



# THE GURUKUL INSTITUTE

PLOT 5C, 2ND FLOOR, COMPLEX, SEC-13, OPP. JAIPURIA SCHOOL,  
VASUNDHARA, GHAZIABAD (U.P.). CELL: 9810780903

## Thermodynamics & Thermochemistry

### Disorder, Entropy and Second Law of Thermodynamics

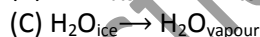
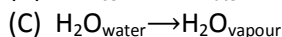
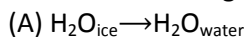
1. The change in entropy with respect to temperature in case of sample is graphically represented below: Carefully analyse the, graph and answer the following:

- What does  $T_1$  and  $T_2$  indicate?
- What does AB curve show?
- What does BC curve show? Why temperature does not change?

2. predict in which of the following, entropy increased/ decreases:

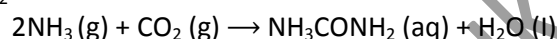
- A liquid crystallizes into a solid.
- Temperature of crystalline solid is raised from 0K to 115 K.
- $2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
- $\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$

3. In which of the following entropy decreases.



4. the enthalpy of vaporization of benzene ( $\text{C}_6\text{H}_6$ ) is  $308 \text{ kJ mol}^{-1}$  at its boiling point ( $80.1^\circ \text{C}$ ). Calculate the entropy change in going from (i) liquid to vapour and (ii) vapour to liquid at  $80.1^\circ \text{C}$ .

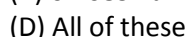
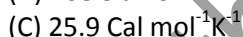
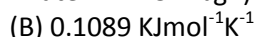
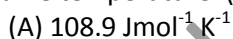
5. calculate the change of entropy  $\Delta_r S_m^\circ$  at 298 K for the reaction in which urea is formed from  $\text{NH}_3$  and  $\text{CO}_2$ .



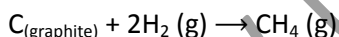
The standard entropy of  $\text{NH}_2\text{CONH}_2$  is  $174.0 \text{ JK}^{-1} \text{ mol}^{-1}$ . For  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  it is 192.3, 213 and  $69.9 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

### Exercise 2:

1. Calculate the entropy change involved in the conversion of one mole of water at 373 K to vapour at the same temperature. (Latent heat of vaporization of water =  $2.257 \text{ kJ g}^{-1}$ )

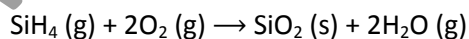


2. Calculate the standard free energy change for the formation of methane at 298K.



Given that  $\Delta H_f^\circ$  of  $\text{CH}_4 = -74.81 \text{ kJ mol}^{-1}$  and  $\Delta S^\circ$  of  $\text{C}_{\text{graphite}}$ ,  $\text{H}_2(\text{g})$  and  $\text{CH}_4(\text{g})$  are  $5.70 \text{ K}^{-1} \text{ mol}^{-1}$ ,  $130.7 \text{ JK}^{-1} \text{ mol}^{-1}$  and  $186.3 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively.

3. Silane,  $\text{SiH}_4$  like methane, burns in air. The product silica (silicon dioxide) is solid quite unlike carbon dioxide.

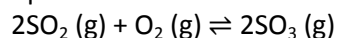


Standard gibbs energy of formation of  $\text{SiO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{SiH}_4$  are 805, -228.6 and  $+52.3$  (all in  $\text{kJ mol}^{-1}$ ) respectively. Calculate the value of  $\Delta_r G^\circ$ .

### Exercise 3:

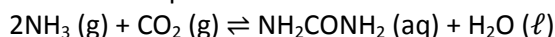
4. The standard Gibbs energies ( $\Delta_f G^\circ$ ) of formation of  $\text{SO}_2(\text{g})$  and  $\text{SO}_3(\text{g})$  are  $-300.0$  and  $-371.1 \text{ kJ mol}^{-1}$  at 300 K respectively.

Calculate  $\Delta G$  and equilibrium constant for the following reaction at 300 K.



5. Calculate  $\Delta_r G^\circ$  for conversion of oxygen to ozone  $3/2\text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$  at 298 K, if  $K_p$  for this conversion is  $2.47 \times 10^{-29}$ .

6. Find out the value of equilibrium constant for the following reaction at 298 K.



Standard Gibbs energy change,  $\Delta_r G^\circ$  at the given temperature is  $-13.6 \text{ kJmol}^{-1}$

- (A) 24  
(C) 240

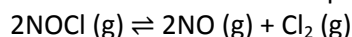
- (C) 12  
(D) 2400

#### Exercise 4.

1. For the equilibrium  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g})$  at 298 K,  $K = 1.8 \times 10^{-7}$ , calculate  $\Delta G^\circ$  for the reaction. ( $R = 8.1314 \text{ JK}^{-1}\text{mol}^{-1}$ )

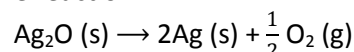
- (A)  $38.484 \text{ KJmol}^{-1}$  (B)  $3.8484 \text{ KJmol}^{-1}$   
(C)  $384.4 \text{ Jmol}^{-1}$  (D) None of these

2. Calculate the value of equilibrium constant,  $K$ , for the reaction at 400 K.



$$(\Delta H^\circ = 80.0 \text{ kJmol}^{-1}, \Delta S^\circ = 120 \text{ JK}^{-1}\text{mol}^{-1} \text{ at } 400 \text{ K}, R = 8.31 \text{ JK}^{-1}\text{mol}^{-1})$$

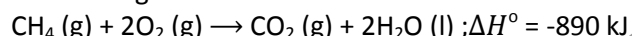
3. For the reaction



$\Delta H$  is  $30.56 \text{ kJmol}^{-1}$  and  $\Delta S$  is  $6.6 \text{ JK}^{-1}\text{mol}^{-1}$  at one atmosphere pressure. Calculate the temperature at which  $\Delta G$  for it will be zero. What will be the direction of reaction at this temperature and at temperatures below this temperature and why?

