



EXERCISE I (JEE MAIN)

Basics

- The word standard in molar enthalpy change implies
 - temperature 298 K and pressure 1 atm.
 - any temperature and pressure 1 atm.
 - any temperature and pressure 1 bar.
 - any temperature and pressure.
- The enthalpy change in a reaction does not depend upon
 - the state of reactants and products.
 - the nature of the reactants and products.
 - different intermediate steps in the reaction.
 - initial and final enthalpy of the system.
- A quantity of 1.6 g sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter decreases by 6.0 K. The heat capacity of the calorimeter system is 1.25 kJ/K. The molar heat of decomposition for NH_4NO_3 is
 - 7.5 kJ/mol
 - 600 kJ/mol
 - 375 kJ/mol
 - 375 kJ/mol
- The difference between enthalpies of reaction at constant pressure and constant volume for the reaction

$$2\text{C}_6\text{H}_6(\text{l}) + 15\text{O}_2(\text{g}) \rightarrow 12\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$$
 at 298 K in kJ is
 - 7.43
 - +3.72
 - 3.72
 - +7.43
- Among the following the reaction for which $\Delta H = \Delta E$ is
 - $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
 - $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
 - $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
 - $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- The heat capacity of bomb calorimeter is 500 J/°C. A 2°C rise in temperature has been observed on the combustion of 0.1 g of methane. What is the value of ΔE per mole of methane?
 - 1 kJ
 - 160 kJ
 - 160 kJ
 - 1 kJ
- For the reaction $\text{C}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$,
 - $\Delta H > \Delta E$
 - $\Delta H < \Delta E$
 - $\Delta H = \Delta E$
 - $|\Delta H| > |\Delta E|$
- The enthalpy of formation of methane(g) at constant pressure is -18,500 cal/mol at 27°C. The enthalpy of formation at constant volume would be
 - 19,700 cal
 - 17,300 cal
 - 18,498.8 cal
 - 18,500 cal
- When 0.18 g of glucose was burnt in a bomb calorimeter, the temperature rose by 4 K. The heat capacity of the calorimeter system is $(\Delta_C H^\circ = -2.8 \times 10^6 \text{ J/mol glucose})$
 - 700 J/K
 - 700 kJ/K
 - 126 J/K
 - 7.0 kJ/K

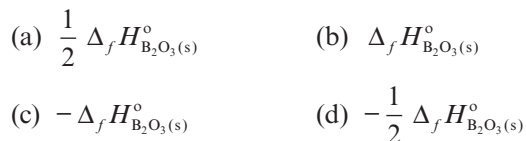
10. Geological conditions are sometimes so extreme that quantities neglected in normal laboratory experiments take on an overriding importance. For example, consider the formation of diamond under geophysically typical conditions. The density of graphite is 2.4 g/cm^3 and that of diamond is 3.6 g/cm^3 at a certain temperature and 500 kbar. By how much does ΔU_{trans} differ from ΔH_{trans} for the graphite to diamond transition?
- (a) 83.33 kJ/mol (b) 0.83 kJ/mol
 (c) $8.33 \times 10^7 \text{ kJ/mol}$ (d) 83.33 J/mol
11. Study the following thermochemical equations.
- $A \rightarrow B; \Delta H = +100 \text{ kcal}$
 $B \rightarrow C; \Delta H = -80 \text{ kcal}$
- The correct order of enthalpies of formation of A, B and C is
- (a) $A < B < C$ (b) $A < C < B$
 (c) $C < A < B$ (d) $B < C < A$

Enthalpy of Formation

12. The standard enthalpy of formation of a substance
- (a) is always positive.
 (b) is always negative.
 (c) is zero.
 (d) may be positive, negative or zero.
13. The enthalpy of formation of ammonia gas is -46.0 kJ/mol . The enthalpy change for the reaction
- $$2\text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$$
- is
- (a) 46.0 kJ (b) 92.0 kJ
 (c) 23.0 kJ (d) -92.0 kJ
14. The enthalpy of formation of $\text{HCl}(\text{g})$ from the following reaction
- $$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + 44 \text{ kcal}$$
- is
- (a) $-44 \text{ kcal mol}^{-1}$ (b) $-22 \text{ kcal mol}^{-1}$
 (c) 22 kcal mol^{-1} (d) $-88 \text{ kcal mol}^{-1}$
15. Formation of ozone from oxygen is an endothermic process. In the upper atmosphere, ultraviolet is the source of energy that drives the reaction. Assuming that both the reactions and the products of the reaction are in standard states, the standard enthalpy of formation of ozone from the following information
- $$3\text{O}_2(\text{g}) \rightarrow 2\text{O}_3(\text{g}), \Delta H^\circ = 286 \text{ kJ}$$
- is
- (a) $+143 \text{ kJ/mol}$ (b) -143 kJ/mol
 (c) $+286 \text{ kJ/mol}$ (d) -286 kJ/mol
16. The $\Delta_f H^\circ$ for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -110.5 and $-241.8 \text{ kJ mol}^{-1}$, respectively. The standard enthalpy change (in kJ) for the reaction
- $$\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$$
- is
- (a) 524.1 (b) 41.2
 (c) -262.5 (d) -41.2
17. The value of $\Delta_f H^\circ$ of $\text{U}_3\text{O}_8(\text{s})$ is $-853.5 \text{ kJ mol}^{-1}$. ΔH° for the reaction
- $$3\text{UO}_2(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{U}_3\text{O}_8(\text{s})$$
- is -76.00 kJ . The value of $\Delta_f H^\circ$ of $\text{UO}_2(\text{s})$ is
- (a) -259.17 kJ/mol (b) -310.17 kJ/mol
 (c) $+259.17 \text{ kJ/mol}$ (d) 930.51 kJ/mol
18. Given enthalpy of formation of $\text{CO}_2(\text{g})$ and $\text{CaO}(\text{s})$ are -94.0 kJ and -152 kJ , respectively, and the enthalpy of the reaction
- $$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$$
- is 42 kJ . The enthalpy of formation of $\text{CaCO}_3(\text{s})$ is
- (a) -42 kJ/mol (b) -202 kJ/mol
 (c) $+202 \text{ kJ/mol}$ (d) -288 kJ/mol
19. The standard enthalpies of formation of $\text{NH}_3(\text{g})$, $\text{CuO}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ are -46 , -155 and -285 kJ/mol , respectively. The enthalpy change when 6.80 g of NH_3 is passed over cupric oxide is
- (a) -59.6 kJ (b) $+59.6 \text{ kJ}$
 (c) -298 kJ (d) -119.2 kJ
20. The standard enthalpies of formation of $\text{H}_2\text{O}(\text{l})$, $\text{Li}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ are -285.8 , -278.5 and -228.9 kJ/mol , respectively. The standard enthalpy change for the below reaction is
- $$2\text{Li}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Li}^+(\text{aq}) + 2\text{OH}^-(\text{aq}) + \text{H}_2(\text{g})$$
- is
- (a) $+443.2 \text{ kJ}$ (b) -443.2 kJ
 (c) -221.6 kJ (d) $+221.6 \text{ kJ}$

Enthalpy of Combustion

21. The standard enthalpy of combustion of solid boron is numerically equal to



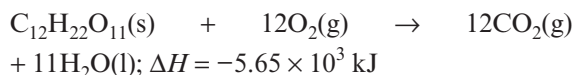
22. The heat evolved in the combustion of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is -680 kcal/mol. The mass of CO_2 produced, when 170 kcal of heat is evolved in the combustion of glucose is

- (a) 45 g (b) 66 g
 (c) 11 g (d) 44 g

23. The standard molar enthalpy of formation of CO_2 is equal to

- (a) zero
 (b) the standard molar enthalpy of combustion of gaseous carbon.
 (c) the sum of standard molar enthalpies of formation of CO and O_2 .
 (d) the standard molar enthalpy of combustion of carbon (graphite).

24. Heat evolved in the complete combustion of 1.026 kg sucrose at constant pressure will be



- (a) 1.695×10^4 kJ (b) 5.65×10^3 kJ
 (c) 1.883×10^3 kJ (d) 3.22×10^4 kJ

25. Enthalpies of combustion of CH_4 , C_2H_4 and C_2H_6 are -890 , -1411 and -1560 kJ/mole, respectively. Which has the highest fuel value (heat produced per gram of the fuel)?

- (a) CH_4 (b) C_2H_6
 (c) C_2H_4 (d) All are same

26. The enthalpy of combustion of methane is -890 kJ. The volume of methane at 0°C and 1 atm to be burnt to produce 2670 kJ heat is

- (a) 33.6 L (b) 67.2 L
 (c) 7.47 L (d) 11.2 L

27. Enthalpies of combustion of CH_4 , C_2H_6 and C_3H_8 are -210 , -370 and -526 kcal/mol, respectively.

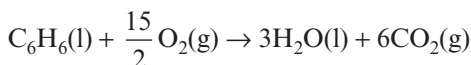
Enthalpy of combustion of hexane can be predicted as

- (a) -840 kcal mol^{-1} (b) -684 kcal mol^{-1}
 (c) -1000 kcal mol^{-1} (d) -500 kcal mol^{-1}

28. For a specific work, on an average a person requires 5616 kJ of energy. How many kilograms of glucose must be consumed if all the required energy has to be derived from glucose only? ΔH for combustion of glucose is -2808 kJ mol^{-1} .

- (a) 0.720 kg (b) 0.36 kg
 (c) 0.18 kg (d) 1.0 kg

29. Benzene burns in oxygen according to the following reactions.



If the standard enthalpies of formation of $\text{C}_6\text{H}_6(\text{l})$, $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ are 11.7 , -68.1 and -94 kcal/mole, respectively, the amount of heat that will liberate by burning 780 g of benzene is

- (a) 7800 kcal (b) 780 kcal
 (c) 78 kcal (d) 608.4 kcal

30. The enthalpy of combustion at 25°C of $\text{H}_2(\text{g})$, cyclohexane(l) and cyclohexene(l) are -241 , -3920 and -3800 kJ/mol, respectively. The enthalpy of hydrogenation of cyclohexene(l) is

- (a) -121 kJ/mol (b) $+121$ kJ/mol
 (c) -242 kJ/mol (d) $+242$ kJ/mol

31. The enthalpy change involved in the oxidation of glucose is -2880 kJ/mol. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk 1 km, what is the maximum distance that a person will be able to walk after eating 120 g of glucose?

- (a) 19.2 km (b) 9.6 km
 (c) 2.4 km (d) 4.8 km

32. A geyser, operating on LPG (liquefied petroleum gas) heats water flowing at the rate of 3.0 litres per minute, from 27°C to 77°C . If the heat of combustion of LPG is $40,000$ J/g, then how much fuel (in g) is consumed per minute? (Specific heat capacity of water is 4200 J/kg-K)

- (a) 15.25 (b) 15.50
 (c) 15.75 (d) 16.00

33. For the allotropic change represented by the equation $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$; $\Delta H = +1.9$ kJ. If 6.0 g of diamond and 6.0 g of graphite is burnt completely in separate experiments, then the heat liberated will be higher by
- (a) 1.9 kJ in case of graphite.
 (b) 1.9 kJ in case of diamond.
 (c) 0.95 kJ in case of diamond.
 (d) 0.95 kJ in case of graphite.

Enthalpy of Neutralization

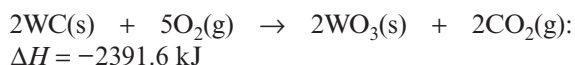
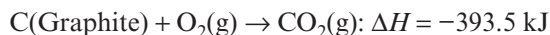
34. Equal volumes of one molar hydrochloric acid and one molar sulphuric acid are neutralized completely by dilute NaOH solution by which X and Y kcal of heat are liberated, respectively. Which of the following is true?
- (a) $X = Y$ (b) $2X = Y$
 (c) $X = 2Y$ (d) $4X = Y$
35. Enthalpy of neutralization of oxalic acid is -25.4 kcal/mol using strong base, NaOH. Enthalpy change for the process $\text{H}_2\text{C}_2\text{O}_4(\text{aq}) \rightarrow 2\text{H}^+(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq})$ is about
- (a) 2.0 kcal (b) -11.7 kcal
 (c) 1.0 kcal (d) 4.0 kcal
36. A solution of 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 again performed using 250 ml of KOH solution and 500 ml of HCl solution and rise in temperature T_2 is again noted. Which of the following is correct?
- (a) $T_1 = T_2$
 (b) T_1 is 2 times as larger as T_2 .
 (c) T_2 is twice larger as T_1 .
 (d) T_1 is 1.5 times as larger as T_2 .
37. Under identical conditions, how many millilitres of 1 M-KOH and 2 M- H_2SO_4 solutions are required to produce a resulting volume of 100 ml with the highest rise in temperature?
- (a) 80, 20 (b) 20, 80
 (c) 60, 40 (d) 50, 50
38. Enthalpy of neutralization of the reaction between $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{NaOH}(\text{aq})$ is -13.2 kcal/eq and that of the reaction between $\text{H}_2\text{SO}_4(\text{aq})$ and $\text{KOH}(\text{aq})$ is -13.7 kcal/eq. The enthalpy of dissociation of $\text{CH}_3\text{COOH}(\text{aq})$ is
- (a) -0.5 kcal eq^{-1} (b) $+0.5$ kcal eq^{-1}
 (c) -26.9 kcal eq^{-1} (d) $+13.45$ kcal eq^{-1}
39. Enthalpy of neutralization of H_3PO_3 by NaOH is -106.68 kJ/mol. If the enthalpy of neutralization of HCl by NaOH is -55.84 kJ/mol, then the $\Delta H_{\text{ionization}}$ of H_3PO_3 into its ions is
- (a) 50.84 kJ/mol (b) 5 kJ/mol
 (c) 10 kJ/mol (d) 2.5 kJ/mol

Hess's Law

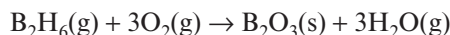
40. Given that $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$; $\Delta H^\circ = -X$ kJ
 $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$; $\Delta H^\circ = -Y$ kJ
 The enthalpy of formation of carbon monoxide will be
- (a) $(2X - Y)/2$ (b) $(Y - 2X)/2$
 (c) $2X - Y$ (d) $Y - 2X$
41. The standard heat of combustion of propane is -2220.1 kJ/mol. The standard heat of vaporization of liquid water is 44 kJ/mol. What is the ΔH° of the following reaction?
- $$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$$
- (a) -2220.1 kJ (b) -2044.1 kJ
 (c) -2396.1 kJ (d) -2176.1 kJ

42. Calculate $\Delta_f H$ for $\text{ZnSO}_4(\text{s})$ from the following data
- $$\text{ZnS}(\text{s}) \rightarrow \text{Zn}(\text{s}) + \text{S (rhombic)}, \quad \Delta H_1 = 44 \text{ kcal/mol}$$
- $$2\text{ZnS}(\text{s}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{ZnO}(\text{s}) + 2\text{SO}_2(\text{g}), \quad \Delta H_2 = -221.88 \text{ kcal/mol}$$
- $$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g}), \quad \Delta H_3 = -46.88 \text{ kcal/mol}$$
- $$\text{ZnSO}_4(\text{s}) \rightarrow \text{ZnO}(\text{s}) + \text{SO}_3(\text{g}), \quad \Delta H_4 = 55.1 \text{ kcal/mol}$$
- (a) -233.48 kcal/mol (b) -343.48 kcal/mol
 (c) -434.84 kcal/mol (d) -311.53 kcal/mol
43. The value of ΔH_{sol} of anhydrous copper (II) sulphate is -66.11 kJ . Dissolution of 1 mole of blue vitriol, [Copper (II) sulphate pentahydrate] is followed by the absorption of 11.5 kJ of heat. The enthalpy of dehydration of blue vitriol is
- (a) -77.61 kJ (b) $+77.61 \text{ kJ}$
 (c) -54.61 kJ (d) $+54.61 \text{ kJ}$
44. The data below refers to gas phase reaction at constant pressure at 25°C .
- $$\text{CH}_3\text{--CH}_3 \rightarrow \text{CH}_3\text{--CH}_2 + \text{H}; \quad \Delta H_1 = +420 \text{ kJ mol}^{-1}$$
- $$\text{CH}_3\text{--CH}_2 \rightarrow \text{CH}_2 = \text{CH}_2 + \text{H}; \quad \Delta H_2 = +168 \text{ kJ mol}^{-1}$$
- From these data, the enthalpy change ΔH for the reaction $2\text{CH}_3\text{--CH}_2 \rightarrow \text{CH}_3\text{--CH}_3 + \text{CH}_2 = \text{CH}_2$ is
- (a) $+250 \text{ kJ}$ (b) $+588 \text{ kJ}$
 (c) -252 kJ (d) -588 kJ
45. Study the following thermochemical data.
- $$\text{S} + \text{O}_2 \rightarrow \text{SO}_2; \quad \Delta H = -298.2 \text{ kJ}$$
- $$\text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3; \quad \Delta H = -98.2 \text{ kJ}$$
- $$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4; \quad \Delta H = -130.2 \text{ kJ}$$
- $$\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}; \quad \Delta H = -287.3 \text{ kJ}$$
- The enthalpy of formation of H_2SO_4 at 298 K will be
- (a) -433.7 kJ (b) -650.3 kJ
 (c) $+320.5 \text{ kJ}$ (d) -813.9 kJ
46. Based on the following thermochemical equations,
- $$\text{H}_2\text{O}(\text{g}) + \text{C}(\text{s}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g}); \quad \Delta H = 131 \text{ kJ}$$
- $$\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \quad \Delta H = -282 \text{ kJ}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \quad \Delta H = -242 \text{ kJ}$$
- $$\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \quad \Delta H = X \text{ kJ}$$
- The value of 'X' will be
- (a) -393 kJ (b) -655 kJ
 (c) $+393 \text{ kJ}$ (d) $+655 \text{ kJ}$
47. Enthalpies of solution of $\text{BaCl}_2(\text{s})$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ are -20.6 kJ/mol and 8.8 kJ/mol , respectively. ΔH hydration of $\text{BaCl}_2(\text{s})$ to $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ is
- (a) -29.4 kJ (b) -11.8 kJ
 (c) 29.6 kJ (d) 11.8 kJ
48. The dissolution of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ in a large volume of water is endothermic to the extent of 3.5 kcal/mol . For the reaction, $\text{CaCl}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{CaCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$; ΔH is -23.2 kcal . The heat of solution of anhydrous CaCl_2 in large quantity of water will be
- (a) $-26.7 \text{ kcal mol}^{-1}$ (b) $-19.7 \text{ kcal mol}^{-1}$
 (c) $19.7 \text{ kcal mol}^{-1}$ (d) $26.7 \text{ kcal mol}^{-1}$
49. For the given two processes
- (i) $\frac{1}{2}\text{P}_4(\text{s}) + 3\text{Cl}_2(\text{g}) \rightarrow 2\text{PCl}_3(\text{l}); \quad \Delta H = -635 \text{ kJ}$
 (ii) $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{s}); \quad \Delta H = -137 \text{ kJ}$
- the value of $\Delta_f H$ of $\text{PCl}_5(\text{s})$ is
- (a) $454.5 \text{ kJ mol}^{-1}$ (b) $-454.5 \text{ kJ mol}^{-1}$
 (c) -772 kJ mol^{-1} (d) -498 kJ mol^{-1}
50. Calculate $\Delta_f H^\circ$ for aqueous chloride ion from the following data.
- $$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g}); \quad \Delta_f H^\circ = -92.4 \text{ kJ}$$
- $$\text{HCl}(\text{g}) + n\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}); \quad \Delta H^\circ = -74.8 \text{ kJ}$$
- $$\Delta_f H^\circ (\text{H}^+, \text{aq.}) = 0.0 \text{ kJ}$$
- (a) 0.0 (b) $+83.6 \text{ kJ}$
 (c) $+167.2 \text{ kJ}$ (d) -167.2 kJ

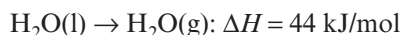
51. Tungsten carbide is very hard and is used to make cutting tools and rock drills. What is the enthalpy of formation (in kJ/mol) of tungsten carbide? The enthalpy change for this reaction is difficult to measure directly, because the reaction occurs at 1400°C. However, the enthalpies of combustion of the elements and of tungsten carbide can be measured easily.



