2$   
 $(C_p)_{\text{O}_2} = 6.26 + 2.746 \times 10^{-3}T - 0.770 \times 10^{-6}T^2$   
 $(C_p)_{\text{CO}} = 6.60 + 1.20 \times 10^{-3}T$   
 to find the temperature interval within which the  $\Delta H$  of the reaction  $\text{C} + \frac{1}{2}\text{O}_2 = \text{CO}$  does not depend on the temperature.
29. If the enthalpy of formation and enthalpy of solution of  $\text{HCl}(\text{g})$  are  $-92.3 \text{ kJ/mol}$  and  $-75.14 \text{ kJ/mol}$  respectively then find enthalpy of formation of  $\text{Cl}^-(\text{aq})$  :
30. Calculate the enthalpy change when infinitely dilute solution of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  are mixed.  $\Delta H_f^\circ$  for  $\text{Ca}^{+2}(\text{aq})$ ,  $\text{CO}_3^{2-}(\text{aq})$  and  $\text{CaCO}_3(\text{s})$  are  $-129.80$ ,  $161.65$ ,  $-288.50 \text{ kcal mol}^{-1}$  respectively.
31. For the reaction,  $\text{cis-2butene} \longrightarrow \text{trans-2butene}$  and  $\text{cis-2butene} \rightarrow 1\text{-butene}$ ,  $\Delta H = -950 \text{ cal/mol}$  and  $\Delta H = 1800 \text{ cal/mol}$  respectively. The heat of combustion of 1-butene is  $-650 \text{ kcal/mol}$ . Determine the heat of combustion of trans-2-butene. Also calculate the bond energy of  $\text{C}=\text{C}$  bond in trans-2-butene. Given B.E. of  $\text{C}=\text{O} = 196$ ,  $\text{O}-\text{H} = 110$ ,  $\text{O}=\text{O} = 118$ ,  $\text{C}-\text{C} = 80$  and  $\text{C}-\text{H} = 98 \text{ kcal/mol}$  respectively.  $\Delta H_v(\text{H}_2\text{O}) = 11 \text{ kcal/mol}$ .
32. Using the data (all values in  $\text{kJ}\cdot\text{mol}^{-1}$  at  $25^\circ\text{C}$ ) given below:  
 (A) Enthalpy of polymerisation of ethylene =  $-72$  (kJ per mole of ethylene)  
 (B) Enthalpy of formation of benzene ( $\ell$ ) =  $49 \text{ KJ/mole}$   
 (C) Enthalpy of vaporization of benzene( $\ell$ ) =  $144 \text{ KJ/mole}$   
 (D) Resonance energy of benzene =  $-152 \text{ KJ/mole}$   
 (E) Heat of formation of gaseous atoms from elements in their standard states  $\text{H} = 436$ ,  $\text{C} = 715$ .  
 (F) Average bond energy of  $\text{C}-\text{H} = 415$ , calculate the bond energy of  $\text{C}-\text{C}$  and  $\text{C}=\text{C}$ .
33. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is  $-56.1 \text{ kJ mol}^{-1}$ . If the enthalpy of ionization of the acid is  $1.5 \text{ kJ mol}^{-1}$  and enthalpy of neutralization of the strong acid with a strong base is  $-57.3 \text{ kJ equiv}^{-1}$ , what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