#### Laws of Thermochemistry

4. from the following data at  $25^\circ \text{C}$



Enthalpy of formation  $\Delta H_f^\circ$  of  $\text{CO}_2$  is  $-393.5 \text{ kJmol}^{-1}$ ,  $\Delta H_f^\circ$  of  $\text{H}_2\text{O}$  is  $-285.9$  and find the enthalpy of formation  $\Delta H_f^\circ$  of  $\text{CH}_4(\text{g})$  and  $\Delta E^\circ$  for its combustion reaction shown above. ( $R = 8.31 \text{ JK}^{-1}\text{mol}^{-1}$ )

5.  $\text{C} + \text{O}_2 \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -94 \text{ Kcals}$   
 $\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}(\text{s}) \quad \Delta H = -26.4 \text{ Kcals}$   
 $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = ?$

6. What is heat evolved using neutralization of HCN by a strong base? Heat of ionization of HCN is  $10.8 \text{ Kcal}$ .

#### Lattice energy of an ionic Crystal

1. What is the expression of lattice energy ( $U$ ) of  $\text{CaBr}_2$  using Born-Haber cycle?  
2. What is the relation between  $\Delta H$  and  $\Delta E$  in this reaction?



- (A)  $\Delta H = \Delta E - RT$  (B)  $\Delta H = \Delta E - \frac{RT}{2}$   
(C)  $\Delta H = \Delta E + RT$  (C)  $\Delta H = \Delta E - 2RT$

#### Exercise 6:

1. For a system  $\text{C}(\text{s}) + \text{O}_2(\text{g}) = \text{CO}_2(\text{g})$  which of the following is correct:

- (A)  $\Delta H = \Delta E$  (B)  $\Delta H > \Delta E$  (C)  $\Delta H < \Delta E$  (D)  $\Delta H = 0$

2.  $\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 3\text{H}_2\text{O} + 6\text{CO}_2(\text{g}) \quad \Delta H = -3264.4 \text{ kJ mole}^{-1}$ . What is the energy evolved when 7.8 gm of benzene is burnt in air at constant temperature and at constant pressure.

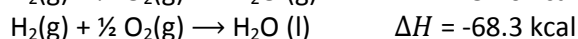
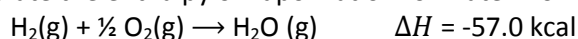
3. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at  $25^\circ \text{C}$  are  $-156$  and  $49 \text{ kJ mol}^{-1}$  respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at  $25^\circ \text{C}$  is  $-119 \text{ kJ mol}^{-1}$ . Use these data to estimate the magnitude of resonance energy of benzene.

#### Bomb Calorimeter

1. Starting with the thermodynamic relationships  $\Delta E = q - P\Delta V$  and  $H = E + PV$  derive the relationship  $\Delta H = qp$ .

#### Problems

1. Calculate the enthalpy of vaporization for water from the following



Also calculate the heat required to change 1 gm H<sub>2</sub>O (l) to H<sub>2</sub>O (g).

2. The standard enthalpy of combustion of H<sub>2</sub>, C<sub>6</sub>H<sub>10</sub> and cyclohexane (C<sub>6</sub>H<sub>12</sub>) are -241, -3800, -3920 kJ mole<sup>-1</sup> at 25° C respectively. Calculate the heat of hydrogenation of cyclohexane.

3. calculate the heat of formation of KOH (s) using the following equations.



4. A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion,  $\Delta H = -2658$  kJ/mol for butane.

5. the heat of solution of anhydrous CuSO<sub>4</sub> is -15.9 kcal and that of CuSO<sub>4</sub>.5H<sub>2</sub>O is 2.8 Kcal. Calculate the heat of hydration of CuSO<sub>4</sub>.

6. Calculate the heat of neutralization from the following data 200 ml of 1M HCl is mixed with 400 ML of 0.5 m NaOH. The temperature rise in calorimeter was found to be 4.4° C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal / ml / degree for solution.

7. Standard heat of formation of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O (l) are - 76.2, - 394.8 and -241.6 kJ mole<sup>-1</sup>. Calculate to amount of heat evolved by burning 1m<sup>3</sup> of CH<sub>4</sub> measured under normal conditions.