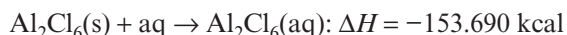
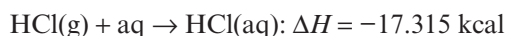
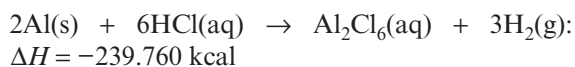
- (a) -38.0 (b) -76.0
(c) -19.0 (d) -1233.8
52. Diborane is a potential rocket fuel which undergoes combustion according to the following reaction.



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



- (a) -2167 kJ/mol (b) -1478 kJ/mol
(c) -2035 kJ/mol (d) -1999 kJ/mol
53. Calculate the enthalpy of formation (in kcal/mol) of anhydrous Al_2Cl_6 from the following data.



- (a) -371.76 (b) -321.960
(c) -218.07 (d) -525.45
54. Which of the following salts shall cause more cooling when one mole of the salt is dissolved in the same amount of water? (Integral heat of solution at 298 K is given for each solute.)

- (a) KNO_3 ; $\Delta H = 35.4 \text{ kJ/mol}$
(b) NaCl ; $\Delta H = 5.35 \text{ kJ/mol}$
(c) KOH ; $\Delta H = -55.6 \text{ kJ/mol}$
(d) HBr ; $\Delta H = -83.3 \text{ kJ/mol}$

55. When 1 mole of Na(s) is dissolved in large volume of water at 298 K and 1 bar, 184 kJ/mol heat is released. When 1 mole of $\text{Na}_2\text{O(s)}$ is dissolved in large volume of water at 298 K and 1 bar, 238 kJ/mol is released. If the enthalpy of formation of water is -286 kJ/mol, then the enthalpy of formation of sodium oxide is

- (a) +54 kJ/mol (b) +156 kJ/mol
(c) -416 kJ/mol (d) -130 kJ/mol

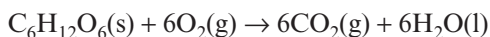
56. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as follows.



The ΔG for the reaction $2\text{ZnS(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{ZnO(s)} + 2\text{SO}_2\text{(g)}$ will be

- (a) -357 kJ (b) -731 kJ
(c) -773 kJ (d) -229 kJ

57. For the following reaction,



which of the following expression is incorrect?

- (a) $\Delta H^\circ_{\text{reaction}} = 6\Delta_f H^\circ(\text{CO}_2, \text{g}) + 6\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - 6\Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{s})$
(b) $\Delta G^\circ_{\text{reaction}} = 6\Delta_f G^\circ(\text{CO}_2, \text{g}) + 6\Delta_f G^\circ(\text{H}_2\text{O}, \text{l}) - 6\Delta_f G^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{s})$
(c) $\Delta S^\circ_{\text{reaction}} = 6S^\circ(\text{CO}_2, \text{g}) + 6S^\circ(\text{H}_2\text{O}, \text{l}) - 6S^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{s})$
(d) $\Delta S^\circ_{\text{reaction}} = 6S^\circ(\text{CO}_2, \text{g}) + 6S^\circ(\text{H}_2\text{O}, \text{l}) - S^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) - 6S^\circ(\text{O}_2, \text{g})$

58. Calculate the free energy change for the reaction: $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$ by using the following data at the reaction temperature of 27°C.

Bond enthalpies (kJ/mol):

$\text{H} - \text{H} = 435$; $\text{Cl} - \text{Cl} = 240$; $\text{H} - \text{Cl} = 430$

Entropies (J/K-mol):

$\text{H}_2 = 130$; $\text{Cl}_2 = 222$; $\text{HCl} = 186$

- (a) -185 kJ (b) -20 kJ
(c) -179 kJ (d) -191 kJ

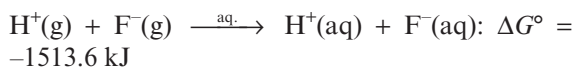
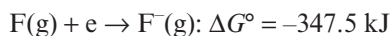
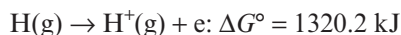
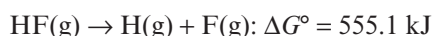
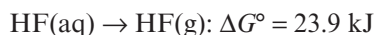
59. The ΔG° values for the hydrolysis of creatine phosphate (creatine-P) and glucose-6-phosphate (G-6-P) are

- (i) Creatine-P + $\text{H}_2\text{O} \rightarrow$ Creatine + P; $\Delta G^\circ = -29.2 \text{ kJ}$
 (ii) G-6-P + $\text{H}_2\text{O} \rightarrow$ G + P; $\Delta G^\circ = -12.4 \text{ kJ}$

The value of ΔG° for the reaction G-6-P + Creatine \rightarrow G + Creatine-P is

- (a) +16.8 kJ (b) -16.8 kJ
 (c) -41.6 kJ (d) +41.6 kJ

60. Calculate the standard free energy change for the ionization $\text{HF}(\text{aq}) \rightarrow \text{H}^+(\text{aq}) + \text{F}^-(\text{aq})$ from the following data.



- (a) -38.1 kJ (b) +38.1 kJ
 (c) -1489.7 kJ (d) -1513.6 kJ

61. Calculate the standard free energy of the reaction at 27°C for the combustion of methane using the given data $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$.

Species	$\text{CH}_4(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
$\Delta_f H^\circ / (\text{kJ mol}^{-1})$	-74.5	0	-393.5	-286.0
$S^\circ / (\text{JK}^{-1} \text{mol}^{-1})$	186	205	216	70

- (a) -891.0 kJ/mol (b) -240 kJ/mol
 (c) -819 kJ/mol (d) -963 kJ/mol

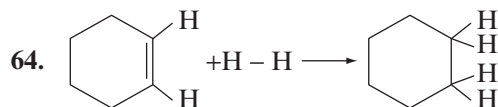
Bond Enthalpy

62. $\Delta_f H^\circ$ for $\text{NF}_3(\text{g})$ is -113 kJ/mol . Bond energy for the N-F bond is 273.5 kJ/mol . The bond energies of N_2 and F_2 , if their magnitudes are in the ratio 6:1, are respectively,

- (a) 822.6, 137.1 kJ/mol
 (b) 979.8, 163.3 kJ/mol
 (c) 943.33, 157.22 kJ/mol
 (d) 762.6, 127.1 kJ/mol

63. Among the following, for which reaction the heat of reaction represents bond energy of HCl?

- (a) $\text{HCl}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{Cl}(\text{g})$
 (b) $2\text{HCl}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})$
 (c) $\text{HCl}(\text{g}) \rightarrow \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g})$
 (d) $\text{HCl}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{Cl}^-(\text{g})$



The bond energies (in kJ/mol) at 25°C are C-C = 346, C-H = 413, H-H = 437, C = C; 611. From these data, the value of ΔH at 25°C for the above reaction is

- (a) -289 kJ mol^{-1} (b) -124 kJ mol^{-1}
 (c) 124 kJ mol^{-1} (d) 289 kJ mol^{-1}

65. Heat absorbed in the reaction $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$ is 182 kJ. Bond energies of H-H = 430 kJ/mole and Cl-Cl = 242 kJ/mole. The H-Cl bond energy is

- (a) 763 kJ/mole (b) 245 kJ/mole
 (c) 336 kJ/mole (d) 154 kJ/mole

66. ΔH for the reaction $2\text{C}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$ is -20.24 kcal/mol . The bond energies (in kcal/mol) of C-C, C-H and H-H are 63, 85.6 and 102.6, respectively. The enthalpy of sublimation of C(s) is

- (a) 124.3 kcal/mol (b) 185.3 kcal/mol
 (c) 158.3 kcal/mol (d) 211.5 kcal/mol

67. Sublimation energy of Ca is 121 kJ/mol. Dissociation energy of Cl_2 is 242.8 kJ/mol, the total ionization energy of $\text{Ca}(\text{g}) \rightarrow \text{Ca}^{2+}(\text{g})$ is 2422 kJ/mol and electron affinity of Cl is -355 kJ/mol . Lattice energy of CaCl_2 is -2430.8 kJ/mol . What is ΔH for the process $\text{Ca}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow \text{CaCl}_2(\text{s})$?

- (a) -355 kJ mol^{-1} (b) $+3550 \text{ kJ mol}^{-1}$
 (c) $-35.5 \text{ kJ mol}^{-1}$ (d) $-1720 \text{ kJ mol}^{-1}$

68. The following are various ΔH values (kJ per mol), $\Delta_f H$ (NaCl) = -411.2; $\Delta_f H$ (Na, g) = 107.3; $\Delta_f H$ (Cl, g) = 121.7; $\Delta_i H$ (Na, g) = 495.4; $\Delta_{eg} H$ (Cl, g) = -348.5. The lattice enthalpy of NaCl(s) is

- (a) 495.4 kJ (b) 107.3 kJ
(c) 411.2 kJ (d) 787.1 kJ

69. The enthalpy of hydrogenation of benzene is -49.8 kcal/mol while its resonance energy is 36.0 kcal/mol. The enthalpy of hydrogenation of cyclohexene is

- (a) -4.6 kcal (b) -28.6 kcal/mol
(c) -85.8 kcal/mol (d) -13.8 kcal/mol

70. The enthalpy of hydrogenation of benzene is -51.0 kcal/mol. If enthalpy of hydrogenation of 1, 4-cyclohexadiene and cyclohexene is -58 kcal/mol and -29 kcal/mol, respectively, then what is the resonance energy of benzene?

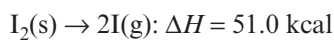
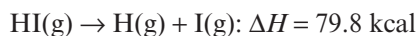
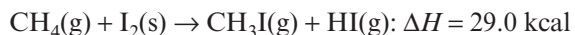
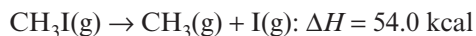
- (a) 29 kcal/mole (b) 36 kcal/mole
(c) 58 kcal/mole (d) 7 kcal/mole

71. Use the following data to calculate the enthalpy of hydration for caesium iodide and caesium hydroxide, respectively.

Compound	Lattice energy (kJ/mol)	$\Delta H_{\text{Solution}}$ (kJ/mol)
CsI	+604	+33
CsOH	+724	-72

- (a) -571 kJ/mol and -796 kJ/mol
(b) 637 kJ/mol and 652 kJ/mol
(c) -637 kJ/mol and -652 kJ/mol
(d) 571 kJ/mol and 796 kJ/mol

72. From the following thermochemical equations, find out the bond dissociation enthalpy of $\text{CH}_3\text{-H}$ bond.



- (a) 125.2 kcal/mol (b) 91.7 kcal/mol
(c) 101.9 kcal/mol (d) 111.8 kcal/mol

73. Estimate the average S-F bond energy in SF_6 . The values of standard enthalpy of formation of $\text{SF}_6\text{(g)}$, S(g) and F(g) are -1100, 275 and 80 kJ/mol, respectively.

- (a) 183.33 kJ/mol (b) 309.17 kJ/mol
(c) 366.37 kJ/mol (d) 345 kJ/mol

74. The enthalpy of atomization of $\text{PH}_3\text{(g)}$ is +954 kJ/mol and that of P_2H_4 is +1.488 MJ/mol. The bond energy of the P-P bond is

- (a) 318 kJ/mol (b) 372 kJ/mol
(c) 216 kJ/mol (d) 534 kJ/mol

75. The standard molar enthalpies of formation of cyclohexane (l) and benzene(l) at 298 K are -156 and +49 kJ/mol, respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 298 K is -119 kJ/mol. Use these data to estimate the magnitude of the resonance energy of benzene.

- (a) 152 kJ/mol (b) 250 kJ/mol
(c) 12 kJ/mol (d) 86 kJ/mol

76. Calculate the magnitude of resonance energy of CO_2 from the following data (in kJ/mol).

Bond energies: $\text{C=O} = 539.0$, $\text{O=O} = 498.0$

Heat of sublimation of $\text{C(s)} = 718.0$

Heat of combustion of $\text{C(s)} = -393.0$

- (a) 255 (b) 531
(c) 138 (d) 247

77. AB , A_2 and B_2 are diatomic molecules. If the bond enthalpies of A_2 , AB and B_2 are in the ratio 2:2:1 and enthalpy of formation AB from A_2 and B_2 is $-100 \text{ kJ mole}^{-1}$, then what is the bond energy of A_2 ?

- (a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 300 kJ mol^{-1} (d) 400 kJ mol^{-1}

78. The lattice energy of solid NaCl is 180 kcal/mol. The dissolution of the solid in water, in the form of ions is endothermic to the extent of 1kcal/mol. If the solvation energies of Na^+ and Cl^- ions are in the ratio 6:5, then what is the enthalpy of hydration of sodium ion?

- (a) -85.6 kcal/mol (b) -97.6 kcal/mol
(c) 82.6 kcal/mol (d) 100 kcal/mol

79. The enthalpy of atomization of graphite is 698.6 kJ/mol and the mean bond enthalpy of C–C bond in diamond is 348.4 kJ/mol. The enthalpy of conversion of graphite into diamond is
- (a) +1.2 kJ/mol (b) +1.8 kJ/mol
(c) -1.2 kJ/mol (d) -1.8 kJ/mol
80. The lattice energy of $\text{Na}_2\text{CO}_3(\text{s})$ is 205 kJ/mol and the hydration energies of Na^+ and CO_3^{2-} ions are -80 and -40 kJ/mol, respectively. The correct prediction about the solubility of Na_2CO_3 in water is (Assume that ΔH is independent of temperature)
- (a) increases with increase in temperature.
(b) decreases with increase in temperature.
(c) unaffected by the change in temperature.
(d) first increases and then decreases with increase in temperature.
-



EXERCISE II (JEE ADVANCED)

Section A (Only one Correct)

1. In a flask, colourless N_2O_4 is in equilibrium with brown coloured NO_2 . At equilibrium, when the flask is heated at 373 K, the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy for this reaction is

(a) negative (b) positive
(c) zero (d) unpredictable

2. $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2(\text{g}) + 8\text{H}_2\text{O}$

The above reaction is endothermic and hence, the actual temperature of the reaction vessel (isolated from the surrounding) may be different from that expected. Given that the initial temperature of the reaction vessel was used in the calculations, how would this affect the predicted value of moles of Cl_2 (n) according to the equation $n = PV/RT$?

(a) It would be greater than the actual value.
(b) It would be less than the actual value.
(c) It would be the same as the actual value.
(d) This cannot be determined from the information given.

3. The molar heat capacities of A, B and C are in the ratio 1:2:3. The enthalpy change for the reaction $\text{A} + \text{B} \rightarrow \text{C}$ at temperature T_1 is ΔH_1 . Assuming that the heat capacities do not change with temperature, the enthalpy change, ΔH_2 , at temperature T_2 ($T_2 > T_1$) will be

(a) greater than ΔH_1 .
(b) equal to ΔH_1 .
(c) less than ΔH_1 .
(d) greater or less than ΔH_1 , depending on the values of T_2 and T_1 .

4. The specific heats of iodine vapours and solid are 0.031 and 0.055 cal/g, respectively. If the enthalpy of sublimation of iodine is 24 cal/g at 200°C, then the enthalpy of sublimation of iodine at 250°C should be

(a) 24 cal/g (b) 22.8 cal/g
(c) 26.4 cal/g (d) 25.2 cal/g

5. A quantity that cannot be directly measured is

(a) heat of formation of $\text{H}_2\text{O}(\text{l})$.
(b) heat of formation of $\text{CH}_4(\text{g})$.
(c) latent heat of fusion of ice.
(d) heat of combustion of ethyl alcohol.

6. Which of the following gas will liberate maximum heat on combustion per gram?

(a) Methane (b) Ethane
(c) Acetylene (d) Ethylene

7. Ethyl chloride is prepared by the reaction of ethylene with hydrogen chloride as



What is the value of ΔU (in kJ) if 70 g of ethylene and 73 g of HCl are allowed to react at 25°C?

(a) -69.8 (b) -180.75
(c) -174.5 (d) -139.6

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

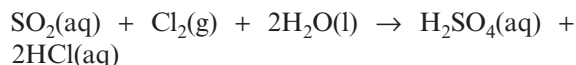


In an experiment, there was absorption of 0.44 kcal when one mole of HAuBr_4 was mixed with 4 moles of HCl. What is the percentage conversion of HAuBr_4 into HAuCl_4 ?