## Exercise # 5

## Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

1. The enthalpies of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283$   $\text{kJ mol}^{-1}$  respectively. The enthalpy of formation of carbon monoxide per mole is [AIEEE 2004]  
 (A) 110.5 kJ (B) 676.5 kJ (C)  $-676.5$  kJ (D)  $-110.5$  kJ
2. If the bond dissociation energies of XY,  $X_2$  and  $Y_2$  (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and  $\Delta H_f$  for the formation of XY is  $-200$   $\text{kJ mol}^{-1}$ . The bond dissociation energy of  $X_2$  will be [AIEEE 2005]  
 (A) 100  $\text{kJ mol}^{-1}$  (B) 200  $\text{kJ mol}^{-1}$  (C) 300  $\text{kJ mol}^{-1}$  (D) 800  $\text{kJ mol}^{-1}$
3. The enthalpy changes for the following processes are listed below: [AIEEE 2006]  
 $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g}); 242.3 \text{ kJ mol}^{-1}$  ;  $\text{I}_2(\text{g}) \rightarrow 2\text{I}(\text{g}); 151.0 \text{ kJ mol}^{-1}$   
 $\text{ICl}(\text{g}) \rightarrow \text{I}(\text{g}) + \text{Cl}(\text{g}); 211.3 \text{ kJ mol}^{-1}$  ;  $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g}); 62.76 \text{ kJ mol}^{-1}$   
 Given that the standard state for iodine and chlorine are  $\text{I}_2(\text{s})$  and  $\text{Cl}_2(\text{g})$ , the standard enthalpy of formation for  $\text{ICl}(\text{g})$  is  
 (A)  $-16.8 \text{ kJ mol}^{-1}$  (B)  $+16.8 \text{ kJ mol}^{-1}$  (C)  $+244.8 \text{ kJ mol}^{-1}$  (D)  $-14.6 \text{ kJ mol}^{-1}$
4.  $(\Delta H - \Delta U)$  for the formation of carbon monoxide (CO) from its elements at 298 K is [AIEEE 2006]  
 ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )  
 (A)  $1238.78 \text{ J mol}^{-1}$  (B)  $-2477.57 \text{ J mol}^{-1}$  (C)  $2477.57 \text{ J mol}^{-1}$  (D)  $-1238.78 \text{ J mol}^{-1}$
5. The standard enthalpy of formation ( $\Delta H_f^\circ$ ) at 398 K for methane,  $\text{CH}_4(\text{g})$  is  $74.8 \text{ kJ mol}^{-1}$ . The additional information required to determine the average energy for C - H bond formation would be : [AIEEE 2007]  
 (A) the dissociation energy of  $\text{H}_2$  and enthalpy of sublimation of carbon  
 (B) latent heat of vapourisation of methane  
 (C) the first four ionization energies of carbon and electron gain enthalpy of hydrogen  
 (D) the dissociation energy of hydrogen molecule,  $\text{H}_2$
6. On the basis of the following thermochemical data : ( $\Delta_f G^\circ_{\text{H}^+(\text{aq})} = 0$ ) [AIEEE 2009]  
 $\text{H}_2\text{O}(\ell) \rightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H = 57.32 \text{ kJ}$   
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\ell); \Delta H = -286.20 \text{ kJ}$   
 The value of enthalpy of formation of  $\text{OH}^-$  ion at  $25^\circ\text{C}$  is :  
 (A)  $-228.88 \text{ kJ}$  (B)  $+228.88 \text{ kJ}$  (C)  $-343.52 \text{ kJ}$  (D)  $-22.88 \text{ kJ}$
7. 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)  $-964 \text{ kJ mol}^{-1}$  (B)  $+352 \text{ kJ mol}^{-1}$  (C)  $+1056 \text{ kJ mol}^{-1}$  (D)  $-1102 \text{ kJ mol}^{-1}$
8. The value of enthalpy change ( $\Delta H$ ) for the reaction  
 $\text{C}_2\text{H}_5\text{OH}(\ell) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$   
 at  $27^\circ\text{C}$  is  $-1366.5 \text{ kJ mol}^{-1}$ . The value of internal energy change for the above reaction at this temperature will be : [AIEEE 2011]  
 (A)  $-1369.0 \text{ kJ}$  (B)  $-1364.0 \text{ kJ}$  (C)  $-1361.5 \text{ kJ}$  (D)  $-1371.5 \text{ kJ}$
9. Consider the reaction :  
 $4\text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{N}_2\text{O}_5(\text{g}); \Delta_r H = -111 \text{ kJ}$   
 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  $\Delta_r H$  value will be:  
 (given,  $\Delta H$  of sublimation for  $\text{N}_2\text{O}_5$  is  $54 \text{ kJ mol}^{-1}$ ) [AIEEE 2011]  
 (A)  $+54 \text{ kJ}$  (B)  $+219 \text{ kJ}$  (C)  $-219 \text{ kJ}$  (D)  $-165 \text{ kJ}$