8. Calculate the heat of reaction of the hydrogenation of acetylene to ethylene at constant volume at 25° C from the following data

(i) Enthalpy of formation of water = -285.8 kJ mol<sup>-1</sup>

(ii) Enthalpy of combustion of acetylene = - 1299.6 kJ mol<sup>-1</sup>

(iii) Enthalpy of combustion of ethylene = -1410.8 kJ mol<sup>-1</sup>

9. From the following data, calculate the bond enthalpies of C---C and C≡N bonds:

(i) Enthalpy of formation of CH<sub>3</sub>CN = 87.86 kJ mol<sup>-1</sup>

(ii) Enthalpy of formation of C<sub>2</sub>H<sub>6</sub> = -83.68 kJ mol<sup>-1</sup>

(iii) Enthalpy of sublimation of graphite = 719.65 kJ mol<sup>-1</sup>

(iv) Enthalpy of dissociation of nitrogen = 945.58 kJ mol<sup>-1</sup>

(v) Enthalpy of dissociation of hydrogen = 435.14 kJ mol<sup>-1</sup>

(vi) C—H bond enthalpy = 414.22 kJ mol<sup>-1</sup>

10. Calculate the heat of formation of acetone from the following data:

Heat of atomization

H = 52.1 kcal/mol

C = 170.9 kcal / mol

O = 59.6 kcal /mol

Average Bond energies

C—H = 99 kcal

C=O = 81 kcal

C—C = 80 kcal

11. An ideal gas having initial pressure P, volume V and temperature T is allowed to expand adiabatically until its volume becomes 5.66 V while its temperature falls to T/2.

(i) How many degrees of freedom do the gas molecules have?

(ii) Obtain an expression for the work done by the gas during the expansion as a function of the initial pressure P and volume V.

12. A sample of solid naphthalene C<sub>10</sub>H<sub>8</sub>, weighing 0.6 g is burnt to CO<sub>2</sub>(g) and H<sub>2</sub>O( ) in a constant volume calorimeter at 298 K. in this experiment the observed temperature rise of the

calorimeter and its contents is 2.27°C. In a separate experiment. The total heat capacity of the calorimeter was found to be 2556 cal/°C. What is  $\Delta E$  for the combustion of one mole of naphthalene? What is  $\Delta H$  for this reaction. Also calculate the enthalpy of formation of naphthalene.

$$\Delta H_f^\circ (\text{H}_2\text{O}, \dots) = -68.32 \text{ kcal/mol}$$

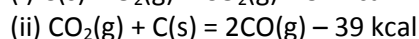
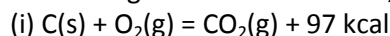
$$\Delta H_f^\circ (\text{CO}_2, \text{g}) = -94.05 \text{ kcal/mol}$$

13. Calculate the resonance energy of acetic acid from the following data:

- (i) Enthalpy of formation of water (l) =  $-286 \text{ kJ mol}^{-1}$
- (ii) Enthalpy of formation of  $\text{CO}_2(\text{g}) = -393.5 \text{ kJ mol}^{-1}$
- (iii) Enthalpy of formation of  $\text{CH}_3\text{CO}_2(\text{g}) = -384.5 \text{ kJ mol}^{-1}$
- (iv) Enthalpy of vapourization of  $\text{H}_2\text{O}(\text{l}) = 168 \text{ kJ mol}^{-1}$
- (v) Enthalpy of dissociation of  $\text{CH}_4(\text{g}) = 1652 \text{ kJ mol}^{-1}$
- (vi) Enthalpy of formation of  $\text{C}_6\text{H}_6(\text{g}) = 90 \text{ kJ mol}^{-1}$
- (vii) Resonance energy of  $\text{C}_6\text{H}_6(\text{g}) = 718.5 \text{ kJ mol}^{-1}$
- (viii) Bond enthalpy of C = C bond =  $617 \text{ kJ mol}^{-1}$
- (ix) Bond enthalpy of C – O bond =  $420 \text{ kJ mol}^{-1}$
- (x) Heat of atomization of gaseous oxygen =  $248 \text{ kJ mol}^{-1}$
- (xi) Heat of atomization of gaseous oxygen =  $217 \text{ kJ mol}^{-1}$

#### OBJECTIVE

1. for the given heat of reaction,



The heat of combustion of  $\text{CO}(\text{g})$  is:

(A) 68 kcal

(B) - 68 kcal

(C) +48 kcal

(D) None

2. The heat of combustion of sucrose,  $\text{C}_{12}\text{H}_{22}\text{O}_{11}(\text{s})$  at constant volume is  $-1348.9 \text{ kcal mol}^{-1}$  at  $25^\circ \text{C}$ , then the heat of reaction at constant pressure, when steam is produced, is

(A)  $-1348.9 \text{ kcal}$

(B)  $-68 \text{ kcal}$

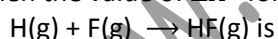
(C)  $+1250 \text{ kcal}$

(D) None

3. For the given reaction



Then the value of  $\Delta H^\circ$  for



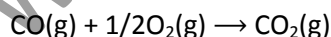
(A) 142 kcal

(B) -132.9 kcal

(C) 132 kcal

(D) 134 kcal

4. At constant temperature and pressure which one of the following statements is correct for the reaction?



(A)  $\Delta H = \Delta E$

(B)  $\Delta H < \Delta E$

(C)  $\Delta H > \Delta E$

(D)  $\Delta H$  is independent physical state of reactant

5. The heats of combustion of yellow phosphorus and red phosphorus are  $-9.19 \text{ kJ}$  and  $-8.78 \text{ kJ}$  respectively, then heat of transition of yellow phosphorus to red phosphorus is