(a) 0.5% (b) 0.6%
(c) 5% (d) 50%

9. When carbon is burnt in a definite amount of oxygen, the product will be CO, if excess amount of carbon is present and the product will be CO₂ if excess amount of O₂ is present. The enthalpies of formation of CO(g) and CO₂(g) are -75 and -95 kcal/mol, respectively. In which of the following case, the amount of heat evolved will be maximum?
- 10 moles of carbon and 4.5 moles of O₂.
 - 24 g of carbon and 64 g of O₂.
 - 4 moles of carbon and 3.5 moles of O₂.
 - 30 g of carbon and 80 g of O₂.
10. The standard molar enthalpies of formation of trinitrotoluene(l), CO₂(g) and H₂O(l) are 65, -395 and -285 kJ/mol, respectively. The density of trinitrotoluene is 1.816 g/ml. Trinitrotoluene can be used as rocket fuel, with the gases resulting from its combustion streaming out of the rocket to give the required thrust. What is the enthalpy density for the combustion reaction of trinitrotoluene?
- 28.34 MJ/L
 - 28.34 kJ/L
 - 27.30 MJ/L
 - 8.59 MJ/L
11. When 1 g equivalent of strong acid reacts with strong base, the heat released is 13.5 kcal. When 1 g equivalent H₂A is completely neutralized against strong base, 13 kcal is released. When 1 g equivalent B(OH)₂ is completely neutralized against strong acid, 10 kcal heat is released. What is the enthalpy change when 1 mole of H₂A is completely neutralized by B(OH)₂?
- 27 kcal
 - 10 kcal
 - 20 kcal
 - 19 kcal
12. The enthalpy change for the reaction, NaOH(aq) + HCl(aq) → NaCl(aq) + H₂O(l) is -57 kJ. Predict the value of the enthalpy change in the following reaction.
- $$\text{Ba(OH)}_2(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$$
- 57 kJ
 - 76 kJ
 - 114 kJ
 - 200 kJ
13. The enthalpy of neutralization of a strong monobasic acid by a strong monoacidic base is -13,700 cal. A certain monobasic weak acid is 10% ionized in a molar solution. If the enthalpy of ionization of the weak acid is +400 cal/mole, then what is the enthalpy of neutralization of one molar solution of the weak acid?
- 13,700 cal
 - 13,340 cal
 - 13,660 cal
 - 13,300 cal
14. In biological cells that have a plentiful supply of O₂, glucose is oxidized completely to CO₂ and H₂O by a process called aerobic oxidation. Muscle cells may be deprived of O₂ during vigorous exercise and in that case, one molecule of glucose is converted to two molecules of lactic acid, CH₃CH(OH)COOH, by a process called anaerobic glycolysis.
- $$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}); \Delta H^\circ = -2880 \text{ kJ/mol}$$
- $$\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{CH}_3\text{CH}(\text{OH})\text{COOH}(\text{s}); \Delta H^\circ = +2530 \text{ kJ/mol}$$
- Which of the following statements is true regarding aerobic oxidation and anaerobic glycolysis with respect to energy change as heat?
- Aerobic oxidation has biological advantage over anaerobic glycolysis by 5410 kJ/mol.
 - Aerobic oxidation has biological advantage over anaerobic glycolysis by 350 kJ/mol
 - Anaerobic glycolysis has biological advantage over aerobic oxidation by 5410 kJ/mol.
 - Anaerobic glycolysis has biological advantage over aerobic oxidation by 350 kJ/mol.
15. The intermediate SiH₂ is formed in the thermal decomposition of silicon hydrides. Calculate ΔH_f° of SiH₂ from the following reactions.
- $$\text{Si}_2\text{H}_6(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{SiH}_4(\text{g}); \Delta H^\circ = -11.7 \text{ kJ/mol}$$
- $$\text{SiH}_4(\text{g}) \rightarrow \text{SiH}_2(\text{g}) + \text{H}_2(\text{g}); \Delta H^\circ = +239.7 \text{ kJ/mol}$$
- $$\Delta_f H^\circ, \text{Si}_2\text{H}_6(\text{g}) = +80.3 \text{ kJ mol}^{-1}$$
- 353 kJ/mol
 - 321 kJ/mol
 - 198 kJ/mol
 - 274 kJ/mol
16. Study the following thermodynamic data given by E. H. P. Cordfunke, A. S. Booji and M. Y. Furkalionk.
- DyCl₃(s) → DyCl₃(aq., in 4.0 M-HCl): $\Delta H^\circ = -180.06 \text{ kJmol}^{-1}$
 - Dy(s) + 3HCl(aq, 4.0 M) → DyCl₃(aq, in 4.0 M-HCl) + 3/2 H₂(g): $\Delta H^\circ = -699.43 \text{ kJ mol}^{-1}$
 - 1/2 H₂(g) + 1/2 Cl₂(g) → HCl(aq, 4.0 M): $\Delta H^\circ = -158.31 \text{ kJ mol}^{-1}$
- What is ΔH_f° of DyCl₃(s) from these data?
- 248.58 kJ mol⁻¹
 - 994.30 kJ mol⁻¹
 - 3977.2 kJ mol⁻¹
 - 1469.2 kJ mol⁻¹

17. The enthalpies of formation of $\text{SO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$, $\text{HCl}(\text{g})$ and $\text{H}_2\text{SO}_4(\text{l})$ are -70.97 , -68.32 , -22.1 and -188.84 (kcal mol^{-1}). The enthalpies of solution of SO_2 , H_2SO_4 and HCl in dilute solution are -8.56 , -22.05 and -17.63 (kcal mol^{-1}), respectively. What is the enthalpy change for the reaction?



- (a) -74.18 kcal (b) -78.97 kcal
(c) -43.71 kcal (d) -87.14 kcal
18. The enthalpy of neutralization of a strong acid by a strong base is -57.32 kJ mol^{-1} . The enthalpy of formation of water is -285.84 kJ mol^{-1} . The enthalpy of formation of aqueous hydroxyl ion is
- (a) $+228.52$ kJ/mol (b) -114.26 kJ/mol
(c) -228.52 kJ/mol (d) $+114.2$ kJ/mol
19. $\Delta_f H^\circ$ for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -94.0 and -68.0 kcal/mol . $\Delta_f H^\circ$ for the propanoic acid is one-third of the enthalpy of combustion of the acid and has the same sign as the latter. The value of $\Delta_f H^\circ$ of propanoic acid is
- (a) -364.5 kcal/mol (b) -729.0 kcal/mol
(c) -121.5 kcal/mol (d) -243.0 kcal/mol
20. The enthalpy change when x g of phenol dissolves in y g of CHCl_3 is given below at a certain temperature.

x	Y	ΔH (kcal)
0.470	120	-0.02
1.410	140	-0.03

Calculate the enthalpy of dilution per mole of phenol, when the second solution is diluted to the concentration of the first by addition of CHCl_3 .

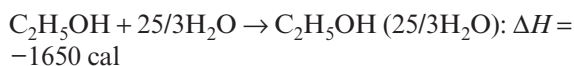
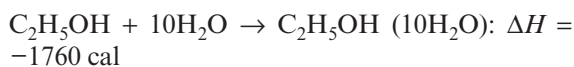
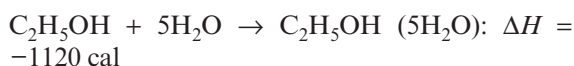
- (a) -4.0 kcal/mol (b) -2.0 kcal/mol
(c) $+4.0$ kcal/mol (d) $+2.0$ kcal/mol
21. Consider the following equations.
- $$\text{CH}_3\text{CH}(\text{OH})\text{CHClCOOH} + 2\text{KOH} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CHClCOOK} + \text{KCl} + 2\text{H}_2\text{O};$$
- $$\Delta H = -14.7 \text{ kcal}$$
- $$\text{CH}_3\text{CH}(\text{OH})\text{CHClCOOK} + \text{KOH} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CHClCOO}^- + \text{K}^+ + \text{H}_2\text{O};$$
- $$\Delta H = -2.7 \text{ kcal}$$
- ΔH for the neutralization of HCl and NaOH is -13.75 kcal/eq . The enthalpy of ionization of $\text{CH}_3\text{CH}(\text{OH})\text{CHClCOOH}$ is

- (a) $+1.75$ kcal/mol (b) $+3.5$ kcal/mol
(c) $+0.875$ kcal/mol (d) -1.75 kcal/mol

22. The enthalpies of formation of $\text{FeO}(\text{s})$ and $\text{Fe}_2\text{O}_3(\text{s})$ are -65.0 and -197.0 kcal/mol , respectively. A mixture of the two oxides contains FeO and Fe_2O_3 in the mole ratio 2:1. If by oxidation it is changed in to a 1:2 mole ratio mixture, then how much of thermal energy will be released per mole of the initial mixture?

- (a) 13.4 kcal (b) 67 kcal
(c) 47.2 kcal (d) 81 kcal

23. Calculate the heat effect produced when a solution of 1 mole of ethanol in 5 moles of water is mixed with a solution of 2 moles of ethanol in 20 moles of water.



- (a) 310 cal is absorbed.
(b) 310 cal is released.
(c) 4640 cal is absorbed.
(d) 4640 cal is released.

24. A solution was prepared by dissolving 7.45 g of KCl in 200 g of H_2O in a calorimeter with a water equivalent of 25 g. The temperature of the water had reduced from 28°C to 25°C . The value of ΔH (in kJ/mol) for dissolving KCl in water is (Specific heat capacity of water is 4.2 J/K-g)

- (a) $+2.52$ (b) $+2.835$
(c) $+25.2$ (d) $+28.35$

25. In an ice calorimeter, a chemical reaction is allowed to occur in thermal contact with an ice-water mixture at 0°C . Any heat liberated by the reaction is used to melt some ice and the volume change of the ice-water mixture indicates the amount of melting. When solutions containing 1.0 millimole each of AgNO_3 and NaCl were mixed in such a calorimeter, both solutions having been pre-cooled to 0°C , 0.20 g of ice melted. Assuming complete reaction in this experiment, what is ΔH for the reaction $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$? Latent heat of fusion of ice at 0°C is 80 cal/g .

- (a) -16 kcal (b) $+16$ kcal
(c) -16 cal (d) $+16$ cal

26. A volume of 4.0 L of a mixture of ethane and methane gases on complete combustion at 300 K produced 6.0 L of carbon dioxide. Find out the amount of heat evolved on burning 1 L of gaseous mixture. The heats of combustion of ethylene and methane are -1573 and -890 kJ per mole, respectively, at 300 K.
- (a) 4926 kJ (b) 50 kJ
(c) 1231.5 kJ (d) 200 kJ
27. A quantity of 0.3 g of carbon was converted into CO_2 producing 2400 cal of heat. When 0.6 g of carbon was converted to CO, 1400 cal of heat were produced. What will be the heat produced when 0.7 g of CO is converted to CO_2 ?
- (a) 1700 cal (b) 1633.33 cal
(c) 700 cal (d) 1000 cal
28. Assume that for a domestic hot water supply, 160 kg of water per day must be heated from 10°C to 60°C and gaseous fuel propane, C_3H_8 , is used for this purpose. What volume of propane gas at STP would have to be used for heating domestic water, with efficiency of 40%? Heat of combustion of propane is -500 kcal/mol and specific heat capacity of water is 1.0 cal/K-g.
- (a) 896 L (b) 908 L
(c) 896 m^3 (d) 908 m^3
29. As a 0.1 mole sample of solid NH_4Cl was dissolved in 50 ml of water, the temperature of the solution decreased. A small electrical immersion heater restored the temperature of the system by passing 0.125 A from a 15 V power supply for a period of 14 min. The value of ΔH for the process $\text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_4\text{Cl(aq)}$ is
- (a) -15.75 kJ (b) $+15.75$ kJ
(c) -787.5 J (d) $+787.5$ J
30. The thermochemical equation for the dissociation of hydrogen gas into atoms may be written as $\text{H}_2 \rightarrow 2\text{H}$; $\Delta H = 432.0$ kJ. What is the ratio of the energy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam? Heat of formation of steam is -240.0 kJ/mol.
- (a) 2.80 (b) 1.80
(c) 0.8 (d) 2.40
31. The most exothermic 'ordinary' chemical reaction for a given mass of reactants is $2\text{H(g)} \rightarrow \text{H}_2\text{(g)}$, where $\Delta E = 103$ kcal. The theoretical decrease in mass on combination of 2.0 moles of hydrogen

atoms to form 1.0 mole of hydrogen molecules, assuming that the energy is released only due to decrease in mass of the system is

- (a) 4.8×10^{-12} kg (b) 4.8×10^{-12} g
(c) 2.4×10^{-12} kg (d) 9.6×10^{-12} kg

32. Calculate the enthalpy of formation (in kcal/mol) of gaseous HCl using the following data.

Substance	$\text{NH}_3\text{(g)}$	HCl(g)	$\text{NH}_4\text{Cl(s)}$
Heat of formation	-11	X	-75
Heat of solution	-8.5	-17.5	+3.9 kcal

$\text{NH}_3\text{(aq)} + \text{HCl(aq)} \rightarrow \text{NH}_4\text{Cl(aq)}$:
 $\Delta H = -12$ kcal

- (a) -44.2 (b) -22.1
(c) -11.05 (d) -28.7
33. Two bars of different metals are heated to 60°C and then immersed in identical insulated containers each containing 200 g of water at 20°C . Will the metal with higher or lower atomic mass cause a greater temperature rise in water?
- (a) Lower atomic mass
(b) Higher atomic mass
(c) Same for both
(d) Cannot be predicted
34. From the following data, calculate the enthalpy change (in kJ/mol) for the combustion of cyclopropane(g) at 298 K. The enthalpy of formation of $\text{CO}_2\text{(g)}$, $\text{H}_2\text{O(l)}$ and propene(g) are -394 , -286 and 20 kJ/mol, respectively. The enthalpy of isomerization of cyclopropane(g) to propene(g) is -33 kJ/mol.
- (a) -2073 (b) -2093
(c) -2060 (d) -2027
35. The reaction of zinc metal with hydrochloric acid was used to produce 1.5 moles of hydrogen gas at 298 K and 1 atm pressure. The magnitude of work done in pushing back the atmosphere is
- (a) 596 cal (b) 894 cal
(c) 447 cal (d) 298 cal
36. The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 7.4 kcal/mol. The molar internal energy change of vaporization is
- (a) 7.4 kcal/mol (b) 8.106 kcal/mol
(c) 6.694 kcal/mol (d) 62.47 kcal/mol

37. Determine the standard enthalpy of the reaction $\text{C}_3\text{H}_8(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g}) + \text{CH}_4(\text{g})$, using the given enthalpies under standard conditions.

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

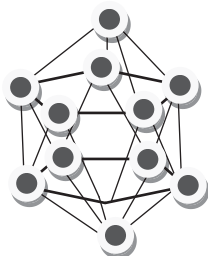
The standard enthalpy of formation of $\text{C}_3\text{H}_8(\text{g})$ is -103.8 kJ/mol .

- (a) -55.7 kJ (b) $+55.7 \text{ kJ}$ (c) -2060.4 kJ (d) $+2060.4 \text{ kJ}$

38. The enthalpy of formation of $\text{KCl}(\text{s})$ from the following data is
- $\text{KOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$: $\Delta H = -13.7 \text{ kcal}$
 - $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$: $\Delta H = -68.4 \text{ kcal}$
 - $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq})$: $\Delta H = -39.3 \text{ kcal}$
 - $\text{K}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + \text{aq} \rightarrow \text{KOH}(\text{aq})$: $\Delta H = -116.5 \text{ kcal}$
 - $\text{KCl}(\text{s}) + \text{aq} \rightarrow \text{KCl}(\text{aq})$: $\Delta H = +4.4 \text{ kcal}$
- (a) $+105.5 \text{ kcal/mol}$ (b) -105.5 kcal/mol
(c) -13.7 kcal/mol (d) -18.1 kcal/mol
39. Calculate ΔH for the following reaction at 298 K , $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$ from the following thermochemical equations.
- $3\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \rightarrow 2\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}_2(\text{g})$: $\Delta H = -46.4 \text{ kJ}$
 - $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightarrow \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$: $\Delta H = 9.0 \text{ kJ}$
 - $\text{Fe}_3\text{O}_4(\text{s}) + \text{CO}(\text{g}) \rightarrow 3\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$: $\Delta H = -41.0 \text{ kJ}$
- (a) -24.8 kJ (b) $+24.8 \text{ kJ}$
(c) -17.97 kJ (d) $+17.97 \text{ kJ}$
40. Calculate the enthalpy of formation (in kcal/mol) of $\text{HI}(\text{g})$ from the following data.
- $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$: $\Delta H = -44.20 \text{ kcal}$
 $\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq})$: $\Delta H = -17.31 \text{ kcal}$
 $\text{HI}(\text{g}) + \text{aq} \rightarrow \text{HI}(\text{aq})$: $\Delta H = -19.21 \text{ kcal}$
 $\text{KOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{KCl}(\text{aq})$: $\Delta H = -13.74 \text{ kcal}$
 $\text{KOH}(\text{aq}) + \text{HI}(\text{aq}) \rightarrow \text{KI}(\text{aq})$: $\Delta H = -13.67 \text{ kcal}$
 $\text{Cl}_2(\text{g}) + 2\text{KI}(\text{aq}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{s})$: $\Delta H = -52.42 \text{ kcal}$
- (a) $+19.21$ (b) -32.87
(c) $+5.94$ (d) $+7.82$
41. Calculate the enthalpy of formation of $\text{I}_2\text{O}_5(\text{s})$ from the following data.
- $\text{I}_2\text{O}_5(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{HIO}_3(\text{aq})$: $\Delta H = +4.0 \text{ kJ}$
 - $\text{KI}(\text{aq}) + 3\text{HClO}(\text{aq}) \rightarrow \text{HIO}_3(\text{aq}) + 2\text{HCl}(\text{aq}) + \text{KCl}(\text{aq})$: $\Delta H = -322.0 \text{ kJ}$
 - $\text{NaOH}(\text{aq}) + \text{HClO}(\text{aq}) \rightarrow \text{NaOCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$: $\Delta H = -44.0 \text{ kJ}$
 - $\text{NaOH}(\text{aq}) + \text{HCl}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$: $\Delta H = -57.0 \text{ kJ}$
 - $2\text{NaOH}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{NaOCl}(\text{aq}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$: $\Delta H = -100.0 \text{ kJ}$
 - $2\text{KI}(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{KCl}(\text{aq}) + \text{I}_2(\text{s})$: $\Delta H = -224.0 \text{ kJ}$
 - $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$: $\Delta H = -285.0 \text{ kJ}$
 - $\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$: $\Delta H = -92.0 \text{ kJ}$
 - $\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{HCl}(\text{aq})$: $\Delta H = -75.0 \text{ kJ}$
- (a) -169.0 kJ (b) -173.0 kJ
(c) -165.0 kJ (d) -177.0 kJ
42. Calculate proton affinity of $\text{NH}_3(\text{g})$ from the following data.
- $\Delta H_{\text{dissociation}} \text{H}_2 = 218 \text{ kJ mole}^{-1}$
 $\Delta H_{\text{dissociation}} \text{Cl}_2 = 124 \text{ kJ mole}^{-1}$
 $\Delta H_f^\circ \text{ of } \text{NH}_3(\text{g}) = -46 \text{ kJ mole}^{-1}$
 $\Delta H_f^\circ \text{ of } \text{NH}_4\text{Cl}(\text{s}) = -314 \text{ kJ mole}^{-1}$
 Ionization energy of $\text{H} = 1310 \text{ kJ mole}^{-1}$
 E.A. of $\text{Cl}(\text{g}) = -348 \text{ kJ mole}^{-1}$
 Lattice energy of $\text{NH}_4\text{Cl}(\text{s}) = -683 \text{ kJ mole}^{-1}$
- (a) $-818 \text{ kJ mole}^{-1}$ (b) $-718 \text{ kJ mole}^{-1}$
(c) $-318 \text{ kJ mole}^{-1}$ (d) $-418 \text{ kJ mole}^{-1}$