## CHEMISTRY FOR JEE MAIN & ADVANCED

10. For complete combustion of ethanol,  $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$ , 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 MAIN 2014]  
 (A)  $-1460.50 \text{ kJ mol}^{-1}$       (B)  $-1350.50 \text{ kJ mol}^{-1}$       (C)  $-1366.95 \text{ kJ mol}^{-1}$       (D)  $-1361.95 \text{ kJ mol}^{-1}$
11. The following reaction is performed at  $298 \text{ K}$  [JEE MAIN 2015]  
 $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$   
 The standard free energy of formation of  $NO(g)$  is  $86.6 \text{ kJ/mol}$  at  $298 \text{ K}$ . What is the standard free energy of formation of  $NO_2(g)$  at  $298 \text{ K}$ ? ( $K_p = 1.6 \times 10^{12}$ )  
 (A)  $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$       (B)  $0.5[2 \times 86,600 - R(298 \ln(1.6 \times 10^{12}))]$   
 (C)  $R(298 \ln(1.6 \times 10^{12}) - 86600)$       (D)  $86600 + R(298) \ln(1.6 \times 10^{12})$
12. 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  $\text{kJ}$ ) of carbon monoxide per mole is:  
 (A)  $676.5$       (B)  $-676.5$       (C)  $-110.5$       (D)  $110.5$

### Part # II

### [Previous Year Questions][IIT-JEE ADVANCED]

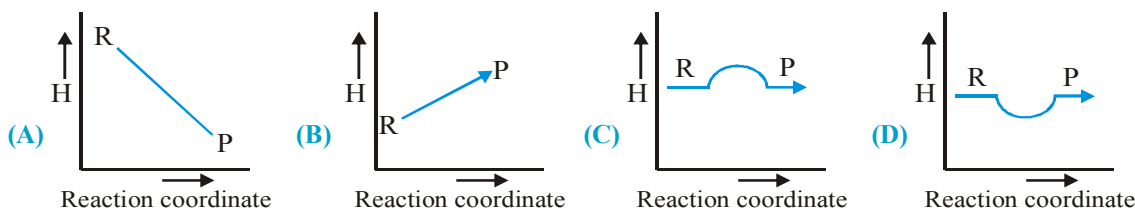
1. In a constant volume calorimeter,  $3.5 \text{ g}$  of a gas with molecular weight  $28$  was burnt in excess oxygen at  $298.0 \text{ K}$ . The temperature of the calorimeter was found to increase from  $298.0 \text{ K}$  to  $298.45 \text{ K}$  due to the combustion process. Given that the heat capacity of the calorimeter is  $2.5 \text{ kJ K}^{-1}$ , the numerical value for the enthalpy of combustion of the gas in  $\text{kJ mol}^{-1}$  is. [JEE 2009]
2. The species which by definition has **ZERO** standard molar enthalpy of formation at  $298 \text{ K}$  is : [JEE 2010]  
 (A)  $Br_2(g)$       (B)  $Cl_2(g)$       (C)  $H_2O(g)$       (D)  $CH_4(g)$
3. The bond energy (in  $\text{kcal mol}^{-1}$ ) of a  $C-C$  single bond is approximately : [JEE 2010]  
 (A)  $1$       (B)  $10$       (C)  $100$       (D)  $1000$
4. Using the data provided, calculate the multiple bond energy ( $\text{kJ mol}^{-1}$ ) of a  $C \equiv C$  bond  $C_2H_2$ . That energy is (take the bond energy of a  $C-H$  bond as  $350 \text{ kJ mol}^{-1}$ ) [JEE 2012]  
 $2C(s) + H_2(g) \longrightarrow C_2H_2(g) \quad \Delta H = 225 \text{ kJ mol}^{-1}$   
 $2C(s) \longrightarrow 2C(g) \quad \Delta H = 1410 \text{ kJ mol}^{-1}$   
 $H_2(g) \longrightarrow 2H(g) \quad \Delta H = 330 \text{ kJ mol}^{-1}$   
 (A)  $1165$       (B)  $837$       (C)  $865$       (D)  $815$
5. The standard enthalpies of formation of  $CO_2(g)$ ,  $H_2O(l)$  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)  $+16.11 \text{ kJ}$



## MOCK TEST

### SECTION - I : STRAIGHT OBJECTIVE TYPE

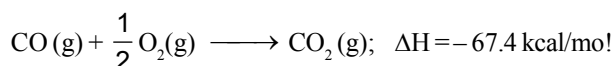
1. Which plot represent an exothermic reaction ?