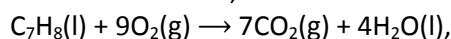
(A)  $-18.69 \text{ kJ}$

(B)  $+1.13 \text{ kJ}$

(C)  $+18.69 \text{ kJ}$

(D)  $-1.13 \text{ kJ}$

6. For the reaction,



the calculated heat of reaction is  $232 \text{ kJ/mol}$  and observed heat of reaction is  $50.4 \text{ kJ/mol}$ , then the resonance energy is

- (A) - 182.2 kJ/mol  
(C) 172 kJ/mol
- (B) + 182.2 kJ/mol  
(D) None

7. Given that

$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ ,  $\Delta H = -115.4$  kcal that the bond energy of H-H and O = O bond respectively is 104 kcal and 119 kcal, then the O—H bond energy in water vapour is

- (A) 110.6 kcal/mol  
(C) 105 kcal/mol
- (B) -110.6 kcal  
(D) none

8. The heat of transition for  $\text{C}_{\text{Diamond}} \rightarrow \text{C}_{\text{amorphous}}$  from the following is

- $\text{C}_{\text{diamond}} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   $\Delta H = -94.3$  kcal  
 $\text{C}_{\text{Diamond}} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   $\Delta H = -97.6$  kcal
- (A) 3.3 kJ/mol  
(C) -3.3 kJ/mol
- (B) 3.3 kcal / mol  
(D) -3.3 kcal/ mol

9. The heat of neutralisation of HCl by NaOH is - 55.9 kJ mol<sup>-1</sup>. If the heat of neutralisation of HCN by NaOH is - 12.1 kJ/mol, the energy of dissociation of HCN is:

- (A) -43.8 kJ  
(C) 68 kJ
- (B) 43.8 kJ  
(D) -68 kJ

10. Heat of neutralization of a strong acid by a strong base is equal to  $\Delta H$  of

- (A)  $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$   
(C)  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$
- (B)  $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$   
(D)  $\text{CH}_3\text{COOH} + \text{NaOH} = \text{CH}_3\text{COONa} + \text{H}_2\text{O}$

### ASSIGNMENTS

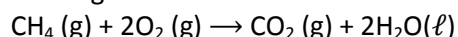
#### Section - I

#### Part - A (Level - I)

- When is the entropy of a perfectly crystalline zero?
- Explain why entropy of a perfectly crystalline substance is less than that of its imperfect crystals.
- Illustrate with an example what is meant by 'Standard free energy of formation' of a compound.
- State the relation between standard free energy change and equilibrium constant of a chemical reaction.
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$  is an endothermic reaction yet it is spontaneous. Explain the reason.
- Define the following terms:
  - State variables of a system
  - Internal energy of a system
- For a reaction,  $K = 1.958 \times 10^{-4}$  at 400 K. what is the value of  $\Delta G^\circ$  at this temperature?  
[ $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ]
- The equilibrium constant at 25°C for the process  $\text{CO}^{3+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq})$  is  $2.0 \times 10^7$ . Calculate the value of  $\Delta G^\circ$  at 25°C. [ $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$ ]. In which direction is the reaction spontaneous when reactants and products are under standard conditions?

9. What is meant by the term 'Free Energy'? What is the necessity of introducing such a function?

56. From the data given below at 298 K for the reaction:



Calculate the enthalpy of formation of  $\text{CH}_4(\text{g})$  at 298 K

Enthalpy of reaction = -890.5 kJ

Enthalpy of formation of  $\text{CO}_2(\text{g}) = -393.5 \text{ kJmol}^{-1}$

Enthalpy of formation  $\text{H}_2\text{O}(\ell) = -286.0 \text{ kJmol}^{-1}$

## Level – II

- The standard heats of formation at 298 K for  $\text{CCl}_4(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{HCl}(\text{g})$  are -25.5, -57.8, -94.1 and -22.1 kcal/mol respectively. Calculate  $\Delta H^\circ$  for the reaction  $\text{CCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g})$ .
- Calculate the standard heat of formation of  $\text{CS}_2(\text{l})$ . Given that the standard heat of combustion of carbon(s), sulphur(s) &  $\text{CS}_2(\text{l})$  are -393.3, -293.72 & -1108.76  $\text{kJ mol}^{-1}$ .
- The bond dissociation energy of gaseous  $\text{H}_2$ ,  $\text{Cl}_2$  and  $\text{HCl}$  are 104, 58, and 103 kcal mole<sup>-1</sup> respectively. Calculate the enthalpy of formation for  $\text{HCl}$  gas.
- An intimate mixture of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}$  is used as solid fuel rocket. Calculate the fuel value per gram and per ml of mixture.  $\Delta H_{\text{Al}_2\text{O}_3} = -399.0$  kcal,  $\Delta H_{\text{Fe}_2\text{O}_3} = 199.0$  kcal, density of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}$  are 5.2 g/ml and 2.7 g/ml respectively.

5. Find the enthalpy of S—S bond from the following data:

- |  |   |
|--|---|
| (i) $\text{C}_2\text{H}_5\text{—S—C}_2\text{H}_5(\text{g})$    | $\Delta H_f^\circ = -147.2 \text{ kJ mol}^{-1}$ |
| (ii) $\text{C}_2\text{H}_5\text{—S—S—C}_2\text{H}_5(\text{g})$ | $\Delta H_f^\circ = -201.9 \text{ kJ mol}^{-1}$ |
| (iii) $\text{S}(\text{g})$                                     | $\Delta H_f^\circ = +222.8 \text{ kJ mol}^{-1}$ |

6. The enthalpy of formation of  $\text{H}_2\text{O}(\text{l})$  is  $-287.7 \text{ kJ mol}^{-1}$  and enthalpy of neutralization of a strong acid and a strong base is  $-56.7 \text{ kJ mol}^{-1}$ . What is the enthalpy of formation of  $\text{OH}^-$  ions?