43. The polymerization of ethylene to linear polyethylene is represented by the reaction
- $$n\text{CH}_2=\text{CH}_2 \rightarrow (-\text{CH}_2-\text{CH}_2-)_n$$
- where n has a large integral value. Given that the average enthalpies of bond dissociation for C=C and C-C at 298 K are +590 and +331 kJ/mol, respectively, the enthalpy of polymerization per mole of ethylene at 298 K is
- (a) -72 kJ (b) +259 kJ
(c) -259 kJ (d) -849 kJ
44. The enthalpy of formation of liquid methyl alcohol in kJ/mol, using the following data (in kJ/mol).
Heat of vaporization of liquid methyl alcohol = 38.
Heat of formation of gaseous atoms from the elements in their standard states: H, 218; C, 715; O, 249.
Average bond energies: C-H, 415; C-O, 356; O-H, 463.
- (a) -190 (b) -702
(c) -626 (d) -266
45. The strain energy (in kJ/mol) of cyclopropane from the following data is
- $$\Delta_f H [\text{C}_3\text{H}_6(\text{g})] = 53.0 \text{ kJ/mol}; \Delta_f H [\text{C}(\text{g})] = 715.0 \text{ kJ/mol}; \Delta_f H [\text{H}(\text{g})] = 218.0 \text{ kJ/mol}$$
- B.E. (C-C) = 356.0 kJ/mol; B.E. (C-H) = 408.0 kJ/mol.
- (a) 770 kJ (b) 116 kJ
(c) 240 kJ (d) 346 kJ
46. Standard enthalpy of formation of gaseous ethane, ethene and benzene from gaseous atoms are -2839, -2275 and -5506 kJ/mol, respectively. The bond enthalpy of C-H bond is 412 kJ/mol. The magnitude of resonance energy of benzene compared with one Kekule structure is
- (a) 24 kJ (b) 52 kJ
(c) 2524 kJ (d) 152 kJ
47. Find the bond energy of S-S bond from the following data.
- $$\text{C}_2\text{H}_5-\text{S}-\text{C}_2\text{H}_5(\text{g}): \Delta H^\circ_f = -148 \text{ kJ},$$
- $$\text{C}_2\text{H}_5-\text{S}-\text{S}-\text{C}_2\text{H}_5(\text{g}): \Delta H^\circ_f = -202 \text{ kJ},$$
- $$\text{S}(\text{g}): \Delta H^\circ_f = 222 \text{ kJ}$$
- (a) 276 kJ/mol (b) 128 kJ/mol
(c) 168 kJ/mol (d) 222 kJ/mol
48. Given the bond dissociation enthalpy of CH₃-H bond as 103 kcal/mol and the enthalpy of formation of CH₄(g) as -18 kcal/mol, find the enthalpy of formation of methyl radical. The dissociation energy of H₂(g) into H (atoms) is 103 kcal/mol.
- (a) -33.5 kcal/mol (b) 33.5 kcal/mol
(c) 18 kcal/mol (d) -9 kcal/mol
49. Calculate the enthalpy of the following homogeneous gaseous reaction
- $$\text{CH}_3\text{COCH}_3 + 2\text{O}_2 \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2 + \text{H}_2\text{O}$$
- from the following data.
- Bond energies (kJ/mol): C-H = 414; C-C = 348; C=O = 580; C-O = 354; O=O = 610; O-H = 462;
Magnitude of resonance energies (kJ/mol): COOH = 118; CO₂ = 140.
- (a) 348 kJ (b) 168 kJ
(c) -168 kJ (d) -348 kJ
50. What is the enthalpy change for the isomerization reaction?
- $$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2 \text{ (A)}$$
- $$\xrightarrow[\Delta]{\text{NaNH}_2} \text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2 \text{ (B)}$$
- Magnitude of resonance energies of A and B are 50 and 70 kJ/mol, respectively.
- Enthalpies of formation of A and B are -2275.2 and -2839.2 kJ/mol, respectively.
- (a) -584 kJ (b) -564 kJ
(c) -544 kJ (d) -20 kJ
51. The bond enthalpies of C-C, C=C and C≡C bonds are 348, 610 and 835 kJ/mol, respectively at 298 K and 1 bar. The enthalpy of polymerization per mole of 2-Butyne at 298 K and 1 bar as shown below is
- $$n\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3(\text{g}) \rightarrow -(\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2)_n - (\text{g})$$
- (a) -123 kJ (b) -132 kJ
(c) -139 kJ (d) -37 kJ
52. The enthalpies of combustion of formaldehyde and paraformaldehyde (a polymer of formaldehyde) are -134 and -732 kcal/mol, respectively. The enthalpy of polymerization per mole of paraformaldehyde is -72 kcal. The molecular formula of paraformaldehyde is
- (a) CH₂O (b) C₆H₁₂O₆
(c) C₃H₆O₃ (d) C₄H₈O₄

53. Boron exists in different allotropic forms. All allotropic form contains icosahedral units (icosahedral is a regular shape with 12 corners and 20 faces) with boron atoms at all 12 corners and all bonds are equivalent. Calculate the heat evolved at constant pressure (in kJ/mole) of boron atom undergoing the above change if the bond dissociation enthalpy of B–B bond is 300 kJ/mol.



- (a) 500 (b) 750
(c) 1500 (d) 900
54. Butane exists in various conformations in nature. At any given instant, the probability that a given butane molecule is in anti, gauche, eclipsed and fully eclipsed conformation is 0.7, 0.2, 0.06 and 0.04, respectively. If the molar enthalpy of

combustion of natural butane is -690 kcal/mol at 25°C , then calculate the enthalpy of combustion of butane if all the butane molecules are in gauche conformation. The potential energy of gauche form is 2 kcal/mol higher than anti form but it is 3 kcal/mol less than eclipsed form and 5.5 kcal/mol less than fully eclipsed form.

- (a) -690 kcal/mol (b) -689 kcal/mol
(c) -691 kcal/mol (d) -692 kcal/mol

55. For an ionic solid MX_2 , where X is monovalent, the enthalpy of formation of the solid from $\text{M}(\text{s})$ and $\text{X}_2(\text{g})$ is 1.5 times the electron gain enthalpy of $\text{X}(\text{g})$. The first and second ionization enthalpies of the metal (M) are 1.2 and 2.8 times of the enthalpy of sublimation of $\text{M}(\text{s})$. The bond dissociation enthalpy of $\text{X}_2(\text{g})$ is 0.8 times the first ionization enthalpy of metal and it is also equal to one-fifth of the magnitude of lattice enthalpy of MX_2 . If the electron gain enthalpy of $\text{X}(\text{g})$ is -96 kcal/mol, then what is the enthalpy of sublimation (in kcal/mol) of the metal (M)?

- (a) 41.38 (b) 52.5
(c) 48.0 (d) 38.27

Section B (One or More than one Correct)

- Which of the following is/are endothermic reaction(s)?
(a) Combustion of methane.
(b) Decomposition of water.
(c) Dehydrogenation of ethane to ethylene.
(d) Conversion of graphite to diamond.
- The enthalpy change for the following process would be expected to be a negative for
(a) $\text{Na}^+(\text{g}) + \text{e}^- \rightarrow \text{Na}(\text{g})$
(b) $\text{F}(\text{g}) + \text{e}^- \rightarrow \text{F}^-(\text{g})$
(c) $\text{Na}^+(\text{g}) + \text{F}^-(\text{g}) \rightarrow \text{NaF}(\text{s})$
(d) $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$
- For which of the following substance(s), the standard enthalpy of formation is/is are zero?
(a) C (graphite) (b) $\text{O}_3(\text{g})$
(c) $\text{I}_2(\text{g})$ (d) $\text{Br}_2(\text{l})$
- Which of the following is/are endothermic compound(s)?
(a) $\text{NO}(\text{g})$ (b) $\text{CO}_2(\text{g})$
(c) $\text{CO}(\text{g})$ (d) $\text{NH}_3(\text{g})$
- Among the following the reaction for which $\Delta H = \Delta E$, is
(a) $\text{PCl}_5(\text{g}) \rightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$
(b) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g})$
(c) $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{g})$
(d) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$
- ΔH of which of the following reaction(s) may be directly taken as enthalpy of combustion of the concerned substance?
(a) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
(b) $2\text{C}_2\text{H}_6(\text{g}) + 7\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$
(c) $\text{C}_3\text{H}_8(\text{g}) + 7/2 \text{O}_2(\text{g}) \rightarrow 3\text{CO}(\text{g}) + 4\text{H}_2\text{O}(\text{l})$
(d) $1/2 \text{N}_2(\text{g}) + 1/2 \text{O}_2(\text{g}) \rightarrow \text{NO}(\text{g})$
- Which of the following reaction(s) is/are endothermic?
(a) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
(b) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
(c) $2\text{CO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g})$
(d) $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6(\text{g})$

8. A volume of 100 ml of 0.5 N- H_2SO_4 solution is neutralized with 200 ml of 0.2 M- NH_4OH in a constant pressure calorimeter which resulted 1.4°C rise in temperature. The heat capacity of the calorimeter system is $1.5 \text{ kJ}/^\circ\text{C}$. Some useful thermochemical equations are as follows:
- $$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} + 57 \text{ kJ}$$
- $$\text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} + 48.1 \text{ kJ}$$
- Which of the following statements are correct?
- Enthalpy of neutralization of HCl vs. NH_4OH is -52.5 kJ/mol .
 - Enthalpy of dissociation (ionization) of NH_4OH is 4.5 kJ/mol .
 - Enthalpy of dissociation (ionization) of CH_3COOH is 4.6 kJ/mol .
 - ΔH for $2\text{H}_2\text{O(l)} \rightarrow 2\text{H}^+(\text{aq}) + 2\text{OH}^-(\text{aq})$ is 114 kJ .
9. From the following data at 25°C , which of the following statement(s) is/are correct?
- $$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g}); \Delta H^\circ = 42 \text{ kJ}$$
- $$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H^\circ = -242 \text{ kJ}$$
- $$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g}); \Delta H^\circ = 436 \text{ kJ}$$
- $$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g}); \Delta H^\circ = 495 \text{ kJ}$$
- $\Delta_f H^\circ$ for the reaction $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$ is 925.5 kJ .
 - $\Delta_f H^\circ$ for the reaction $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$ is 502 kJ .
 - Enthalpy of formation of $\text{H}(\text{g})$ is -218 kJ/mol .
 - Enthalpy of formation of $\text{OH}(\text{g})$ is 42 kJ/mol .
10. Which of the following molecules will have different values of standard molar enthalpy of formation, one calculated using bond energy concept and other calculated calorimetrically?
- C_2H_6
 - 1,3-Butadiene
 - 1,4-Cyclohexadiene
 - N_2O
11. Consider the following isomerization process.
- $$\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2(\text{g})$$
- $$\rightarrow \text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3(\text{g})$$
- Which of the following statement(s) is/are true regarding this process?
- The process is exothermic.
 - Enthalpy change of reaction = Resonance enthalpy of product.
 - The magnitude of enthalpy of combustion of product is less than that of reactant.
 - The magnitude of enthalpy of hydrogenation of product is greater than that of reactant.
12. α -maltose can be hydrolysed to glucose according to the following reaction.
- $$\alpha\text{-C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow 2\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$$
- The standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$, $\text{C}_6\text{H}_{12}\text{O}_6(\text{aq})$ and $\alpha\text{-C}_{12}\text{H}_{22}\text{O}_{11}(\text{aq})$ are -285 , -1263 and -2238 kJ/mol , respectively. Which of the following statement(s) is/are true?
- The hydrolysis reaction is exothermic.
 - Heat liberated in combustion of 1.0 mole of α -maltose is smaller than the heat liberated in combustion of 2.0 mole of glucose neglecting the effect of hydration.
 - Increase in temperature will increase the degree of hydrolysis of α -maltose.
 - Enthalpy of reaction will remain the same even if solid α -maltose is taken in the reaction.
13. In certain areas where coal is cheap, artificial gas is produced for house hold use by the 'water gas' reaction.
- $$\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}(\text{g})$$
- Assume that coke is 100% carbon. Given ΔH_c (kcal/mol) at 25°C : $\text{H}_2(\text{g}) = -68.0$; $\text{CO}(\text{g}) = -68.0$; $\text{C}(\text{s}) = -94.0$. Select the correct option(s) from the following.
- The maximum heat obtainable at 25°C from the combustion of 1.2 kg of coke is 9400 kcal.
 - The maximum heat obtainable at 25°C from burning water gas produced from 1.2 kg of coke is 13,600 kcal.
 - The maximum heat obtainable at 25°C from burning 1.2 kg of water gas is 5440 kcal.
 - The maximum heat obtainable at 25°C from burning water gas or burning the same mass of coke will be same.
14. At 300 K, 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 kJ/mol , respectively. The enthalpy of combustion of benzoic acid(s) at 300 K is
- -3201 kJ/mol , at constant pressure.
 - -3199.75 kJ/mol , at constant pressure.
 - -3201 kJ/mol , at constant volume.
 - -3199.75 kJ/mol , at constant volume.

15. For the reaction, $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$; $\Delta H = -35.0 \text{ kcal}$ at 300 K. If 6.0 moles of NO reacts with 3.0 moles of O_2 at constant pressure of 1.0 atm and temperature 300 K to form NO_2 , then which of the following statement(s) is/are correct?
- (a) The magnitude of work done by the system is 1.8 kcal.
- (b) The amount of heat released by the reaction is 35 kcal.
- (c) The internal energy of system decreased by 103.2 kcal.
- (d) The internal energy of system decreased by 106.8 kcal.

4. **Solution I:** 1 mole of H_2SO_4 dissolved in 5 moles of water.
- (a) -64.66 kJ
(b) -66.18 kJ
(c) -208.33 kJ
(d) -55.15 kJ
5. **Solution II:** 1 mole of H_2SO_4 dissolved in 10 moles of water.
- (a) -69.44 kJ
(b) -63.56 kJ
(c) -416.67 kJ
(d) -58.59 kJ
6. **Solution III:** 1 mole of H_2SO_4 dissolved in large excess of water.
- (a) Indeterminate (b) zero
(c) -750 kJ (d) -75 kJ
7. **Solution IV:** Solution I + 5 moles of water.
- (a) -63.56 kJ (b) -55.15 kJ
(c) $+8.41 \text{ kJ}$ (d) -8.41 kJ
8. **Solution V:** Solution II + large excess of water.
- (a) Indeterminate (b) -63.56 kJ
(c) -11.44 kJ (d) -75 kJ

Comprehension III

Study the following thermochemical equations



9. Which oxidizing agent will generate the greatest amount of energy for 1 mole of $\text{H}_2(\text{g})$?
- (a) $\text{O}_2(\text{g})$ (b) $\text{O}_3(\text{g})$
(c) $\text{H}_2\text{O}_2(\text{g})$ (d) All are same
10. Which oxidizing agent will generate the greatest amount of energy for 1 g of oxidizing agent?
- (a) $\text{O}_2(\text{g})$ (b) $\text{O}_3(\text{g})$
(c) $\text{H}_2\text{O}_2(\text{g})$ (d) All are same
11. Which of the reaction will generate the greatest amount of energy on a total mass basis of reactants?
- (a) H_2-O_2 (b) H_2-O_3
(c) $\text{H}_2-\text{H}_2\text{O}_2$ (d) All are same
-

Comprehension IV

The thermal effects of reactions in liquid NH_3 at -33°C were measured by observing the quantity of liquid NH_3 vaporized by the process of interest. The heat of vaporization of NH_3 at -33°C is 320.0 cal/g. When 0.98 g of NH_4Br was dissolved in 20 g of liquid NH_3 , 0.25 g of NH_3 was vaporized ($\text{Br} = 80$).

12. The molar heat of solution of NH_4Br in liquid NH_3 at this concentration is
- (a) +80.0 cal (b) -80.0 cal
(c) -8.0 kcal (d) +8.0 kcal
13. When 0.49 g of NH_4Br was dissolved in 20 g of liquid NH_3 containing an equimolar amount of KNH_2 , 0.80 g of ammonia was vaporized. The ΔH for the reaction
- $$\text{NH}_4^+(\text{NH}_3, \text{l}) + \text{NH}_2^-(\text{NH}_3, \text{l}) \rightarrow 2\text{NH}_3(\text{l})$$
- at 240 K is
- (a) -256.0 cal (b) +256.0 cal
(c) +51.2 kcal (d) -51.2 kcal
-

Comprehension V

Use the data (all values are in kJ per mole at 25°C) given below to answer the following.

Enthalpy of formation of $\text{CH}_3\text{CN} = +88.0$

Enthalpy of formation of $\text{C}_3\text{H}_8 = -85.0$

Enthalpy of sublimation of graphite = 719.0

Enthalpy of dissociation of nitrogen = 948.0

Enthalpy of dissociation of hydrogen = 435.0

Bond enthalpies: $\text{C}-\text{H} = 414.0$; $\text{C}-\text{N} = 378.0$; $\text{N}-\text{H} = 426.0$

14. The bond enthalpy of $\text{C}-\text{C}$ bond (kJ/mol) is
- (a) 250.0 (b) 335.0
(c) 223.33 (d) 248.5
15. The bond enthalpy of $\text{C}\equiv\text{N}$ bond (kJ/mol) is
- (a) 987.5 (b) 811.5
(c) 899.5 (d) 890.0
16. The enthalpy of hydrogenation of CH_3CN (kJ/mol) is
- (a) -288.5 (b) +288.5
(c) -89.5 (d) +89.5
-

Comprehension VI

An intimate mixture of hydrogen gas and a theoretical amount of air at 27°C and a total pressure of 1 atm is exposed in a closed rigid vessel. If the process occurs under adiabatic condition, then using the following data, answer the following questions.

Given: (i) $C_{P,m} = 6.9$ cal/K-mol (ii) $C_{P,m} = 8.2$ cal/K-mol (iii) $\Delta_f H [\text{H}_2\text{O(g)}] = -55.85$ kcal (iv) Air contains 20% O_2 and 80% N_2 , by volume

17. The values of $C_{P,m}$ of $\text{N}_2(\text{g})$ and $\text{H}_2\text{O(g)}$ (in cal/K-mol) should be
(a) 6.9, 6.9 (b) 6.9, 8.2
(c) 8.2, 8.2 (d) 8.2, 6.9
18. What will be the maximum temperature (approximately) attained if the process occurs in adiabatic container?
(a) 3800 K (b) 3500 K
(c) 2540 K (d) 300 K
19. What will be the final pressure (approximately)?
(a) 10.86 atm (b) 12.67 atm
(c) 14.78 atm (d) 1.0 atm
20. If at initial temperature, T_1 , E_1 is the internal energy and at higher temperature T_2 , E_2 is the internal energy, then
(a) $E_1 > E_2$ (b) $E_1 < E_2$
(c) $E_1 = E_2$ (d) Unpredictable

Comprehension VII

When 0.1 mole of $\text{C}_8\text{H}_{18}(\text{l})$ at 300 K is completely burned at constant pressure in stoichiometric amount of oxygen gas at 300 K, yielding as products gaseous H_2O , CO and CO_2 at 800 K, the process yielding 87.3 kcal of heat to the surrounding.

$\Delta_f H$ (kcal/mol): $\text{C}_8\text{H}_{18}(\text{l}) = -74.0$, $\text{CO}_2(\text{g}) = -94.0$, $\text{CO(g)} = -26.5$, $\text{H}_2\text{O(g)} = -58.0$

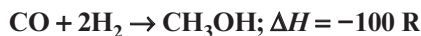
Molar heat capacity at constant pressure (cal/K-mol): $\text{CO(g)} = 7.0$, $\text{CO}_2(\text{g}) = 8.0$, $\text{H}_2\text{O(g)} = 6.0$

Assume that all $\Delta_f H$ are independent of temperature.