2. If  $\Delta H$  is the change in enthalpy and  $\Delta E$  the change in internal energy accompanying a gaseous reaction

- (A)  $\Delta H$  is always greater than  $\Delta E$   
 (B)  $\Delta H < \Delta E$  only if the number of moles of the products is greater than the number of the reactants  
 (C)  $\Delta H$  is always less than  $\Delta E$   
 (D)  $\Delta H < \Delta E$  only if the number of moles of the products is less than the number of moles of the reactants

3.  $C(s) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H = -94.3 \text{ kcal/mol}$



Calculate  $\Delta H$  for  $C(s) \longrightarrow C(g)$  in kcal/mol.

- (A) 171                      (B) 154                      (C) 117                      (D) 145
4. The standard heat of combustion of solid boron is equal to :  
 (A)  $\Delta H^\circ_f(B_2O_3)$                       (B)  $1/2 \Delta H^\circ_f(B_2O_3)$                       (C)  $2\Delta H^\circ_f(B_2O_3)$                       (D)  $1/2 \Delta H^\circ_f(B_2O_3)$
5. The heat of combustion of sucrose ( $C_{12}H_{22}O_{11}$ ) is 1350 kcal. How much of heat will be liberated when 17.1 g of sucrose is burnt ?  
 (A) 67.5 kcal                      (B) 13.5 kcal                      (C) 40.5 kcal                      (D) 25.5 kcal
6. One mole of anhydrous  $MgCl_2$  dissolves in water and liberates 25 cal/mol of heat.  $\Delta H_{\text{hydration}}$  of  $MgCl_2 = -30 \text{ cal/mol}$ . Heat of dissolution of  $MgCl_2 \cdot H_2O$  is  
 (A) +5 cal/mol                      (B) -5 cal/mol                      (C) 55 cal/mol                      (D) -55 cal/mol
7. Enthalpy of neutralization of  $H_3PO_3$  acid is  $-106.68 \text{ kJ/mol}$  using NaOH. If enthalpy of neutralization of HCl by NaOH is  $-55.84 \text{ kJ/mol}$ . Calculate  $\Delta H_{\text{ionization}}$  of  $H_3PO_3$  into its ions :  
 (A) 50.84 kJ/mol                      (B) 5 kJ/mol                      (C) 2.5 kJ/mol                      (D) None of these
8. The bond dissociation energy of gaseous  $H_2$ ,  $Cl_2$  and HCl are 104, 58 and 103 kcal  $\text{mol}^{-1}$  respectively. The enthalpy of formation for HCl gas will be  
 (A) -44.0 kcal                      (B) -22.0 kcal                      (C) 22.0 kcal                      (D) 44.0 kcal
9. Heat of hydrogenation of ethene is  $x_1$  and that of benzene is  $x_2$ . Hence, resonance energy is :  
 (A)  $x_1 - x_2$                       (B)  $x_1 + x_2$                       (C)  $3x_1 - x_2$                       (D)  $x_1 - 3x_2$
10. AB,  $A_2$  and  $B_2$  are diatomic molecules. If the bond enthalpies of  $A_2$ , AB &  $B_2$  are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from  $A_2$  and  $B_2$  is  $-100 \text{ kJ/mol}^{-1}$ . What is the bond enthalpy of  $A_2$ .  
 (A) 400 kJ/mol                      (B) 200 kJ/mol                      (C) 100 kJ/mol                      (D) 300 kJ/mol