7. Determine the enthalpy of the reaction

$\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) + \text{CH}_6(\text{g}) + \text{at } 25^\circ \text{C}$ , using the given enthalpy of combustion values under standard conditions.

Compound	$\text{H}_2(\text{g})$	$\text{CH}_4(\text{g})$	$\text{C}_2\text{H}_6(\text{g})$	$\text{C}(\text{graphite})$
$\Delta H^\circ / \text{kJ mol}^{-1}$	-285.8	-890.0	-1560.0	-393.5

The standard enthalpy of formation of  $\text{C}_3\text{H}_8(\text{g})$  is  $-103.8 \text{ kJ / mole}$

8. Calculate the heat of dissociation of  $\text{N}_2\text{O}_4$  into  $\text{NO}_2$  from the data

- |  |                                 |
|--|---------------------------------|
| $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO};$            | $\Delta H = 43.1 \text{ kcal}$  |
| $\text{N}_2 + 2\text{O}_2 \rightarrow \text{N}_2\text{O}_4;$ | $\Delta H = -1.87 \text{ kcal}$ |
| $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2;$          | $\Delta H = 26.1 \text{ kcal}$  |

9. At 400K, the standard enthalpies of formation of  $\text{C}_6\text{H}_5\text{COOH}(\text{s})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are -408, -393 and  $-286 \text{ kJ mol}^{-1}$  respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) constant volume ( $R = 8.31 \text{ J mole}^{-1} \text{ K}^{-1}$ )

10. From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298K. The enthalpy of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and propene (g) are -393.5, -285.8 and  $20.42 \text{ kJ mol}^{-1}$  respectively. The enthalpy of isomerisation of cyclopropane to propene is  $-33.0 \text{ kJ mol}^{-1}$ .

11. Heat of formation of propene is  $-21 \text{ kcal/mol}$ . Heat of sublimation  $\text{C}(\text{graphite})$  is  $170 \text{ kcal}$ . Bond energies of C—H, H—H and C—C bonds are 99, 104 and 80 kcal respectively. Calculate bond energy of C=C in propene.

12. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

13. How much heat is required to change 10g ice at  $0^\circ \text{C}$  to steam at  $100^\circ \text{C}$ ? Latent heat of fusion and vapour for  $\text{H}_2\text{O}$  are 80 cal/g and 540 cal/g respectively. Specific heat of water is 1 cal/g.

14. The heat of combustion of acetylene is 312 kcal. If heat of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are 94.38 and 68.38 kcal respectively, calculate C  $\equiv$  C bond energy. Given that heat of atomization of C and H are 150.0 and 51.5 kcal respectively and C—H bond energy is 93.64 kcal.

15. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as is required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (With X litre/ hour of CH<sub>4</sub> and 6X litre/ hour of O<sub>2</sub>) is to be readjusted for butane, C<sub>4</sub>H<sub>10</sub>. In order to get the same to incomplete combustion, etc are same for both the fuels and gases behave ideally.  
Heats of combustion: CH<sub>4</sub> = 809 kJ/mol, C<sub>4</sub>H<sub>10</sub> = 2878 kJ / mol.

16. The polymerization of ethylene to linear polyethylene is represented by the following reaction  
 $n\text{CH}_2 = \text{CH}_2 \rightarrow (-\text{CH}_2 - \text{CH}_2 -)_n$  (n = large integer value)  
 Calculate the enthalpy of polymerization per mol of enthalpy 298 K if average enthalpies of bond dissociation for C = C and C – C are 590 and 331 kJ mol<sup>-1</sup> respectively.

17. Determine the resonance energy of gaseous benzene from the following data.

If  $\Delta H_{diss}^{\circ}(\text{H}_2, \text{g}) = 435.9 \text{ kJ mol}^{-1}$ ,  $\Delta H_{sub}^{\circ}(\text{C, graphite}) = 718.4 \text{ kJ mol}^{-1}$ ,  
 $\Delta H_f^{\circ}(\text{Benzene, g}) = 82.9 \text{ kJ mol}^{-1}$ ,  $\epsilon_{C=C} = 591.3 \text{ kJ mol}^{-1}$

18. Two moles of a perfect gas undergo the following processes:

- A reversible isobaric expansion from (1.0 atm, 20.0 L) To (1.0 atm, 40.0 L).
  - A reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L).
  - A reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L).
- (i) Sketch with labels each of the processes on the same P–V diagram.  
 (ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.  
 (iii) What will be the values of  $\Delta U$ ,  $\Delta H$  and  $\Delta S$  for the overall process?

#### PART – B

#### Multiple Choice Questions (Single Option correct)

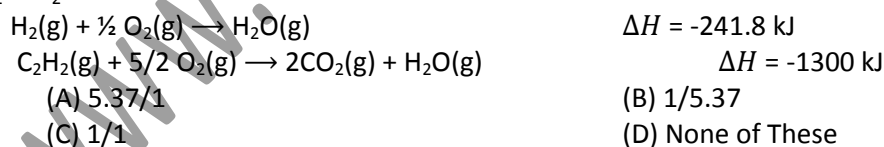
1. In which case of mixing of a strong acid and a base each of 1 N concentration, temperature increase is highest.