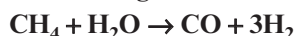
21. The value of $\Delta_c H$ of $\text{C}_8\text{H}_{18}(\text{l})$ is (in kcal/mol) assuming the formation of $\text{H}_2\text{O(g)}$
(a) +1200.0 (b) +660.0
(c) -1200.0 (d) -660.0
22. The value of $\Delta_r H$ for the reaction $\text{C}_8\text{H}_{18}(\text{l}) + \frac{17}{2} \text{O}_2(\text{g}) \rightarrow 8\text{CO(g)} + 9\text{H}_2\text{O(g)}$ is (in kcal/mol)
(a) +1200.0 (b) +660.0
(c) -1200.0 (d) -660.0
23. How many moles of CO_2 are produced?
(a) 0.1 (b) 0.8
(c) 0.4 (d) 0.05
24. How many moles of H_2O are produced?
(a) 0.1 (b) 0.9
(c) 0.45 (d) 1.8
25. What is the magnitude of work done by the system?
(a) 1.045 kcal (b) 2.09 kcal
(c) 0.96 kcal (d) 5.7 kcal

Comprehension VIII

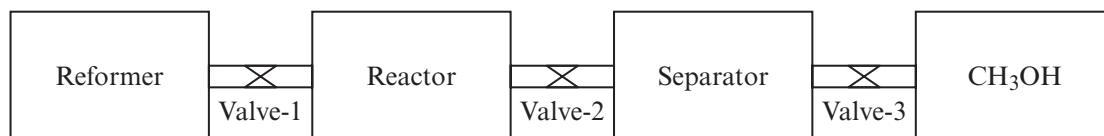
A factory is producing methanol based on the following reaction.



Hydrogen and carbon monoxide are obtained by the following reaction.



Three units of factory, namely reformer (for the production of H_2 and CO), reactor (for the production of methanol from CO and H_2) and separator (to separate CH_3OH from CO and H_2) are schematically shown in the following figure.



The flow of methanol from Valve-3 is 1000 mol/sec. The factory is so designed that 2/3rd of the CO is converted to CH₃OH. Assume that the reformer reaction goes to completion.

26. What is the flow of CO and H₂ at Valve-1?
(a) CO = 3000 mol/sec; H₂ = 9000 mol/sec
(b) CO = 1500 mol/sec; H₂ = 3000 mol/sec
(c) CO = 1000 mol/sec; H₂ = 2000 mol/sec
(d) CO = 1500 mol/sec; H₂ = 4500 mol/sec
27. What is the flow of CO and H₂ at Valve-2?
(a) CO = 500 mol/sec; H₂ = 1000 mol/sec
(b) CO = 500 mol/sec; H₂ = 2500 mol/sec
(c) CO = 500 mol/sec; H₂ = 2000 mol/sec
(d) CO = 500 mol/sec; H₂ = 1500 mol/sec
28. Amount of energy released in methanol reactor in one minute is
(a) 12,000 kcal
(b) 1200 kcal
(c) 6000 kcal
(d) 600 kcal

Comprehension IX

When 12 g of carbon reacted with oxygen to form CO and CO₂ at 298 K and constant pressure, 53.2 kcal of heat was liberated and no carbon remained. Heat of formation of CO and CO₂ are -26.0 and -94.0 kcal/mole, respectively.

29. Moles of CO formed is
(a) 0.4
(b) 0.5
(c) 0.6
(d) 1.0
30. Mass of oxygen reacted with carbon is
(a) 16 g
(b) 32 g
(c) 24 g
(d) 22.4 g

Comprehension X

The bond dissociation enthalpy of the first H-S bond in hydrogen sulphide is 376.0 kJ/mol. The enthalpies of formation of H₂S(g) and S(g) are -20.0 and 277.0 kJ/mol, respectively. The bond dissociation enthalpy of H-H bond is 436.0 kJ/mol.

31. The enthalpy of formation of the free radical HS is
(a) 138 kJ/mol
(b) -138 kJ/mol
(c) -10 kJ/mol
(d) 357 kJ/mol
32. The bond dissociation enthalpy of the free radical HS is
(a) 138 kJ/mol
(b) 276 kJ/mol
(c) 357 kJ/mol
(d) 376 kJ/mol

Comprehension XI

For the reaction at 25°C, X₂O₄(l) → 2XO₂(g), ΔE° = 2.1 kcal and ΔS° = 20 cal/K.

33. The value of ΔG° for the reaction is
(a) -2.7 kcal
(b) -9.25 kcal
(c) +2.7 kcal
(d) +9.25 kcal
34. The reaction is
(a) Spontaneous and exergonic.
(b) Non-spontaneous and exergonic.
(c) Spontaneous and endergonic.
(d) Non-spontaneous and endergonic.
-

Section D (Assertion – Reason)

The following questions consist of two statements. Mark the answer as follows.

- (a) If both statements are CORRECT, and **Statement II** is the CORRECT explanation of **Statement I**.
(b) If both statements are CORRECT, and **Statement II** is NOT the CORRECT explanation of **Statement I**.
(c) If **Statement I** is CORRECT, but **Statement II** is INCORRECT.
(d) If **Statement I** is INCORRECT, but **Statement II** is CORRECT.

1. **Statement I:** On increasing the temperature, the enthalpy of reaction may increase, decrease or remain constant.

Statement II: On changing the temperature, the enthalpies of reactants and products may change to same or different extent depending on their heat capacities.

2. **Statement I:** Standard enthalpy of isomerization of an enantiomer into the other is zero.

Statement II: The two enantiomers of any chiral compound have the same enthalpy of formation.

3. **Statement I:** Heat evolved in the neutralization of either 1 mole of HCl or 1 mole of H_2SO_4 with NaOH is same.

Statement II: Both HCl and H_2SO_4 are strong acids.

4. **Statement I:** When a salt is dissolved in water, the temperature of solution decreases.

Statement II: Solubility of any salt in water may be endothermic or exothermic.

5. **Statement I:** If 5 ml of an acid solution is completely neutralized by adding 5 ml of a base solution, then the temperature of solution increases by $x^\circ\text{C}$. If 20 ml of the same acid solution is completely neutralized by adding 20 ml of the same base solution, then the temperature of the solution increases by $4x^\circ\text{C}$.

Statement II: Heat liberated in the second case will be four times the heat liberated in the first case.

6. **Statement I:** The solubility of any gas in any liquid is an exothermic process.

Statement II: All the gases are highly soluble in any liquid.

7. **Statement I:** For all the salts completely soluble in water, the magnitude of sum of the enthalpies of hydration of ions is greater than the magnitude of lattice enthalpy of the salt.

Statement II: If the magnitude of sum of enthalpies of hydration of ions is less than the lattice enthalpy of the salt, then the salt is completely insoluble in water.

8. **Statement I:** The magnitude of enthalpy of combustion of diamond is greater than that of graphite.

Statement II: Graphite is thermodynamically more stable form of carbon than diamond.

9. **Statement I:** The magnitude of enthalpy of combustion of 2-Butene is less than that of 1-Butene.

Statement II: 2-Butene is thermodynamically more stable than 1-Butene.

10. **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 salt like NaCl, KCl, etc., which do not form hydrates is 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 difference in the molecular masses of hydrated and anhydrous salts. The substance with large molecular mass usually shows positive enthalpy changes on dissolutions.

Section E (Column Match)

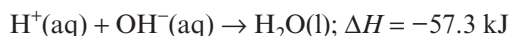
1. Match the columns.

Column I (Reaction)	Column II (Process)
(A) $\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}$	(P) Combustion
(B) $\text{CO(g)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	(Q) Neutralization
(C) $\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$	(R) Formation
(D) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(l)}$	(S) Used in fuel cell

2. Match the columns.

Column I (Reaction)	Column II (Relation)
(A) $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl(g)}$	(P) $\Delta H = \Delta U + RT$
(B) $2\text{N}_2\text{O(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$	(Q) $\Delta H = \Delta U$
(C) $\text{H}_2(\text{g}) + \text{I}_2(\text{s}) \rightarrow 2\text{HI(g)}$	(R) $\Delta H = \Delta U - 2RT$
(D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$	(S) $\Delta H = \Delta U - RT$

3. Column I contains some chemical reactions and Column II contains some ΔH values (in kJ). Match the correct ΔH in Column II for the chemical reaction in Column I with the help of the following thermochemical equations given.



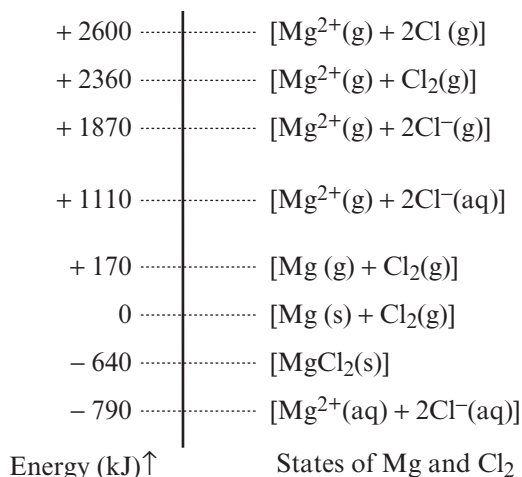
$$\Delta H_{\text{Solution}} \text{ of HA(g)} = -70.7 \text{ kJ/mol}$$

$$\Delta H_{\text{Solution}} \text{ of BOH(g)} = 20 \text{ kJ/mol}$$

$\Delta H_{\text{Ionization}}$ of HA = 15 kJ/mol and BOH is a strong base.

Column I (Chemical reactions)	Column II (ΔH values in kJ)
(A) $\text{HA(aq)} + \text{BOH(aq)} \rightarrow \text{BA(aq)} + \text{H}_2\text{O}$	(P) -42.3
(B) $\text{HA(g)} + \text{BOH(g)} \rightarrow \text{BA(aq)} + \text{H}_2\text{O}$	(Q) -93
(C) $\text{HA(g)} \rightarrow \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$	(R) -55.7
(D) $\text{B}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{OH(aq)}$	(S) 0

4. Carefully observe the given diagrams which indicate the standard enthalpy of formation of different states of one mole of Mg and two moles of Cl atoms and match the entries in Column I and II provided.



Column I	Column II
(A) $\Delta_f H [\text{Mg}^{2+}(\text{aq})]$	(P) -1900 kJ/mol
(B) $\Delta_f H [\text{Cl}^-(\text{aq})]$	(Q) +460 kJ/mol
(C) $\Delta H_{\text{Hydration}} [\text{Mg}^{2+}(\text{g})]$	(R) -625 kJ/mol
(D) Lattice enthalpy of $\text{MgCl}_2(\text{s})$	(S) +2510 kJ/mol

5. Match the columns.

Column I	Column II ($\Delta_f H$ is also known as)
(A) $\text{C (Graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	(P) $\Delta H_{\text{formation}}$
(B) $\text{C (Graphite)} \rightarrow \text{C(g)}$	(Q) $\Delta H_{\text{combustion}}$
(C) $\text{HCl(aq)} + \text{OH}^-(\text{aq}) \rightarrow \text{Cl}^-(\text{aq}) + \text{H}_2\text{O(l)}$	(R) $\Delta H_{\text{atomization}}$
	(S) $\Delta H_{\text{neutralization}}$

6. Match the columns.

Column I	Column II
(A) Sb(s)	(P) $\Delta_f H^\circ = +ve$ $\Delta_f S^\circ = +ve$
(B) O ₃ (g)	(Q) $\Delta_f H^\circ = 0$ $\Delta_f S^\circ = 0$
(C) I ₂ (g)	(R) $\Delta_f H^\circ = +ve$ $\Delta_f S^\circ = -ve$
(D) CO(g)	(S) $\Delta_f H^\circ = -ve$ $\Delta_f S^\circ = +ve$

7. Match the columns.

Column I	Column II
(A) $2\text{HCl(g)} \rightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$	(P) $\Delta H = +\text{ve}$ $\Delta S = +\text{ve}$
(B) $2\text{O}_3\text{(g)} \rightarrow 3\text{O}_2\text{(g)}$	(Q) $\Delta H = -\text{ve}$ $\Delta S = +\text{ve}$
(C) $\text{MgCO}_3\text{(s)} \rightarrow \text{MgO(s)} + \text{CO}_2\text{(g)}$	(R) $\Delta H = -\text{ve}$ $\Delta S = -\text{ve}$
(D) $2\text{NO}_2\text{(g)} \rightarrow \text{N}_2\text{O}_4\text{(g)}$	(S) $\Delta H = +\text{ve}$ $\Delta S \approx +\text{ve}$

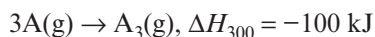
8. Match the columns

Column I	Column II
(A) $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}$	(P) $\Delta H = \Delta U$
(B) $2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)}$	(Q) $\Delta H > \Delta U$
(C) $\text{PCl}_5\text{(g)} \rightarrow \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}$	(R) $\Delta H < \Delta U$
(D) $\text{C}_2\text{H}_4\text{(g)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$	(S) $ \Delta H > \Delta U $
	(T) $ \Delta H < \Delta U $

9. Match the columns.

Column I	Column II
(A) $\text{C(Diamond)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	(P) $\Delta_r H^\circ = \Delta_c H^\circ$
(B) $\text{C(Graphite)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$	(Q) $\Delta_r H^\circ = \Delta_f H^\circ$
(C) $\text{H}_2\text{(g)} \rightarrow 2\text{H(g)}$	(R) $\Delta_r H^\circ = \Delta_{\text{atomization}} H^\circ$
(D) $\text{CH}_4\text{(g)} \rightarrow \text{C(g)} + 4\text{H(g)}$	(S) $\Delta_r H^\circ = \Delta_{\text{bond}} H^\circ$

10. Some thermochemical details are given as follows.



The standard boiling points of A(l) and A₃(l) are 300 K and 400 K, respectively.

Molar heat capacities at constant pressure (in J/K-mol): A(l) = 40; A(g) = 20; A₃(l) = 50; A₃(g) = 30

Match the columns on the basis of these details.

Column I	Column II
(A) $\text{A(l)} \rightarrow \text{A(g)}$ $\Delta_{\text{vap}} H_{400}$	(P) -84 kJ/mol
(B) $\text{A}_3\text{(l)} \rightarrow \text{A}_3\text{(g)}$ $\Delta_{\text{vap}} H_{300}$	(Q) $+23 \text{ kJ/mol}$
(C) $3\text{A(l)} \rightarrow \text{A}_3\text{(l)}$ ΔH_{300}	(R) $+52 \text{ kJ/mol}$
(D) $3\text{A(l)} \rightarrow \text{A}_3\text{(l)}$ ΔH_{400}	(S) -77 kJ/mol

Section F (Subjective)

Single-digit Integer Type

- Volumes of 50 ml of 1 M-NaOH and 50 ml of 1 M-HCl both at the same temperature were mixed in a calorimeter of very small heat capacity. A temperature rise of 411 K was recorded. In a second experiment, the HCl was replaced by 50 ml of 1 M-HCOOH. The temperature rise was 321 K. The enthalpy of ionization (in kcal/mol) of HCOOH is
- The heat evolved on combustion of 1 g of starch, $(\text{C}_6\text{H}_{10}\text{O}_5)_x$ into $\text{CO}_2\text{(g)}$ and $\text{H}_2\text{O(l)}$ is 4.6 kcal. Heat of formation of $\text{CO}_2\text{(g)}$ and $\text{H}_2\text{O(l)}$ are -94.2 and -68.4 kcal/mol, respectively. The magnitude of standard enthalpy of formation of 1 g of starch (in kcal) is

- 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 required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with 'X' L/hr of methane and '6X' L/hr of oxygen) is to be adjusted for butane. In order to get same calorific output, what should be the supply of oxygen (in L/hr) with 1 L/hr supply of butane? Assume that losses due to incomplete combustion, etc., are the same for both fuels and that the gases behave ideally. Enthalpies of combustion; methane = -800 kJ/mol; butane = -3120 kJ/mol.
- The enthalpy of neutralization of monobasic acid in decinormal solution by a dilute solution of KOH is $-12,200$ cal. The enthalpy of neutralization of strong acid by strong base is $-13,700$ cal. Assuming that the acid is 25% dissociated in decinormal solution, the enthalpy of dissociation of the acid (in kcal/mole) is
- A volume of 1.642 L sample of a mixture of methane gas and oxygen measured at 298 K and 1.192 atm, was allowed to react at constant pressure in a calorimeter which together with its content had a heat capacity of 1260 cal/K. The complete combustion of methane to carbon dioxide and water caused a temperature rise in calorimeter 0.667 K. The volume percent of methane in original mixture is (Given the heat of combustion of methane is -210 kcal/mole)
- A solution of 6.3 g of haemoglobin (molar mass = 64,000 g/mol) in 25 ml of solution shows a temperature rise of 0.03°C for complete oxygenation. Each mole of haemoglobin binds 4 moles of oxygen. If the heat capacity of the solution is 4.2 J/K-ml, then the amount of heat released per mole of oxygen bound (in kJ) is
- Two solutions, initially at 25°C , were mixed in an insulated bottle. One contained 200 ml of 0.4 M weak monoprotic acid solution. The other contained 100 ml of a solution having 0.5 mole NaOH per litre. After mixing, the temperature rose to 26°C . Assume that the densities of both the solutions are 1.0 g/ml and that their specific heat capacities are 1.0 cal/g-K. The amount of heat evolved (in kcal) in the neutralization of 1 mole of the acid is
- In solid NH_3 , each NH_3 molecule has six other NH_3 molecules as nearest neighbours. The enthalpy of sublimation of $\text{NH}_3(\text{s})$ at its melting point is 30.4 kJ/mol and estimated value of enthalpy of sublimation of $\text{NH}_3(\text{s})$, where there were no hydrogen bonds is 15.4 kJ/mol. What is the average strength of hydrogen bonds in solid NH_3 in kJ/mol?
- When 3.0 g graphite is burnt in limited supply of oxygen at 298 K and 1 bar, 7.5 kcal heat is released. No solid is left and the gaseous product formed is not absorbed in aqueous KOH solution. When 4.0 g graphite is burnt in excess supply of oxygen at 298 K and 1 bar, 32 kcal heat is released. No solid residue is left and the gaseous product formed is absorbed completely in aqueous KOH solution. When 4.0 g $\text{CO}_2(\text{g})$ is decomposed completely into $\text{CO}(\text{g})$ and $\text{O}_2(\text{g})$ at 29 K and 1 bar, the enthalpy of system increases (in kcal) by
- The enthalpies of neutralization of a weak acid HA and a weak acid HB by NaOH are -6900 cal/equivalent and -2900 cal/equivalent, respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA and one equivalent of HB, the enthalpy change was -3900 cal. If the base is distributed between HA and HB in the ratio 1 : x, the value of 'x' is

Four-digit Integer Type

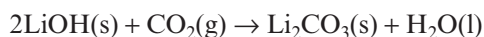
- The heat of total cracking of hydrocarbons ΔH_{TC} is defined as ΔH at 298.15 K and 101.325 kPa for the following process.

$$\text{C}_n\text{H}_m + \left(2n - \frac{m}{2}\right) \text{H}_2(\text{g}) \rightarrow n\text{CH}_4(\text{g})$$

The values of ΔH_{TC} is -65.2 kJ for C_2H_6 and -87.4 kJ for C_3H_8 . Calculate ΔH (in kJ) for

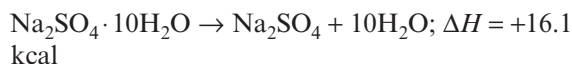
$$\text{CH}_4(\text{g}) + \text{C}_3\text{H}_8(\text{g}) \rightarrow 2\text{C}_2\text{H}_6(\text{g})$$
- An athlete takes 20 breaths per minute at room temperature. The air inhaled in each breath is 164.2 ml which contains 20% oxygen by volume, while exhaled air contains 10% oxygen by volume. Assuming that all the oxygen consumed is used for converting glucose into carbon dioxide and water, how much heat is produced (in kJ) in the body in one hour? Body temperature is 310 K and enthalpy of combustion of glucose is -3100 kJ/mol at 310 K.

