

## Topic : Thermodynamics &amp; Thermochemistry

## Type of Questions

Single choice Objective ('-1' negative marking) Q.1 to Q.5

(3 marks, 3 min.)

M.M., Min.

[15, 15]

Subjective Questions ('-1' negative marking) Q.6 to Q.10

(4 marks, 5 min.)

[20, 25]

1. Given the following standard enthalpies of reaction :
  - Enthalpy of formation of water = - 68.3 kCal/mol
  - Enthalpy of combustion of acetylene = - 310.6 kCal/mol
  - Enthalpy of combustion of ethylene = - 337.2 kCal/mol

Calculate the heat of reaction for the hydrogenation of acetylene at constant volume and 25°C.
2. The internal energy change of the combustion of  $C_6H_6$  (g) and  $C_2H_2$  (g) at 300 K are - 800 Kcal/mole and - 300 Kcal/mole respectively. What is the enthalpy of polymerisation of  $C_2H_2$  (g) to  $C_6H_6$  (g) per mole of  $C_6H_6$  (g) produced ?  $C_6H_6$  (g),  $C_2H_2$  (g) and  $C_2H_6$  (g) behave ideally.  $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$ .
   
 (A) - 100 K Cal/mol      (B) - 101.2 K Cal/mol      (C) - 98.8 K Cal/mol      (D) - 103.6 K Cal/mol
3. The dissociation energy of  $CH_4$  is 360 kCal/mol and of ethane is 620 kCal/mol. Calculate C – C bond energy.
4. Estimate  $\Delta_r H$  for  $2 C_4H_{10}$  (g)  $\rightarrow C_8H_{18}$  (g) +  $H_2$  (g). Given bond energy of C – C and C – H are 347 and 441  $\text{kJmol}^{-1}$ . The enthalpy of formation of H (g) atom is  $217.5 \text{ kJmol}^{-1}$ .
5. The average energy required to break a P – P bond in  $P_4$  (s) into gaseous atoms is 53.3 kcal  $\text{mol}^{-1}$ . The bond dissociation energy of  $H_2$ (g) is 104.3  $\text{kcalmol}^{-1}$ ;  $\Delta H_f^0$  of  $PH_3$ (g) from  $P_4$ (s) is 5.4  $\text{kcalmol}^{-1}$ . The P-H bond energy in kcal  $\text{mol}^{-1}$  is : [Neglect presence of Vanderwaal forces in  $P_4$ (s)]
   
 (A) 85.2      (B) 57.6      (C) 77      (D) 63.3
6. Using the data (all values are in kilocalories per mole at 25°C) given below, calculate the bond energy of C – H and C – C bonds.
 

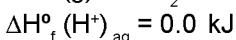
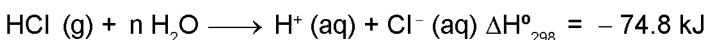
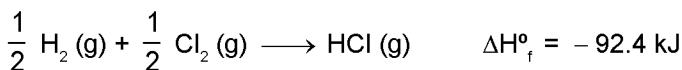
$\Delta H_f^0$ combustion (ethane) g = - 372 ;	$\Delta H_f^0$ combustion (propene) g = - 530
$\Delta H^0$ for C (graphite) $\rightarrow C$ (g) = 172 ;	Bond energy of H – H bond = 104
$\Delta H_f^0$ of $H_2O$ (l) = - 68 ;	$\Delta H_f^0$ of $CO_2$ (g) = - 94
7. Determine the enthalpy change of the reaction:  $C_3H_8$  (g) +  $H_2$  (g)  $\rightarrow C_2H_6$  (g) +  $CH_4$  (g) at 25 °C , using the given enthalpy of combustion values under standard condition :
 

Compound	$H_2$ (g)	$CH_4$ (g)	$C_2H_6$ (g)	C (graphite)
$\Delta H^0$ (kJ/mole)	- 286	- 890	- 1560	- 393.5