- (A) 20 ml acid - 30 ml alkali  
 (B) 40 ml acid – 40 ml alkali  
 (C) 25 ml acid – 25 ml alkali  
 (D) 35 ml acid – 35 ml alkali

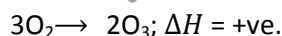
2. The heat of combustion of carbon is 394 kJ/mol. The heat evolved in combustion of  $6.023 \times 10^{22}$  atoms of carbon is

- (A) 3940 kJ  
 (B) 394.0 kJ  
 (C) 39.4 kJ  
 (D) 0.394 kJ

3. Equal volumes of C<sub>2</sub>H<sub>2</sub> & H<sub>2</sub> are combusted under identical condition. The ratio of heat evolved for C<sub>2</sub>H<sub>2</sub> & H<sub>2</sub> is



4. For the reaction



We can say that

- (A) Ozone is more stable than oxygen  
 (B) Ozone is less stable than oxygen and ozone decomposes forming oxygen readily  
 (C) Oxygen is less stable than ozone and oxygen readily forms ozone  
 (D) None

5. When certain amount of ethylene was combusted 6226 kJ/mol heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O<sub>2</sub> (at NTP) that entered into the reaction is

- (A) 296.5 ml  
 (B) 296.5 lit  
 (C) 6226 x 22.4 lit  
 (D) 22.4 lit

6. if total enthalpies of reactants and products are  $H_R$  &  $H_P$  respectively, then for an endothermic reaction.

- (A)  $H_R < H_P$  (B)  $H_R = H_P$   
(C)  $H_R > H_P$  (D)  $H_R \geq H_P$

7. for a system  $C(s) + O_2(g) = CO_2(g)$

- (A)  $\Delta H = \Delta E$  (B)  $\Delta H > \Delta E$   
(C)  $\Delta H < \Delta E$  (D)  $\Delta H = 0$

8. The heat evolved in combustion if 112 litre of water gas at NTP (mixture of equal volume of  $H_2(g)$  and  $CO(g)$ ) is

- $H_2(g) + \frac{1}{2} O_2(g) = H_2O(g)$   $\Delta H = -241.8$  kJ  
 $CO(g) + \frac{1}{2} O_2(g) = CO_2(g)$   $\Delta H = -283$  kJ  
(A) 241.8 kJ (B) 296.5 kJ  
(C) 131.2 kJ (D) 1586 kJ

9. The enthalpy of neutralisation of the given reaction

- $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O + y$  kcal is  
(A) y kcal (B) -y kcal  
(C) + y/2 kcal (D) -y/2 kcal

10. when solute remains in equilibrium with given solvent then

- (A)  $\Delta H_{\text{hydration}} = \text{Lattice energy}$   
(B)  $\Delta H_{\text{hydration}} < \text{Lattice energy}$   
(C)  $\Delta H_{\text{hydration}} > \text{Lattice energy}$   
(D) None of these

11. At equilibrium condition, the value of Gibbs free energy change,  $\Delta G$  is

- (A) Equal to zero (B) Greater than one  
(C) Less than one (D) Equal to one

12. For spontaneous reaction the value of change in Gibbs free energy, ( $\Delta G$ ) is

- (A) Negative (B) Positive  
(C) Greater than one (D) One

13. Which of the following is the heat of combustion?

- (A)  $C(\text{graphite}) + \frac{1}{2} O_2(g) \rightarrow CO(g) + x$  cal  
(B)  $C(\text{diamond}) + O_2(g) \rightarrow CO_2(g) + y$  cal  
(C)  $C(\text{diamond}) + \frac{1}{2} O_2(g) \rightarrow CO(g) + z$  cal  
(D) None

14. Given that

- $A(s) \rightarrow A(l)$   $\Delta H = x$   
 $A(l) \rightarrow A(g)$   $\Delta H = y$

The heat of sublimation of A will be

- (A)  $x - y$  (B)  $x + y$   
(C)  $x$  or  $y$  (D)  $-x + y$

15. Heat of formation of a compound is equal to magnitude to its

- (A) Heat of Reaction  
(B) Heat of decomposition  
(C) Heat of combustion  
(D) Heat of solution

16. Given  $\Delta H_{\text{ioniz}}(\text{HCN}) = 45.2$  kJ mol<sup>-1</sup> &  $\Delta H_{\text{ioniz}}(\text{CH}_3\text{COOH}) = 2.1$  kJ/mol

- (A)  $pK_a(\text{HCN}) = pK_a(\text{CH}_3\text{COOH})$   
(B)  $pK_a(\text{HCN}) > pK_a(\text{CH}_3\text{COOH})$

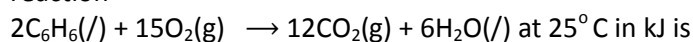


- (C)  $pK_a(\text{HCN}) < pK_a(\text{CH}_3\text{COOH})$   
 (D)  $pK_a(\text{HCN}) = \frac{45.17}{2.07} pK_a(\text{CH}_3\text{COOH})$

17. AB, A<sub>2</sub> and B<sub>2</sub> are diatomic molecules. If the bond enthalpies of A<sub>2</sub>, AB & B<sub>2</sub> are in the ratio 1 : 1 : 0.5 and enthalpy of formation of AB from A<sub>2</sub> and B<sub>2</sub> = 100 kJ/mol<sup>-1</sup>. What is the bond enthalpy of A<sub>2</sub>?