- The heat of combustion of glycogen is about 432 kJ/mol of carbon. Assume that the average rate of heat loss by an adult male is 150 W. If we were to assume that all the heat comes from the oxidation of glycogen, how many units of glycogen (1 mole carbon per unit) must be oxidized per day to provide for this heat loss?
- Only gases remains after 15.0 g of carbon is treated with 20 L of air at 380 K and 8.21 atm pressure. (Assume 19% by volume oxygen, 80% nitrogen, 1% carbon dioxide). Determine the amount of heat evolved (in kcal) under constant pressure. Enthalpies of formation of $\text{CO}_2(\text{g})$ and $\text{CO}(\text{g})$ are -96.0 and -26.0 kcal/mol, respectively.
- Ethanol was oxidized to acetic acid in a catalyst chamber at 18°C . What should be rate of removal of heat (in kcal/hr) to maintain the reaction chamber at 18°C with the feed rate of 2.3 kg ethanol per hour, along with excess oxygen to the system at 18°C , with a 40 mole percent yield based on ethanol? The enthalpies of formation of $\text{H}_2\text{O}(\text{l})$, $\text{C}_2\text{H}_5\text{OH}(\text{l})$ and $\text{CH}_3\text{COOH}(\text{l})$ are, respectively -68 , -66 and -118 kcal/mol.
- The carbon dioxide exhaled in the breath of astronaut is often removed from the spacecrafts by reaction with lithium hydroxide.



Assume that each astronaut requires 2100 kcal of energy per day. Further assume that this energy is obtained only from the combustion of glucose into $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$. The standard enthalpies of formation of glucose, CO_2 and water are -1280 , -395 and -285 kJ/mol, respectively. The minimum mass (in g) of LiOH required per astronaut per day to react completely with all the CO_2 produced is

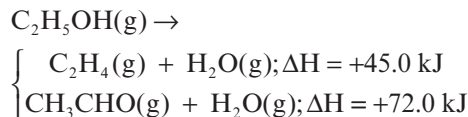
- The reversible reaction



goes completely to the right at temperature above 32.4°C and remains completely on the left below this temperature. This system has been used in some solar houses for heating at night with the energy absorbed from the sun's radiation during the day. How many litres of fuel gas could be saved per night by the reversal of the dehydration of a

fixed charge of 100 kg $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$? Assume that the fuel value of the gas is $10,000$ kcal/ m^3 .

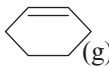
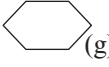
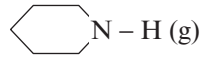
- Ethanol can undergo decomposition to form two sets of products as follows.



If the molar ratio of $\text{C}_2\text{H}_4(\text{g})$ to $\text{CH}_3\text{CHO}(\text{g})$ in the product is 8:1, the heat absorbed in decomposition of 2.5 mole of ethanol(g) (in kJ) is

- A slice of banana weighing 2.5 g was burnt in a bomb calorimeter and produced a temperature rise of 3.0 K. In the same calorimeter, combustion of a 0.305 g sample of benzoic acid produced a temperature rise of 4.0 K. The heat of combustion of benzoic acid at constant volume is -800 kcal/mol. If an average banana weighs 125 g, then how many calories can be obtained from one average banana?
- The enthalpy of formation of liquid water at 25°C is -286 kJ. Given $C_p = 75.4$ J/K-mol for $\text{H}_2\text{O}(\text{l})$ and 33.4 J/K-mol for $\text{H}_2\text{O}(\text{g})$ and that the molar enthalpy of vaporization of liquid water at 125°C is 40.8 kJ/mol. The enthalpy of dissociation (in kJ/mol) of $\text{H}_2\text{O}(\text{g})$ into H_2 and O_2 gases at 25°C is
- For the hypothetical reaction, $2\text{B}(\text{g}) \rightarrow \text{B}_2(\text{g}); \Delta C_p [\text{J/K}^{-1}] = 2.0 \times 10^{-2} \text{ T} [\text{K}]$ and $\Delta H_{300} = -4.0$ kJ/mol. Estimate the absolute temperature at which $\Delta H = 0$ for this reaction.
- The value of heat of combustion per CH_2 unit of cyclopropane is -697 kJ/mol. Calculate its strain energy. Given that the heats of formation of $\text{C}(\text{g})$, $\text{H}(\text{g})$, carbon dioxide and water are 715, 218, -393 and -285 kJ/mol, respectively, and C-C and C-H bond energies are 356 and 408 kJ/mol, respectively.
- The hydrogen bond between F^- and CHCOOH is very strong and its strength may be analysed by setting up a Born-Haber cycle with the following data (in kJ/mol). Lattice energy of $\text{KF} \cdot \text{CH}_3\text{COOH}$, 734; enthalpy of vaporization of CH_3COOH , 20; enthalpy of solution of KF , 35; solvation energy of $\text{K}^+(\text{g})$, -325 ; solvation energy of F^- , -389 ; enthalpy of formation of $\text{KF} \cdot \text{CH}_3\text{COOH}(\text{s})$ from $\text{KF}(\text{s})$ and $\text{CH}_3\text{COOH}(\text{l})$, -25 . Find the energy of the hydrogen bond between F^- and CH_3COOH in the gas phase (in kJ/mol).

14. Find the bond enthalpy (in kJ/mol) of 'three centre two electron bond' in B_2H_6 from the following data. $\Delta_f H^\circ [BH_3(g)] = 100 \text{ kJ/mol}$; $\Delta_f H^\circ [B_2H_6(g)] = 36 \text{ kJ/mol}$; $\Delta H_{\text{Atomization}} [B(s)] = 565 \text{ kJ/mol}$; $\Delta H_{\text{Atomization}} [H_2(g)] = 436 \text{ kJ/mol}$.
15. Calculate the enthalpy change (in kcal) for the reaction $XeF_4 \rightarrow Xe^+ + F^- + F_2 + F$. The average Xe – F bond enthalpy is 34 kcal/mol, first ionization enthalpy of Xe is 279 kcal/mol, electron gain enthalpy of fluorine is –85 kcal/mol and bond dissociation enthalpy of F_2 is 38 kcal/mol.
16. Calculate $\Delta H_{\text{vap}} [CH_3COOH(l)]$ in kJ/mol from the following data.
- $\Delta H_{\text{Solution}} [KF \cdot CH_3COOH(s)]$ in glacial acetic acid = –3 kJ/mol
- $\Delta H_{\text{Solution}} [KF(s)]$ in glacial acetic acid = +35 kJ/mol
- The strength of H-bond between $F^-(g)$ and $CH_3COOH(g)$ = +46 kJ/mol
- Lattice enthalpy of $KF \cdot CH_3COOH(s)$ = +734 kJ/mol
- Lattice enthalpy of $KF(s)$ = +797 kJ/mol
17. Estimate $\Delta_f H^\circ [\text{Pyridine}(l)]$ (in kJ/mol) from the given data.

Compound	$\Delta_f H^\circ$ (kJ/mol)
$CH_2 = N - CH_3(g)$	+44
$CH_3 - NH - CH_3(g)$	–18
 (g)	–37
 (g)	–156
 N – H (g)	–50

Magnitude of resonance energy of pyridine = 125 kJ/mol

$$\Delta H_{\text{vap}, 298 \text{ K}} [\text{Pyridine}(l)] = 40 \text{ kJ/mol}$$

18. The standard molar enthalpies of formation of $IF_3(g)$ and $IF_5(g)$ are –470 kJ and –847 kJ, respectively. Valence shell electron-pair repulsion theory predicts that $IF_5(g)$ is square pyramidal in shape in which all I – F bonds are equivalent while $IF_3(g)$ is T-shaped (based on trigonal-bipyramidal geometry) in which I – F bonds are of different lengths. It is observed that the axial I – F bonds in IF_3 are equivalent to the I – F bonds in IF_5 . Calculate the equatorial I – F bond strength (in kJ/mol) in IF_3 . Some other details given are as follows.
- $I_2(s) \rightarrow I_2(g)$: $\Delta H = 62 \text{ kJ}$
- $F_2(g) \rightarrow 2F(g)$: $\Delta H = 155 \text{ kJ}$
- $I_2(g) \rightarrow 2I(g)$: $\Delta H = 149 \text{ kJ}$
19. The standard molar enthalpies of formations of $H_2O(l)$ and $H_2O_2(l)$ are –286 and –188 kJ/mol, respectively. Molar enthalpies of vaporization of H_2O and H_2O_2 are 44 and 53 kJ, respectively. The bond dissociation enthalpy of $O_2(g)$ is 498 kJ/mol. Calculate the bond dissociation enthalpy (in kJ/mol) of O – O bond in H_2O_2 , assuming that the bond dissociation enthalpy of O – H bond is same in both H_2O and H_2O_2 .
20. Enthalpy of the reaction $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$ is –84.54 kJ. Magnitude of enthalpies of formation of $Ag^+(aq)$ and $Br^-(aq)$ is in 8:9 ratio but their signs are opposite. Enthalpy of formation of $AgBr$ is –99.54 kJ/mol. The magnitude of enthalpy of formation of $Ag^+(aq)$ (in kJ/mol) is

Answer Keys**Exercise I****Basics**

1. (c) 2. (c) 3. (d) 4. (a) 5. (b) 6. (c) 7. (b) 8. (b) 9. (a) 10. (a)
11. (b)

Enthalpy of Formation

12. (d) 13. (b) 14. (b) 15. (a) 16. (b) 17. (a) 18. (d) 19. (a) 20. (b)

Enthalpy of Combustion

21. (a) 22. (b) 23. (d) 24. (a) 25. (a) 26. (b) 27. (c) 28. (b) 29. (a) 30. (a)
31. (d) 32. (c) 33. (c)

Enthalpy of Neutralization

34. (b) 35. (a) 36. (d) 37. (a) 38. (b) 39. (b)

Hess's Law

40. (b) 41. (b) 42. (a) 43. (b) 44. (c) 45. (d) 46. (a) 47. (a) 48. (b) 49. (b)
50. (d) 51. (a) 52. (c) 53. (b) 54. (a) 55. (c) 56. (b) 57. (c) 58. (d) 59. (a)
60. (b) 61. (c)

Bond Enthalpy

62. (c) 63. (a) 64. (b) 65. (b) 66. (a) 67. (a) 68. (d) 69. (b) 70. (b) 71. (a)
72. (d) 73. (b) 74. (c) 75. (a) 76. (b) 77. (d) 78. (b) 79. (b) 80. (a)
-

Answer Keys**Exercise II****Section A (Only one Correct)**

1. (b) 2. (b) 3. (b) 4. (d) 5. (b) 6. (a) 7. (d) 8. (c) 9. (a) 10. (a)
11. (d) 12. (d) 13. (b) 14. (a) 15. (d) 16. (b) 17. (a) 18. (c) 19. (c) 20. (b)
21. (a) 22. (a) 23. (b) 24. (d) 25. (a) 26. (b) 27. (a) 28. (b) 29. (b) 30. (a)
31. (a) 32. (b) 33. (a) 34. (b) 35. (b) 36. (c) 37. (a) 38. (b) 39. (a) 40. (c)
41. (a) 42. (b) 43. (a) 44. (d) 45. (b) 46. (b) 47. (a) 48. (b) 49. (d) 50. (d)
51. (a) 52. (b) 53. (b) 54. (c) 55. (a)

Section B (One or More than one Correct)

1. (b), (c), (d) 2. (a), (b), (c) 3. (a), (d) 4. (a)
5. (b) 6. (a) 7. (a), (b) 8. (a), (b), (d)
9. (a), (d) 10. (b), (d) 11. (a), (b), (c) 12. (a), (b)
13. (a), (b), (c) 14. (a), (d) 15. (c)

Section C

Comprehension I

1. (c) 2. (c) 3. (c)

Comprehension II

4. (d) 5. (b) 6. (d) 7. (d) 8. (c)

Comprehension III

9. (c) 10. (b) 11. (b)

Comprehension IV

12. (c) 13. (d)

Comprehension V

14. (b) 15. (c) 16. (a)

Comprehension VI

17. (b) 18. (a) 19. (a) 20. (c)

Comprehension VII

21. (c) 22. (d) 23. (c) 24. (b) 25. (b)

Comprehension VIII

26. (d) 27. (b) 28. (a)

Comprehension IX

29. (c) 30. (d)

Comprehension X

31. (a) 32. (c)

Comprehension XI

33. (a) 34. (a)

Section D (Assertion – Reason)

1. (a) 2. (a) 3. (d) 4. (d) 5. (d) 6. (c) 7. (c) 8. (a) 9. (a) 10. (c)

Section E (Column Match)

1. $A \rightarrow R; B \rightarrow P; C \rightarrow Q; D \rightarrow P, R, S$
2. $A \rightarrow Q; B \rightarrow S; C \rightarrow P; D \rightarrow R$
3. $A \rightarrow P, B \rightarrow Q; C \rightarrow R; D \rightarrow S$
4. $A \rightarrow Q; B \rightarrow R; C \rightarrow P; D \rightarrow S$
5. $A \rightarrow P, Q; B \rightarrow P, R; C \rightarrow S$
6. $A \rightarrow Q; B \rightarrow R; C \rightarrow P; D \rightarrow S$
7. $A \rightarrow S; B \rightarrow Q; C \rightarrow P; D \rightarrow R$
8. $A \rightarrow P; B \rightarrow Q, T; C \rightarrow Q, S; D \rightarrow R, S$
9. $A \rightarrow P; B \rightarrow P, Q; C \rightarrow R, S; D \rightarrow R$
10. $A \rightarrow Q; B \rightarrow R; C \rightarrow S; D \rightarrow P$

Section F (Subjective)

Single-digit Integer Type

1. (3) 2. (1) 3. (5) 4. (2) 5. (5) 6. (8) 7. (6) 8. (5) 9. (6) 10. (3)

Four-digit Integer Type

- | | | | | |
|------------|------------|------------|------------|------------|
| 1. (0043) | 2. (0400) | 3. (0030) | 4. (0085) | 5. (2400) |
| 6. (0216) | 7. (0500) | 8. (0120) | 9. (0075) | 10. (0241) |
| 11. (0700) | 12. (0120) | 13. (0060) | 14. (0455) | 15. (0292) |
| 16. (0021) | 17. (0085) | 18. (0272) | 19. (0142) | 20. (0120) |
-



HINTS AND EXPLANATIONS

EXERCISE I (JEE MAIN)

Basics

1. For standard state, the pressure should be 1 bar, but temperature, any specified temperature.

2. Enthalpy is a state function.

3. As the temperature is decreased, the reaction must be endothermic.

Heat absorbed in reaction = Heat released by calorimeter

$$= c \cdot \Delta T = 1.25 \times 6 = 7.5 \text{ kJ}$$

$$\therefore \Delta H = +\frac{7.5}{1.6} \times 80 = +375 \text{ kJ/mol}$$

$$4. \Delta H - \Delta E = \Delta n_g \cdot RT = (12 - 15) \times \frac{8.314}{1000} \times 298 \\ = -7432.7 \text{ J}$$

5. For $\Delta H = \Delta E$, $\Delta n_g = 0$

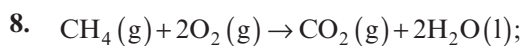
6. Heat released by reaction = $c \cdot \Delta T = 500 \times 2 = 1000 \text{ J}$

$$\therefore \Delta E = -\frac{1000}{0.1} \times 16 = -160 \text{ kJ/mol}$$

$$7. \Delta n_g = 1 - \frac{1}{2} = \frac{1}{2}$$

$\Delta H = \Delta E + \Delta n_g RT$ and $\Delta H, \Delta E$ are -ve, hence

$$\Delta H < \Delta E.$$



$$\Delta n_g = 1 - 3 = -2$$

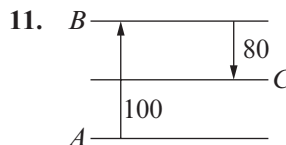
Now,

$$\Delta E = \Delta H - \Delta n_g RT = (-18500) - (-2) \times 2 \times 300 \\ = -17300 \text{ cal/mol}$$

9. Heat released by reaction = $c \cdot \Delta T$

$$\text{or } \frac{2.8 \times 10^6}{180} \times 0.18 = c \times 4 \Rightarrow c = 700 \text{ J/K}$$

$$10. \Delta H - \Delta U = P \cdot \Delta V = P[V_D - V_G] \\ = 500 \times 10^3 \times 10^5 \frac{\text{N}}{\text{m}^2} \left[\frac{12}{3.6} - \frac{12}{2.4} \right] \times 10^{-6} \text{ m}^3 \\ = -8.33 \times 10^4 \text{ J/mol}$$



Enthalpy of Formation

12. $\Delta_f H^\circ = 0$, +ve or -ve

13. $\Delta H = 2 \times 46.0 = 92 \text{ kJ}$

$$14. \Delta_f H_{\text{HCl}(\text{g})} = -\frac{44}{2} = -22 \text{ kcal/mol}$$

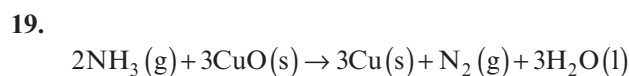
$$15. \Delta_f H_{\text{O}_3(\text{g})}^\circ = -\frac{286}{2} = 143 \text{ kJ/mol}$$

16.

$$\Delta_r H^\circ = \sum \Delta_f H^\circ_{\text{Products}} - \sum \Delta_f H^\circ_{\text{Reactants}} \\ = [\Delta_f H^\circ_{\text{CO}(\text{g})} + \Delta_f H^\circ_{\text{H}_2\text{O}(\text{g})}] \\ - [\Delta_f H^\circ_{\text{CO}_2(\text{g})} + \Delta_f H^\circ_{\text{H}_2(\text{g})}] \\ = [(-110.5) + (-241.8)] \\ - [(-393.5) + 0] = 41.2 \text{ kJ}$$

$$\begin{aligned}
 17. \quad \Delta_r H^\circ &= \sum \Delta_f H^\circ_{\text{Products}} - \sum \Delta_f H^\circ_{\text{Reactants}} \\
 &= \left[\Delta_f H^\circ_{\text{U}_3\text{O}_8(\text{s})} \right] - \left[3 \times \Delta_f H^\circ_{\text{UO}_2(\text{s})} + \Delta_f H^\circ_{\text{O}_2(\text{g})} \right] \\
 \text{or, } -76.0 &= (-853.5) - \left[3 \times \Delta_f H^\circ_{\text{UO}_2(\text{s})} + 0 \right] \\
 \therefore \Delta_f H^\circ_{\text{UO}_2(\text{s})} &= -259.17 \text{ kJ/mol}
 \end{aligned}$$

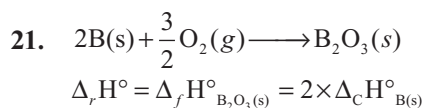
$$\begin{aligned}
 18. \quad \Delta H &= \sum \Delta_f H_{\text{Products}} - \sum \Delta_f H_{\text{Reactants}} \\
 \text{or, } 42 &= [(-152) + (-74)] - [\Delta_f H_{\text{CaCO}_3(\text{s})}] \\
 \therefore \Delta_f H_{\text{CaCO}_3(\text{s})} &= -288 \text{ kJ/mol}
 \end{aligned}$$