SECTION - II : MULTIPLE CORRECT ANSWER TYPE

11. Which of the reaction defines molar  $\Delta H_f^\circ$ ?
- (A)  $\text{CaO(s)} + \text{CO}_2\text{(g)} \longrightarrow \text{CaCO}_3\text{(s)}$       (B)  $\frac{1}{2} \text{Br}_2(\ell) + \frac{1}{2} \text{H}_2\text{(g)} \longrightarrow \text{HBr(g)}$
- (C)  $\text{N}_2\text{(g)} + 2\text{H}_2\text{(g)} + \frac{3}{2} \text{O}_2\text{(g)} \longrightarrow \text{NH}_4\text{NO}_3\text{(s)}$       (D)  $\frac{1}{2} \text{I}_2\text{(s)} + \frac{1}{2} \text{H}_2\text{(g)} \longrightarrow \text{HI(g)}$
12. Consider the reactions
- (i)  $\text{S (rhombic)} + 3/2 \text{O}_2\text{(g)} \longrightarrow \text{SO}_3\text{(g)}, \Delta H_1$
- (ii)  $\text{S (monoclinic)} + 3/2 \text{O}_2\text{(g)} \longrightarrow \text{SO}_3\text{(g)}, \Delta H_2$
- (iii)  $\text{S (rhombic)} + \text{O}_3\text{(g)} \longrightarrow \text{SO}_3\text{(g)}, \Delta H_3$
- (iv)  $\text{S (monoclinic)} + \text{O}_3\text{(g)} \longrightarrow \text{SO}_3\text{(g)}, \Delta H_4$
- (A)  $\Delta H_1 < \Delta H_2 < \Delta H_4$  (magnitude only)      (B)  $\Delta H_1 < \Delta H_3 < \Delta H_4$  (magnitude only)
- (C)  $\Delta H_1 < \Delta H_2 = \Delta H_3 < \Delta H_4$  (magnitude only)      (D)  $\Delta H_1 + \Delta H_4 = \Delta H_2 + \Delta H_3$

SECTION - III : ASSERTION AND REASON TYPE

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

- (A) Statement-1 is true, Statement-2 is true and Statement-2 is correct explanation for Statement-1
- (B) Statement-1 is true, Statement-2 is true and Statement-2 is not correct explanation for Statement-1
- (C) Statement-1 is true, Statement-2 is false
- (D) Statement-1 is false, Statement-2 is true
- (E) Both Statements are false

13. **Statement-1** : Heat of neutralisation of perchloric acid,  $\text{HClO}_4$ , with  $\text{NaOH}$  is same as that of  $\text{HCl}$  with  $\text{NaOH}$ .  
**Statement-2** : Both  $\text{HCl}$  and  $\text{HClO}_4$  are strong acids.
14. **Statement-1** : In the following reaction :  $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ ;  $\Delta H = \Delta U - RT$   
**Statement-2** :  $\Delta H$  is related to  $\Delta U$  by the equation,  $\Delta H = \Delta U + \Delta n_g RT$

SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension # 1

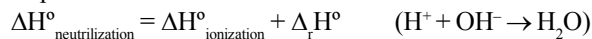
Enthalpy of neutralization is defined as the enthalpy change when 1 mole of acid/base is completely neutralized by base/acid in dilute solution.

For strong acid and strong base neutralization net chemical change is



$\Delta H_{\text{ionization}}^\circ$  of aqueous solution of strong acid and strong base is zero.

When a dilute solution of a weak acid or base is neutralized, the enthalpy of neutralization is some what less because of the absorption of heat in the ionization of the weak acid or base, for weak acid/base



15. If enthalpy of neutralization of  $\text{CH}_3\text{COOH}$  by  $\text{NaOH}$  is  $-49.86 \text{ kJ/mol}$  then enthalpy of ionization of  $\text{CH}_3\text{COOH}$  is:  
 (A)  $5.98 \text{ kJ/mol}$       (B)  $-5.98 \text{ kJ/mol}$       (C)  $105.7 \text{ kJ/mol}$       (D) None of these
16. What is  $\Delta H^\circ$  for complete neutralization of strong diacidic base  $\text{A(OH)}_2$  by  $\text{HNO}_3$  ?  
 (A)  $-55.84 \text{ kJ}$       (B)  $-111.68 \text{ kJ}$       (C)  $55.84 \text{ kJ/mol}$       (D) None of these

17. Under the same condition how many mL of 0.1 M NaOH and 0.05 M  $H_2A$  (strong diprotic acid) solution should be mixed for a total volume of 100 mL produce the highest rise in temperature :
- (A) 25 : 75                      (B) 50 : 50                      (C) 75 : 25                      (D) 66.66 : 33.33