- (A) 400 kJ/mol (B) 200 kJ/mol  
 (C) 100 kJ/mol (D) 300 kJ/mol

18. The difference between the heat of reaction of constant pressure and constant volume for the reaction



- (A) -7.43 (B) 3.72  
 (C) -3.72 (D) 7.43

19. In which case, a reaction is possible at any temperature?

- (A)  $\Delta H < 0, \Delta S > 0$  (B)  $\Delta H < 0, \Delta S < 0$   
 (C)  $\Delta H > 0, \Delta S > 0$  (D) None

### Multiple Choice Questions (Multiple Options Correct)

1. The criteria for the spontaneity of a process are

- (A)  $(dG)_{T,p} < 0$  (B)  $(dE)_{S,V} < 0$   
 (C)  $(dH)_{S,p} < 0$  (D)  $(dS)_{E,V} < 0$

2. Which of the following statements are not correct?

- (A) The standard value of absolute entropy of elementary substance is taken as zero.  
 (B) Work done in isothermal expansion is greater than that in the adiabatic expansion for same increase in volume  
 (C) During adiabatic expansion of a real gas, there is no change in the enthalpy of the system  
 (D) Expansion against vacuum is very large and hence work done is also very large

3. Which of the following relationship are correct?

- (A)  $\frac{\Delta H - \Delta E}{\Delta n \times T} = \text{Constant}$  (B)  $\Delta G = -T\Delta S_{\text{Total}}$   
 (C)  $K = e^{-\Delta G^\circ / RT}$  (D)  $\left[\frac{\partial (\Delta H)}{\partial T}\right]_p = \Delta C_p$

4. Identify the intensive quantities from the following

- (A) Enthalpy (B) Temperature  
 (C) Volume (D) Refractive index

5. Which of the following reactions are endothermic reactions?

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

### Numerical Based

1. The molar heat capacity of water at constant pressure P, is 36 kJ<sup>-1</sup>mol<sup>-1</sup>. When 1 kJ of heat is supplied to 100 gram of water which is free to expand, the increase in temperature of water is kelvin is  
 2. The heat of neutralization of a weak acid with strong base is -5.7 kcal. Then find the enthalpy of dissociation of weak acid in Kcal.

### Comprehension Type

Read The paragraph carefully and answer the following questions

In a fuel cell (device used for producing electricity directly from a chemical reaction), methanol is used as a fuel and oxygen gas is used as an oxidizer. The standard enthalpy of combustion of

methanol is  $-726 \text{ kJmol}^{-1}$ . The standard free energies of formation of  $\text{CH}_3\text{OH}(\ell)$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\ell)$  are  $-166.3$ ,  $-394.4$  and  $-237.1 \text{ kJmol}^{-1}$  respectively.

- The standard free energy change of the reaction will be  
 (A)  $-597.8 \text{ kJmol}^{-1}$  (B)  $-298.9 \text{ kJmol}^{-1}$   
 (C)  $-465.2 \text{ kJmol}^{-1}$  (D)  $-702.3 \text{ kJmol}^{-1}$
- The efficiency of the fuel cell will be  
 (A) 96.7% (B) 66.2%  
 (C) 41.3% (D) 85.1%
- The standard internal energy change of the cell reaction will be  
 (A)  $-727.24 \text{ kJmol}^{-1}$  (B)  $-724.76 \text{ kJmol}^{-1}$   
 (C)  $-728.48 \text{ kJmol}^{-1}$  (D)  $-723.42 \text{ kJmol}^{-1}$

### Match the following

Column - 1	Column - 2
(A) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$	(p) $\Delta S = 0$
(B) $2\text{KI}(\text{aq}) + \text{HgI}_2(\text{aq}) \rightarrow \text{K}_2[\text{HgI}_4](\text{aq})$	(q) $\Delta S < 0$
(C) $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{aq})$	(r) $\Delta H > 0$
(D) $\text{NH}_3(\text{g}) + \text{HCl}(\text{g}) \rightarrow \text{NH}_5\text{Cl}(\text{s})$	(s) $\Delta H < 0$
	(t) $\Delta n_g < 0$