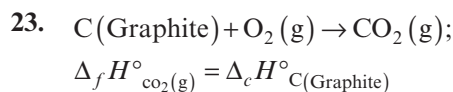
$$\begin{aligned}
 \Delta_r H &= \sum \Delta_f H_{\text{Products}} - \sum \Delta_f H_{\text{Reactants}} \\
 &= [0 + 0 + 3 \times (-285)] - [2 \times (-46) + 3 \times (-155)] \\
 &= -298 \text{ kJ} \\
 \therefore \Delta H_{\text{required}} &= -\frac{298}{2 \times 17} \times 6.8 = 59.6 \text{ kJ}
 \end{aligned}$$

$$\begin{aligned}
 20. \quad \Delta_r H &= \sum \Delta_f H_{\text{products}} - \sum \Delta_f H_{\text{Reactants}} \\
 &= \left[2 \times \Delta_f H_{\text{Li}^+(\text{aq})} + 2 \times \Delta_f H_{\text{OH}^-(\text{aq})} + \Delta_f H_{\text{H}_2(\text{g})} \right] \\
 &\quad - \left[2 \times \Delta_f H_{\text{Li}(\text{s})} + 2 \times \Delta_f H_{\text{H}_2\text{O}(\text{l})} \right] \\
 &= [2 \times (-278.5) + 2 \times (-228.9) + 0] \\
 &\quad - [2 \times 0 + 2 \times (-285.8)] \\
 &= -443.2 \text{ KJ}
 \end{aligned}$$

Enthalpy of Combustion



$$\begin{aligned}
 22. \quad \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) &\longrightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}); \\
 \Delta H &= -680 \text{ Kcal} \\
 \text{For } 680 \text{ Kcal, } 6 \times 44 \text{ gm CO}_2 &\text{ is produced} \\
 \text{Hence, for } 170 \text{ Kcal, mass of CO}_2 &\text{ produced} \\
 &= \frac{6 \times 44}{680} \times 170 = 66 \text{ gm}
 \end{aligned}$$



$$24. \quad \frac{5.65 \times 10^3}{342} \times 1026 = 1.695 \times 10^4 \text{ kJ}$$

$$\begin{aligned}
 25. \quad \text{For CH}_4 : \frac{890}{16} &= 55.625 \text{ kJ/gm} \\
 \text{For C}_2\text{H}_4 : \frac{1411}{28} &= 50.393 \text{ kJ/gm} \\
 \text{For C}_2\text{H}_6 : \frac{1560}{30} &= 52.0 \text{ kJ/gm}
 \end{aligned}$$

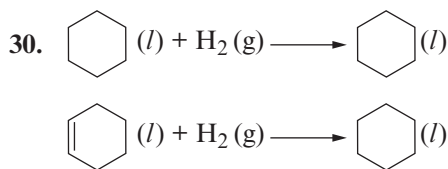
$$\begin{aligned}
 26. \quad \text{Moles of CH}_4 \text{ burned} &= \frac{2670}{890} = 3 \\
 \therefore \text{Volume of CH}_4 &= 3 \times 22.4 = 67.2 \text{ l}
 \end{aligned}$$

$$\begin{aligned}
 27. \quad \text{Increase in } |\Delta_c H| \text{ per unit increase in CH}_2 &\text{ is} \\
 \frac{(370 - 210) + (526 - 370)}{2} &= 158
 \end{aligned}$$

$$\begin{aligned}
 \therefore \text{Expected } \Delta_c H \text{ of} \\
 \text{C}_6\text{H}_{14} &= (-210) + 5 \times (-158) = -1000 \text{ kcal/mol}
 \end{aligned}$$

$$28. \quad \text{Mass of glucose needed} = \frac{5616}{2808} \times 130 = 360 \text{ g}$$

$$\begin{aligned}
 29. \quad \Delta_c H^\circ_{\text{Benzene}} &= \Delta_r H \\
 &= \sum \Delta_f H_{\text{Products}} - \sum \Delta_f H_{\text{Reactants}} \\
 &= 7800 \text{ kcal}
 \end{aligned}$$



$$\begin{aligned}
 \Delta H &= \sum \Delta_c H_{\text{Reactants}} - \sum \Delta_c H_{\text{Products}} \\
 &= [(-3800) + (-241)] - [(-3920)] \\
 &= -121 \text{ KJ/mol}
 \end{aligned}$$

31. Heat released from 120 gm glucose

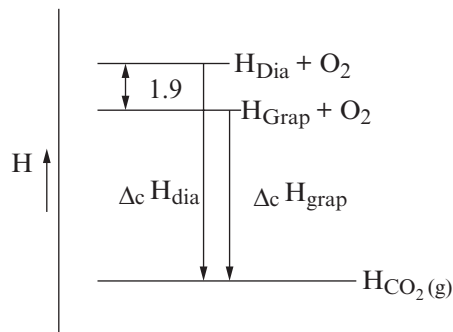
$$= \frac{2880}{180} \times 120 = 1920 \text{ kJ}$$

$$\therefore \text{Distance } \frac{1920}{100} \times \frac{25}{100} = 4.8 \text{ km}$$

32. Heat released by constitution of LPG = Heat absorbed by water

$$w \times 40000 = 3 \times 4200 \times 50 \Rightarrow w = 15.75 \text{ gm}$$

- 33.



Heat liberated is greater for diamond by $\frac{1.9}{12} \times 6 = 0.95 \text{ kJ}$

Enthalpy of Neutralization

34. Moles of H^+ from $\text{H}_2\text{SO}_4 = 2 \times \text{Moles of } \text{H}^+$ from HCl

35. $\Delta H = (-25.4) - 2 \times (-13.7) = 2.0 \text{ kcal/mol}$

36. $q = (1000 \times d) \times s \times T_1$

$$\therefore \frac{q}{2} = (1000 \times d) \times s \times T_2 \quad (\text{KOH is limiting reagent})$$

$$\therefore T_1 = 1.5 T_2$$

37. For maximum rise in temperature, both should react completely.

$$V \times 1 = (100 - V) \times 2 \times 2 \Rightarrow V = 80 = V_{\text{KOH}}$$

38. $\Delta H = (-13.2) - (-13.7) = +0.5 \text{ kcal / eq.}$

39. $\Delta H = (-106.68) - 2 \times (-55.84) = 5 \text{ kJ/mol}$

Hess's Law

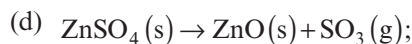
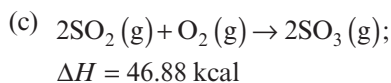
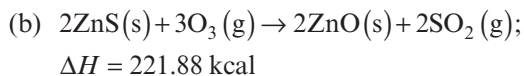
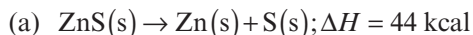
40. $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H^\circ = -x \text{ KJ}$

$$-\frac{1}{2} \times [2\text{CO(g)} + \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}); \Delta H^\circ = -y \text{ kJ}]$$

$$\text{C(s)} + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO(g)}; \Delta H^\circ = (-x) - \frac{1}{2}(-y) = \frac{y-2x}{2}$$

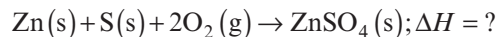
41. $\Delta H^\circ = (-2220.1) + 4 \times 44 = -2044.1 \text{ kJ}$

42. Given thermo chemical equations are:



$$\Delta H = 55.1 \text{ kcal}$$

Required thermochemical equation is

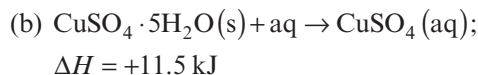


$$\text{From } \frac{1}{2}(b) + \frac{1}{2}(c) - (a) - (d);$$

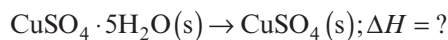
$$\Delta H = \frac{1}{2}(-221.88) + \frac{1}{2}(-46.88) - (44) - (55.1)$$

$$= -233.48 \text{ kcal}$$

43. Given T.C.E. are

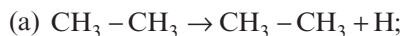


Required T.C.E. is

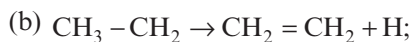


$$\text{From } (b) - (a); \Delta H = 11.5 - (-66.11) = 77.61 \text{ kJ}$$

44. Given T.C.E. are

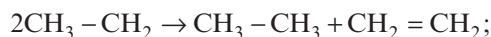


$$\Delta H = 420 \text{ kJ}$$



$$\Delta H = 168 \text{ kJ}$$

Required T.C.E. is



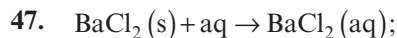
$$\Delta H = ?$$

$$\text{From } (b) - (a); \Delta H = 168 - 420 = -252 \text{ kJ}$$

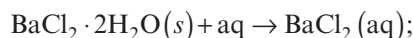
45. Adding all the given T.C.E.,

$$\Delta_f H_{\text{H}_2\text{SO}_4} = -813.9 \text{ kJ/mol}$$

46. Adding all the given T.C.E.: $X = -393$

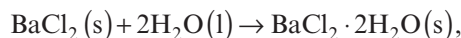


$$\Delta H = -20.6 \text{ kJ}$$



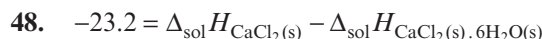
$$\Delta H = 8.8 \text{ kJ}$$

Hence, for the reaction,

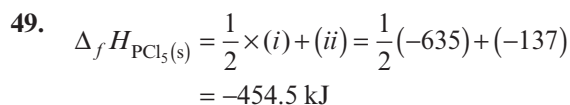


$$\Delta H = (-20.6) - (8.8)$$

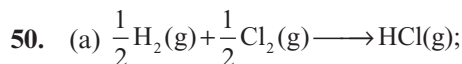
$$= -29.4 \text{ kJ}$$



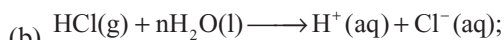
$$\therefore \Delta_{\text{sol}} H_{\text{CaCl}_2(s)} = (-23.2) + (3.5) = -19.7 \text{ kcal/mol}$$



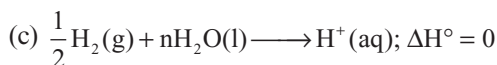
$$= -454.5 \text{ kJ}$$



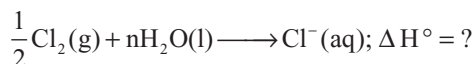
$$\Delta H^\circ = -92.4 \text{ kJ}$$



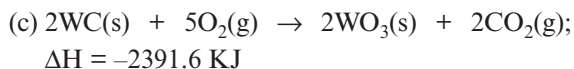
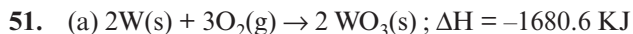
$$\Delta H^\circ = -74.8 \text{ kJ}$$



Required T.C.E. is

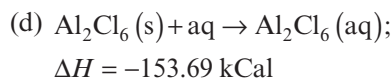
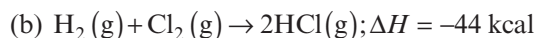
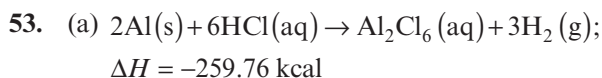
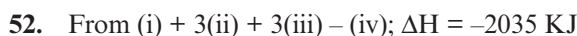


$$\text{From } (a) + (b) - (c); \Delta H^\circ = -167.2 \text{ kJ}$$

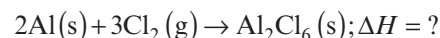


Required T.C.E. is $\text{W}(s) + \text{C}(s) \rightarrow \text{WC}(s); \Delta H = ?$

$$\text{From } \frac{1}{2}(a) + (b) - \frac{1}{2}(c); \Delta H = -38.0 \text{ kJ}$$



Required T.C.E. is

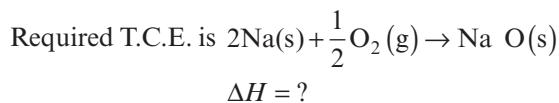
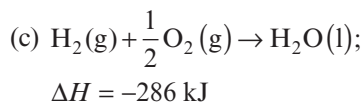
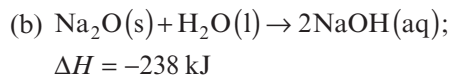
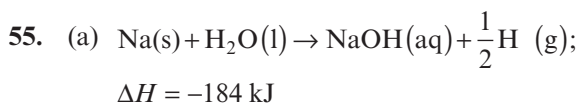


From (a) + 3(b) + 6(c) - (d);

$$\Delta H = (-239.76) + 3(-44) + 6(-17.315) - (-153.69)$$

$$= -321.96 \text{ kcal}$$

54. For more cooling, heating absorbed on dissolution should be high.



From $2(a) - (b) + (c);$

$$\Delta H = 2(-184) - (-238) + (-286) = -416 \text{ kJ}$$

56. From (a) – (b) + (c);
 $\Delta H = (-544) - (-293) + (-480) = -731 \text{ kJ}$
57. $\Delta(\text{S.F.}) = \sum (\text{S.F.})_{\text{Products}} - \sum (\text{S.F.})_{\text{Reactants}}$
58. From (ii) – (i);
 $\Delta G^\circ = (-12.4) - (-29.2) = +16.8 \text{ kJ}$
59. From (a) + (b) + (c) + (d) + (e)
 Now
 $\Delta G^\circ = (23.9) + (555.1) + (1320.2) + (-347.5) + (-1513.6)$
 $= +38.1 \text{ kJ}$
60. $\Delta_r H^\circ = \left[\Delta_f H_{\text{CO}_2(\text{g})} + 2 \times \Delta_f H_{\text{H}_2\text{O}(\text{l})} \right]$
 $- \left[\Delta_f H_{\text{CH}_4(\text{g})} + 2 \times \Delta_f H_{\text{O}_2(\text{g})} \right]$
 $= [(-393.5) + 2(-286)] - [(-74.5) + 2 \times 0] = -891 \text{ kJ}$

$$\Delta_r S^\circ = \left[S_{\text{CO}_2(\text{g})} + 2 \times S_{\text{H}_2\text{O}(\text{l})} \right] - \left[\Delta_f S_{\text{CH}_4(\text{g})} + 2 \times S_{\text{O}_2(\text{g})} \right]$$

$$= [216 + 2 \times 70] - [186 + 2 \times 205] = -240 \text{ J/K}$$

Now,

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ = (-891) - 300 \times \left(\frac{-240}{1000} \right)$$

$$= -819 \text{ kJ}$$

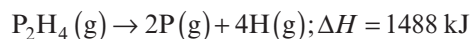
61. $\Delta H = \sum (\text{B.E.})_{\text{Reactants}} - \sum (\text{B.E.})_{\text{Products}}$
 $= (435 + 240) - (2 \times 430) = -185 \text{ KJ}$
 $\Delta S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}}$
 $= (2 \times 186) - (130 + 222) = 20 \text{ J/K}$

Now, $\Delta G = \Delta H - T \cdot \Delta S = (-185) - 300 \times \frac{20}{1000}$
 $= -191 \text{ kJ}$

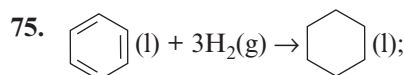
Bond Enthalpy

62. $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{F}_2(\text{g}) \rightarrow \text{NF}_3(\text{g}); \Delta H = -113 \text{ kJ}$
 Now, $-113 = \left[\frac{1}{2} \times x + \frac{3}{2} \times \frac{x}{6} \right] - (3 \times 273.5)$
 $\therefore x = 943.33 \text{ kJ}$
63. Only one bond cleavage should involve in this reaction.
64. $\Delta H = (\text{B.E.}_{\text{C-C}} + \text{B.E.}_{\text{H-H}}) - (2 \times \text{B.E.}_{\text{C-H}})$
 $= [(611 - 346) + 437] - (2 \times 413) = -124 \text{ kJ}$
65. $+182 = (430 + 242) - (2 \times \text{B.E.}_{\text{H-Cl}})$
 $\therefore \text{B.E.}_{\text{H-Cl}} = 245 \text{ kJ/mol}$
66. $-20.24 = \left[2 \times \Delta_{\text{sol}} H_{\text{C(s)}} + 3 \times 102.6 \right] - [63 + 6 \times 85.6]$
 $\therefore \Delta_{\text{sub}} H_{\text{C(s)}} = 124.28 \text{ kcal/mol}$
67. $\Delta H = 121 + 242.8 + 2422 - 2 \times (355) - 2430.8$
 $= -355 \text{ kJ}$
68. $-411.2 = 107.3 + 121.7 + 495.4 - 348.5 - (\text{L.E.})$
 $\therefore \text{L.E.} = 787.1 \text{ kJ}$
69. Required $\Delta H = - \left[\frac{49.8 + 36.0}{3} \right] = -28.6 \text{ kcal/mol}$
70. $|\text{R.E.}| = 29 \times 3 - 51 = 36 \text{ kcal/mol}$
71. $\Delta_{\text{Lattice}} H + \Delta_{\text{Hydration}} H = \Delta_{\text{solution}} H$
 For CSI : $\Delta_{\text{Hid}} H = 33 - 604 = -571 \text{ kJ}$
 For CsOH : $\Delta_{\text{Hid}} H = (-72) - 724 = -796 \text{ kJ}$
72. From (a) + (b) + (c) – (d),
 $\text{CH}_3 - \text{H}(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H}(\text{g}); \Delta H = 54 + 29 + 79.8 - 51$
 $= 111.8 \text{ kcal/mol}$
73. $\text{SF}_6(\text{g}) \rightarrow \text{S}(\text{g}) + 6\text{F}(\text{g})$
 $\Delta H = (275 + 6 \times 80) - (-1100) = 6 \times \text{B.E.}_{\text{S-F}}$
 $\therefore \text{B.E.}_{\text{S-F}} = 309.17 \text{ kJ/mol}$

74. $\text{PH}_3(\text{g}) \rightarrow \text{P}(\text{g}) + 3\text{H}(\text{g}); \Delta H = 954 \text{ kJ}$
 $\therefore 3 \times \text{B.E.}_{\text{P-H}} = 954 \Rightarrow \text{B.E.}_{\text{P-H}} = 318 \text{ kJ/mol}$

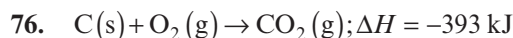


$\therefore \text{B.E.}_{\text{P-P}} + 4 \times \text{B.E.}_{\text{P-H}} = 1488$
 $\Rightarrow \text{B.E.}_{\text{P-P}} = 216 \text{ kJ/mol}$



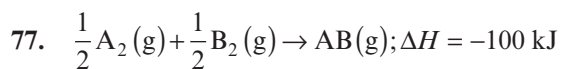
$\Delta H = (-156) - (49 + 0) = -205 \text{ kJ}$

$\therefore \text{Magnitude of resonance energy} = 3 \times 119 - 205$
 $= 152 \text{ kJ}$



Now, $(-393) = [718 + 498] - 2 \times 539 - |\text{R.E.}|_{\text{CO}_2}$

$\therefore |\text{R.E.}|_{\text{CO}_2} = 531 \text{ kJ/mol}$

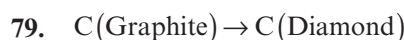


Now, $(-100) = \left[\frac{1}{2} \times x + \frac{1}{2} \times \frac{x}{2} \right] - x \Rightarrow x = 400$



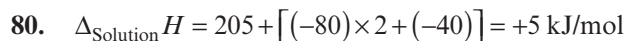
or, $180 + (6x + 5x) = 1 \Rightarrow x = -16.27$

$\therefore \Delta_{\text{Hyd}}H_{\text{Na}^+} = 6x = -97.64 \text{ kcal/mol}$



$\Delta H = 698.6 - 2 \times 348.4 = 1.8 \text{ kJ/mol}$

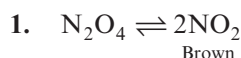
(In diamond, there is 2 C–C bonds per C-atom)



As the solubility is endothermic, it should increase with increase in temperature.