## SECTION - V : MATRIX - MATCH TYPE

- | 18. | Column - I   | Column - II                               |
|-----|--|---|
|     | (A) $C(s, \text{graphite}) + O_2(g) \longrightarrow CO_2(g)$ | (p) $\Delta H^\circ_{\text{combustion}}$  |
|     | (B) $C(s, \text{graphite}) \longrightarrow C(g)$             | (q) $\Delta H^\circ_{\text{formation}}$   |
|     | (C) $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$     | (r) $\Delta H^\circ_{\text{atomization}}$ |
|     | (D) $CH_4(g) \longrightarrow C(g) + 4H(g)$                   | (s) $\Delta H^\circ_{\text{sublimation}}$ |

## SECTION - VI : SUBJECTIVE TYPE

19. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.
- (i) 18 gm of graphite on complete combustion evolve 590 KJ heat  
(ii) 15889 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 50 kJ/mol  
(iv) Density of  $C_6H_6(l) = 0.87 \text{ gm/ml}$
20. Given the following reactions :
- I :  $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g), \Delta H_I = 16.18 \text{ kcal}$   
II :  $N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g), \Delta H_{II} = 2.31 \text{ kcal}$
- Which is more stable between  $N_2O_4$  &  $NO_2$  at low temperature
21. When 0.36g of glucose was burned in a bomb calorimeter (Heat capacity  $640 \text{ JK}^{-1}$ ) the temperature rise by 10 K. Calculate the standard molar enthalpy of combustion.

**ANSWER KEY**

**EXERCISE - 1**

1. D 2. D 3. A 4. D 5. B 6. D 7. D 8. A 9. A 10. B 11. C 12. D 13. A  
 14. B 15. A 16. A 17. B 18. C 19. C 20. A 21. B 22. C 23. B 24. A 25. C 26. C  
 27. A 28. C 29. D 30. B 31. B 32. A 33. A 34. C 35. A 36. B 37. C 38. D 39. A  
 40. B 41. B 42. C

**EXERCISE - 2 : PART # I**

1. B 2. A 3. B 4. B 5. C 6. D 7. D  
 8. A 9. A 10. A 11. A, B, C, D 12. A, B 13. B 14. C  
 15. A, B, D 16. B, C, D 17. A, B, D

**PART # II**

1. A 2. D 3. C 4. C 5. A 6. D 7. B 8. A 9. D 10. A

**EXERCISE - 3 : PART # I**

1.  $A \rightarrow (p, q), B \rightarrow (q, r, s), C \rightarrow (p), D \rightarrow (r)$   
 2.  $A \rightarrow (q), B \rightarrow (p), C \rightarrow (r), D \rightarrow (s)$   
 3.  $A \rightarrow (q), B \rightarrow (r), C \rightarrow (s), D \rightarrow (p), E \rightarrow (t)$   
 4.  $A \rightarrow (r), B \rightarrow (s), C \rightarrow (p), D \rightarrow (q)$

**PART # II**

- Comprehension # 1 :** 1. A 2. D  
**Comprehension # 2 :** 1. A 2. B 3. B  
**Comprehension # 3 :** 1. B 2. A 3. C  
**Comprehension # 4 :** 1. B 2. (i) B (ii) C  
**Comprehension # 5 :** 1. (i)  $\Delta H = (v + w + x + y + z)$  (ii)  $w/2$  (iii)  $y/2$  (iv)  $z/2$   
 2. (i)  $y$  (ii)  $w$   
 3.  $-124 \text{ kJ/mol}$  4.  $-62 \text{ kJ/mol}$  6. 39

## EXERCISE - 5 : PART # I

1. B 2. D 3. B 4. A 5. A 6. A 7. B 8. B 9. D 10. C 11. B 12. C

## PART # II

1. 9 2. B 3. C 4. D 5. D

## MOCK TEST

1. A                    2. D                    3. D                    4. B                    5. A  
6. A                    7. B                    8. B                    9. C                    10. A  
11. B,C,D    12. A,B,D    13. A                    14. D                    15. A  
16. B                    17. B  
18.  $A \rightarrow (p,q), B \rightarrow (q,r,s), C \rightarrow (p), D \rightarrow (r)$