### Section - II

- The enthalpy change for the reaction  $\text{F}_2(\text{g}) + 2\text{HCl}(\text{g}) \rightarrow 2\text{HF}(\text{g}) + \text{Cl}_2(\text{g})$  at 298 K is  $-357.6 \text{ kJmol}^{-1}$ . If the standard enthalpy of formation,  $(\Delta H_f^\circ)$  of HCl is  $-92.3 \text{ kJmol}^{-1}$ , the  $\Delta H_f^\circ$  of HF at 298 K is  
 (A)  $-265.3 \text{ kJmol}^{-1}$  (B)  $+265.3 \text{ kJmol}^{-1}$   
 (C)  $-224.9 \text{ kJmol}^{-1}$  (D)  $-271.1 \text{ kJmol}^{-1}$
- The temperature of 5 ml of a strong acid increases by  $5^\circ \text{C}$  when 5 ml of a strong base is added to it. If 10 ml of each is mixed, temperature should increase by  
 (A)  $5^\circ \text{C}$  (B)  $10^\circ \text{C}$   
 (C)  $15^\circ \text{C}$  (D) cannot be known
- The dissociation energy of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  are respectively 360 & 620 k. cal/mole. The bond energy of C—C is  
 (A) 260 kcal/mole (B) 180 kcal/mole  
 (C) 130 kcal/mole (D) 80 kcal/mole
- If a reaction of  $\Delta H < 0$  and  $\Delta S < 0$ , the reaction proceeds furthest in the forward direction at:  
 (A) Low temperature (B) High temperature  
 (C) All temperature (D) No temperature
- The heat of combustion of propane  $\text{C}_3\text{H}_8(\text{g})$  is  $\Delta H = -2220 \text{ kJ/mol}$ . For the combustion of  $1.00 \text{ m}^3$  of  $\text{C}_3\text{H}_8(\text{g})$  measured at  $25^\circ \text{C}$  and 1 atm pressure,  $\Delta H =$   
 (A)  $-2220 \text{ kJ}$   
 (B)  $+(1.00/22.4) \times 2220 \text{ kJ}$   
 (C)  $-(1.00 / 22.4) \times (298 / 273) \times 2220 \text{ kJ}$   
 (D)  $1000/(0.082 \times 298) \times 2220 \text{ kJ}$
- The heat of solution of NaOH (s) is  $-42.6 \text{ kcal/mole}$  NaOH is dissolved in water, the solution temperature.  
 (A) increases

- (B) Decreases  
(C) Remains Constant  
(D) Either Increases or decreases depending on how much NaOH is dissolved

7. Two moles of an ideal gas at 2 bar and 27° C expand isothermally against a constant pressure of 1 bar. The work done by the gas is equal to

- (A) 3.5 kJ (B) 2.5 kJ  
(C) 1.5 kJ (D) 4.5 kJ

8. One mole of a perfect gas expands isothermally to ten times its original volume. The change In entropy is

- (A) 0.1 R (B) 2.303 R  
(C) 10.0 R (D) 100.0 R

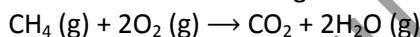
9. Which of The following pairs is correctly matched?

- (i) Arrhenius equation : Variation of enthalpy of a reaction with temperature  
(ii) Kirchhoff equation : Variation of rate constant with temperature  
(iii) Second law of thermodynamics : Entropy of an isolated system tends to increase and reach a maximum value  
(iv) Hess's law of constant heat summation : Enthalpy change in a reaction is always constant and independent of the manner in which the reaction occurs

Select the correct answer using the codes given below :

- (A) (i), (ii), (iii) and (iv) (B) (i), (ii) and (iii)  
(C) (iii) and (iv) (D) (i) and (ii)

10. Given that the standard change of enthalpy of the reaction



is -802 kJ and the enthalpies of formation of CO<sub>2</sub>(g) are -394 and -242 kJ/mol respectively, the enthalpy of formation of CH<sub>4</sub>(g) is

- (A) -152 kJ/mol (B) -76 kJ/mol  
(C) +76 kJ/mol (D) +152 kJ/mol

11. If a certain mass of gas is made to undergo separately adiabatic and isothermally expansion to the same pressure, starting from the same initial condition of temperature and pressure, then, as compared to that of isothermal expansion, in the case of adiabatic expansion, the final

- (A) volume and temperature will be higher  
(B) Volume and temperature will be lower  
(C) temperature will be lower but the final volume will be higher  
(D) Volume will be lower but the final temperature will be higher

12. The dissolution of NH<sub>4</sub>Cl in water is endothermic even though NH<sub>4</sub>Cl dissolves in water spontaneously. Which one of the following best explain the behaviour?

- (A) The bonds in solid NH<sub>4</sub>Cl are weak  
(B) The entropy driving force causes dissolution  
(C) Endothermic processes are energetically favourable  
(D) The dissolving process is unrelated to energy

13. In an adiabatic process, if q is the heat absorbed by the system and w is the work done on the system then

- (A)  $q = w$   
(C)  $du = w$

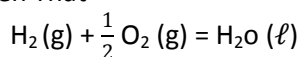
- (B)  $q = -w$   
(D)  $du = q$

14. Two moles of nitrogen were taken as the working substance of a Carnot cycle in which the source and sink temperature were  $227^\circ\text{C}$  and  $27^\circ\text{C}$  respectively. If 100 kJ of heat was absorbed during the isothermal expansion stage of the gas, then the work done in the entire cycle would be

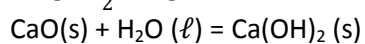
- (A) 40 kJ  
(C) 20 kJ

- (B) 30 kJ  
(D) 60 kJ

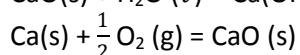
15. Given That



$$\Delta H = -68.3 \text{ Kcal}$$



$$\Delta H = -15.3 \text{ Kcal}$$



$$\Delta H = -151.8 \text{ Kcal}$$

The enthalpy of formation of  $\text{Ca}(\text{OH})_2(\text{s})$  is

- (A) -300.6 Kcal  
(C) -265.8 Kcal

- (B) -180.4 Kcal  
(D) -235.4 Kcal

www.thegurukulinstitute.in