The standard enthalpy of formation of  $C_3H_8$  (g) is - 104 kJ/mole.
8. The standard molar enthalpies of formation of cyclohexane ( $\ell$ ) and benzene ( $\ell$ ) at 25° C are -156 and +49  $\text{KJ mol}^{-1}$  respectively. The standard enthalpy of hydrogenation of cyclohexene ( $\ell$ ) at 25°C is -119  $\text{KJ mol}^{-1}$ . Use these data to estimate the resonance energy of benzene in  $\text{KJ mol}^{-1}$ .
9. The enthalpy of solution of anhydrous  $CuSO_4$  is - 15.9 kCal/mol and that of  $CuSO_4 \cdot 5 H_2O$  is 2.8 kCal/mol. Calculate the enthalpy of hydration of  $CuSO_4$ .
10. Calculate  $\Delta H_f^0$  for chloride ion (aq) from the following data :
 
$$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow HCl(g) \quad \Delta H_f^0 = - 92.4 \text{ kJ}$$

$$HCl(g) + n H_2O \rightarrow H^+(aq) + Cl^-(aq) \quad \Delta H_{298}^0 = - 74.8 \text{ kJ}$$

$$\Delta H_f^0(H^+)_{aq} = 0.0 \text{ kJ}$$



# Answer Key

## DPP No. # 52

1. - 41.104 kCal. 2. (B) 3. 80 kCal/mol. 4. 100 kJ/mol. 5. (C)  
6. C - H = 99 kCal ; C - C = 82 kCal 7. - 56.5 kJ. 8. -152 KJ mol<sup>-1</sup>  
9. - 18.7 kCal 10. - 167.2 kJ/mol.

## Hints & Solutions

### DPP No. # 52

1. - 41.104 kCal.
2.  $C_6H_6(g) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$   $\Delta_r u_1 = -800 \text{ kcal/mole}$   
 $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$   $\Delta_r u_2 = -300 \text{ kcal/mole}$   
 $\therefore 3C_2H_2(g) \longrightarrow C_6H_6(g)$   $\Delta_r u = -100 \text{ kcal/mole}$   
 $\Delta_r H = \Delta_r u + (-2) \times 2 \times 300 \times 10^{-3}$   
 $\Delta_r H = -100 - 1.2 = -101.2 \text{ kcal/mol.}$
3. 80 kCal/mol.
4. 100 kJ/mol.
5.  $P_4(s) \rightarrow 4P(g)$   $\Delta H = 53.2 \times 6$   
 $H_2(g) \rightarrow 2H(g)$   $\Delta H = 104.2$   
 $\frac{1}{4}P_4(s) + \frac{3}{2}H_2(g) \rightarrow PH_3(g)$   $\Delta H = 5.5$   
 $\frac{1}{4} \times 6 \times 53.2 + \frac{3}{2} \times 104.2 - 3\epsilon_{P-H} = 5.5$   
 $\Rightarrow \epsilon_{P-H} = 76.866 \text{ i.e. } 76.9 \text{ kcal mol}^{-1}$
6. C - H = 99 kCal ; C - C = 82 kCal
7. - 56.5 kJ.

8.  $-152 \text{ KJ mol}^{-1}$



$$\Delta H_{\text{calculated}} = 3 \times (-119) = -357 \text{ KJ mol}^{-1}$$

$$\Delta H_{\text{experimental}} = \sum (\Delta H_f^\circ)_{\text{product}} - \sum (\Delta H_f^\circ)_{\text{reactant}}$$

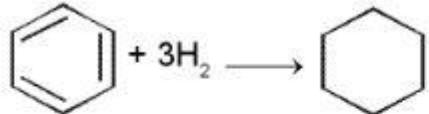
$$\text{or } \Delta H_{\text{expt}} = -156 - (49 + 0) = -205 \text{ KJ mol}^{-1}$$

$$\text{Resonance energy} = -357 - (-205) = -152 \text{ KJ mol}^{-1}$$

9.  $-18.7 \text{ kCal}$

10.  $-167.2 \text{ kJ/mol.}$

8.  $-152 \text{ KJ mol}^{-1}$   
 $-152 \text{ KJ mol}^{-1}$



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