EXERCISE II (JEE ADVANCE)

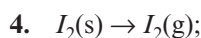
Section A (Only one Correct)



On heating, colour deepens means reaction is endothermic ($\Delta H = +\text{ve}$).

2. As the process is endothermic but no heat is absorbed from surrounding, the temperature of the system will decrease, As initial temperature is used, the calculated mole will be lower.

3. $\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = \Delta(C_P) = (3x) - (x + 2x) = 0$
 $\Rightarrow \Delta H_2 = \Delta H_1$



$\Delta H_1 = 24 \text{ cal/gm}$ at $T_1 = 473 \text{ K}$

$\Delta H_2 = ?$ at $T_2 = 523 \text{ K}$

$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{P, \text{I}_2(\text{g})} - C_{P, \text{I}_2(\text{s})}$

$\Rightarrow \frac{\Delta H_2 - 24}{523 - 473} = 0.055 - 0.031$

$\therefore \Delta H_2 = 25.2 \text{ cal/gm}$

5. For direct measurement, reaction must occur directly in the conditions to measure heat.

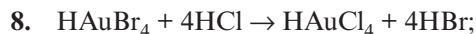
6. Greater the mass per cent of hydrogen, greater is the calorific value.

7. For the reaction:

$\Delta U = \Delta H - \Delta n_g \cdot RT = (-72.3) - (-1) \times \frac{8.314}{1000} \times 298$
 $= -69.8 \text{ kJ}$

As HCl is limiting reagent, for the given amount,

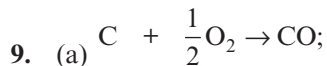
$\Delta U = 2 \times (-69.8) = -139.6 \text{ kJ}$



$$\Delta H = (-28) - (-36.8)$$

$$= 8.8 \text{ kcal}$$

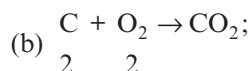
$$\therefore \text{Percentage reaction} = \frac{0.44}{8.8} \times 100 = 5\%$$



$$\begin{matrix} 9.0 & 4.5 \end{matrix}$$

$$\Delta H = -75 \text{ kcal}$$

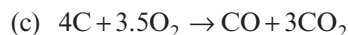
$$\text{Heat evolved} = 75 \times 9 = 675 \text{ kcal}$$



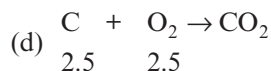
$$\begin{matrix} 2 & 2 \end{matrix}$$

$$\Delta H = -95 \text{ kcal}$$

$$\text{Heat evolved} = 95 \times 2 = 190 \text{ kcal}$$



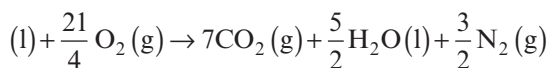
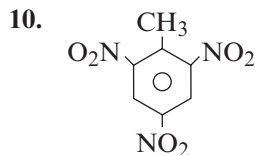
$$\text{Heat evolved} = 75 \times 1 + 95 \times 3 = 360 \text{ kcal}$$



$$\begin{matrix} 2.5 & 2.5 \end{matrix}$$

$$\Delta H = -95 \text{ kcal}$$

$$\text{Heat evolved} = 95 \times 2.5 = 237.5 \text{ kcal}$$



$$\Delta H = 7 \times (-395) + \frac{5}{2} \times (-285) - (65)$$

$$= -3542.5 \text{ kJ/mol}$$

$$= -\frac{3542.5}{227} \times 1.816 \text{ kJ/mol}$$

$$= -28.34 \text{ kJ/mol} = -28.34 \text{ MJ/L}$$

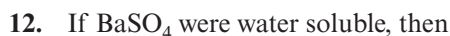


$$= 2 \times (13.5 - 13) = 1 \text{ kcal/mol}$$



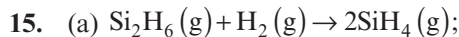
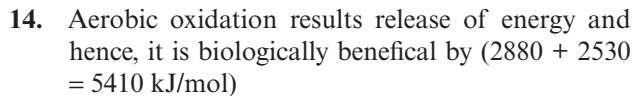
$$= 2 \times (13.5 - 10) = 7 \text{ kcal/mol}$$

$$\therefore \text{Required } \Delta H = 2 \times 13.5 - 1 - 7 = -19 \text{ kcal}$$



$$\Delta H_{\text{expected}} = 2 \times (-57) = -114 \text{ kJ}$$

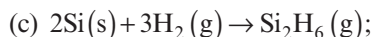
13. Required $\Delta H = -(13700 - 400 \times 0.9) = -13340 \text{ cal}$



$$\Delta H = -11.7 \text{ kcal}$$

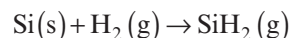


$$\Delta H = +239.7 \text{ kcal}$$

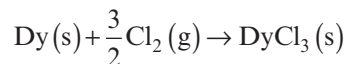


$$\Delta H = +80.3 \text{ kcal}$$

Required thermochemical equation is



$$\text{From (b)} + \frac{1}{2}(\text{a}) + \frac{1}{2}(\text{c}): \Delta H = +274 \text{ kcal/mol}$$



From (ii) + 3 × (iii) - (i), we get:

$$\Delta H = (-699.43) + 3(-158.31) - (-180.06)$$

$$= -994.3 \text{ kJ/mol}$$



$$\Delta H = [(-188.84) + (-22.05) + 2(-22.1) + 2(-17.63)]$$

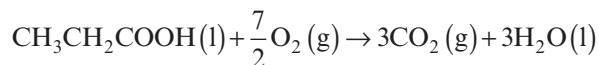
$$- [(-70.97) + (-8.56) + 0 + 2(-68.32)] = -74.18 \text{ kcal}$$



$$\Delta H = \Delta_f H_{\text{H}_2\text{O}(l)} - [\Delta_f H_{\text{H}^+(\text{aq})} + \Delta_f H_{\text{OH}^-(\text{aq})}]$$

$$\text{or, } -57.32 = (-285.84) - [0 + \Delta_f H_{\text{OH}^-(\text{aq})}]$$

$$\therefore \Delta_f H_{\text{OH}^-(\text{aq})} = -228.52 \text{ kJ/mol}$$



$$\Delta_c H_{\text{CH}_3\text{CH}_2\text{COOH}(l)} = [3 \times \Delta_f H_{\text{CO}_2(g)} + 3 \times \Delta_f H_{\text{H}_2\text{O}(l)}]$$

$$- [\Delta_f H_{\text{CH}_3\text{CH}_2\text{COOH}(l)} + \frac{7}{2} \times \Delta_f H_{\text{O}_2(g)}]$$

$$\text{or, } 3 \times \Delta_f H_{\text{CH}_3\text{CH}_2\text{COOH}(l)}$$

$$= [3(-94) + 3(-68)] - [\Delta_f H_{\text{CH}_3\text{CH}_2\text{COOH}(l)} + 0]$$

$$\therefore \Delta_f H_{\text{CH}_3\text{CH}_2\text{COOH}(l)} = -121.5 \text{ kcal/mol}$$

20. $\text{pH}(\text{solution II}) \rightarrow \text{pH}(\text{solution I})$

$$\Delta H = \left(\frac{-0.02}{0.47} \times 94 \right) - \left(\frac{-0.03}{1.410} \times 94 \right) = -2 \text{ kcal/mol}$$

21. $\Delta H_{\text{required}} = [(-14.7) - (-2.7)] - [-13.75]$

$$= +1.75 \text{ kcal/mol}$$

22. $2\text{FeO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3; \Delta H = (-197) - 2(-65)$

$$= -67 \text{ kcal}$$

Initial	$2a$	a
Final	$2a - 2x$	$a + x$

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

and heat released = $67x$ kcal

\therefore Heat released per mole of initial mixture

$$= \frac{67x}{3a} = 13.4 \text{ kcal}$$

23. $3\text{C}_2\text{H}_5\text{OH} + 25\text{H}_2\text{O} \rightarrow 3\text{C}_2\text{H}_5\text{OH}(25\text{H}_2\text{O});$

$$\Delta H_{\text{theo}} = (-1120) + 2(-1760)$$

$$= -4640 \text{ kcal}$$

$$\Delta H_{\text{exp}} = 3(-1650) = -4950 \text{ cal}$$

As experimentally, more heat is released means the mixing is exothermic by $(4950 - 4640) = 310 \text{ cal}$.

24. Heat absorbed in solubility = Heat released from solution

$$= m.s.\Delta T$$

$$= (200 + 25) \times 4.2 \times 3$$

$$= 2835 \text{ J}$$

$$\therefore \Delta H = + \frac{2835}{7.45} \times 74.5 = +28350 \text{ J}$$

25. Heat released by reaction = Heat gained by ice

$$= m.L = 0.2 \times 80 = 16 \text{ cal}$$

$$\Delta H = - \frac{16}{10^{-3}} = -16 \times 10^3 \text{ cal}$$

26. let $\text{C}_2\text{H}_6 = x\text{L}$, then $\text{CH}_4 = (4 - x)\text{L}$
 Volume of CO_2 produced, $2x + (4 - x) = 6 \Rightarrow x = 2$
 \therefore Total heat evolved

$$= \left(\frac{-1}{2} \times 1573 + \frac{1}{2} \times 890 \right) \times \frac{1}{0.0821 \times 300} = 50 \text{ kJ}$$

27. $\text{C} + \text{O}_2 \rightarrow \text{CO}_2; \Delta H = - \frac{2400}{0.3} \times 12 = -96000 \text{ cal}$

$$\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}; \Delta H = - \frac{1400}{0.6} \times 12 = -28000 \text{ cal}$$

Now, $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2;$

$$\Delta H = -(-96000) - (-28000) = -68000 \text{ cal}$$

$$\therefore \text{Heat produced} = \frac{68000}{28} \times 0.7 = 1700 \text{ cal}$$

28. Heat liberated from propane = Heat absorbed by water

or, $n \times 500 \times 10^3 \times \frac{40}{100} = 160 \times 10^3 \times 1 \times 50$

$$\Rightarrow n = 40$$

29. $q = v.i.t = 15 \times 0.125 \times (14 \times 60) \text{ J} = 1575 \text{ J}$

$$\therefore \Delta H = \frac{1575}{0.1} \times 1 = 15750 \text{ J/mol}$$

30. $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}); \Delta H_1 = -240 \text{ kJ}$

$$2\text{H}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g});$$

$$\Delta H_2 = -(240 + 432) = -672 \text{ kJ}$$

$$\therefore \frac{\Delta H_2}{\Delta H_1} = \frac{-672}{-240} = 2.8$$

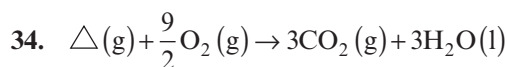
31. $\Delta m = \frac{E}{C^2} = \frac{103 \times 10^3 \times 4.2}{(3 \times 10^8)^2} = 4.8 \times 10^{-12} \text{ kg}$

32. $-12 = [(-75) + (+3.9)]$

$$- [(-11) + (-8.5) + x + (-17.5)]$$

$$\therefore X = -22.1 \text{ kcal/mol}$$

33. Dulong and petit's law : Atomic mass \times Specific heat $\cong 6.4$ for greater temperature rise, heat lost should be high.

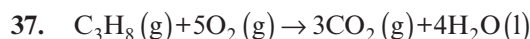


$$\begin{aligned}\Delta_C H_{\text{cyclopropane}} &= \left[3 \times \Delta_f H_{CO_2(g)} + 3 \times \Delta_f H_{H_2O(l)} \right] \\ &- \left[\Delta_f H_{\text{cyclopropane}} + \frac{9}{2} \times \Delta_f H_{O_2(g)} \right] \\ &= \left[3 \times (-394) + 3 \times (-286) \right] - \left[\{(33) + (20)\} + \frac{9}{2} \times 0 \right] \\ &= -2093 \text{ kJ/mol}\end{aligned}$$

35. $w = -P \cdot V_{H_2} = -nRT = -1.5 \times 2 \times 298 = -894 \text{ cal}$

36. $w = -nRT = -1 \times 2 \times 353 = -706 \text{ cal}$

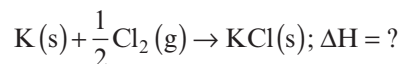
$$\therefore \Delta U = q + w = 7.4 + \left(-\frac{706}{1000} \right) = 6.694 \text{ kcal/mol}$$



$$\begin{aligned}\Delta_C H_{C_3H_8(g)} &= \left[3 \times \Delta_f H_{CO_2(g)} + 4 \times \Delta_f H_{H_2O(l)} \right] \\ &- \left[\Delta_f H_{C_3H_8(g)} + 5 \times \Delta_f H_{O_2(g)} \right] \\ &= \left[3(-393.5) + 4(-285.8) \right] \\ &- (-103.8) = -2219.9 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta_f H_{\text{required}} &= - \left[\Delta_C H_{C_2H_6(g)} + \Delta_C H_{CH_4(g)} \right] \\ &+ \left[\Delta_C H_{C_3H_8(g)} + \Delta_C H_{H_2(g)} \right] \\ &= - \left[(-1560.0) + (-890.0) \right] \\ &+ \left[(-2219.9) + (-285.8) \right] \\ &= -55.7 \text{ kJ}\end{aligned}$$

38. The required thermochemical equation is



From (iv) + (iii) - (v) + (i) - (ii): we get,

$$\begin{aligned}\Delta H &= (-116.5) + (-39.3) - (4.4) + (-13.7) - (-68.4) \\ &= -105.5 \text{ Kcal}\end{aligned}$$

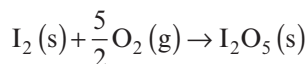
39. From $\frac{1}{3} \times (i) + 2 \times (ii) + \frac{2}{3} \times (iii)$: we get,

$$\begin{aligned}\Delta H_{\text{Required}} &= \frac{1}{3}(-46.4) + 2(9.0) + \frac{2}{3}(-41) \\ &= -24.8 \text{ kJ}\end{aligned}$$

40. For the reaction, $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(s) \rightarrow HI(g)$;

$$\begin{aligned}\Delta H_{\text{Required}} &= \frac{1}{2}(-44.20) - \frac{1}{2}(-52.42) + (-17.31) \\ &- (-19.21) + (-13.74) - (-13.67) \\ &= 5.94 \text{ kcal}\end{aligned}$$

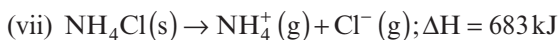
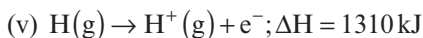
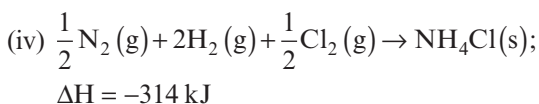
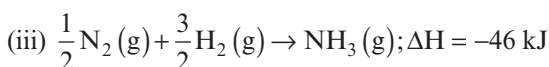
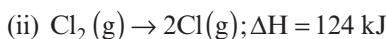
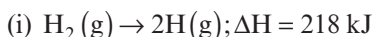
41. The required thermochemical equation is



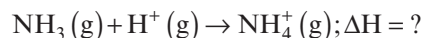
From $2 \times (ii) + 6 \times (v) + 5 \times (vii) - (i) - 6 \times (iii) - 6 \times (iv) - (vi) - 10 \times (viii) - 10 \times (ix)$, we get,

$$\begin{aligned}\Delta H_{\text{Required}} &= 2(-322) + 6(-100) \\ &+ 5(-255) - (4.0) - 6(-44) \\ &- 6(-57) - (-224) - 10(-92) - 10(-75) \\ &= -169 \text{ kJ}\end{aligned}$$

42. Given thermochemical equations are



Required thermochemical equations are



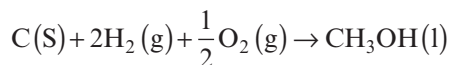
From (vii) + (iv) - (iii) - $\frac{1}{2}$ (ii) - $\frac{1}{2}$ (i) - (v) - (vi)

$$\begin{aligned}\Delta H_{\text{required}} &= (683) + (-314) - (-46) - \frac{1}{2} \times (124) \\ &- \frac{1}{2} \times (218) - (1310) - (-348) \\ &= -718 \text{ kJ/mol}\end{aligned}$$

43. In such polymerization, one sigma bond is formed on cleavage of one pi bond.

$$\Delta H_{\text{required}} = (\text{B.E.}_{\text{C-C}\pi\text{bond}}) - (\text{B.E.}_{\text{C-C}\sigma\text{bond}}) \\ = (590 - 331) - (331) = -72 \text{ kJ/mole}$$

44. Required thermochemical equation is



$$\Delta H = [715 + 4 \times 218 + 249] - [3 \times 415 + 356 + 463] - 38 \\ = -266 \text{ kJ}$$

45. $3\text{C(s)} + 3\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_6(\text{g}); \Delta H_{\text{exp}} = 53 \text{ kJ}$

$$\Delta H_{\text{theo}} = [3 \times 715 + 6 \times 218] - [3 \times 356 + 6 \times 408] \\ = -63 \text{ kJ}$$

$$\therefore \text{Strain energy} = \Delta H_{\text{exp}} - \Delta H_{\text{theo}} = 116 \text{ kJ}$$

46. $2\text{C(g)} + 6\text{H(g)} \rightarrow \text{C}_2\text{H}_6(\text{g})$

$$\Delta H = -2839 = [0 + 0] - [\text{B.E.}_{\text{C-C}} + 6 \times 412] \\ \Rightarrow \text{B.E.}_{\text{C-C}} = 367 \text{ kJ}$$



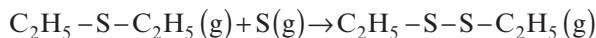
$$\Delta H = -2275 = [0 + 0] - [\text{B.E.}_{\text{C=C}} + 4 \times 412] \\ \Rightarrow \text{B.E.}_{\text{C=C}} = 627 \text{ kJ}$$



$$\Delta H = -5506 \\ = [0 + 0] - [3 \times 367 + 3 \times 627 + 6 \times 412] - \text{R.E.}$$

$$\therefore \text{R.E.} = 52 \text{ kJ/mol}$$

- 47.



$$\Delta H = (-202) - [(-143) + 222] = -276 \text{ kJ}$$

$$\text{B.E.}_{\text{S-S}} = 276 \text{ kJ/mol}$$

48. $\text{CH}_4(\text{g}) \rightarrow \text{CH}_3(\text{g}) + \text{H(g)}$

$$103 = \left[\Delta_f H_{\text{CH}_3(\text{g})} + \frac{103}{2} \right] - [-18]$$

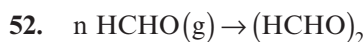
$$\Rightarrow \Delta_f H_{\text{CH}_3(\text{g})} = 33.5 \text{ kcal/mol}$$

$$49. \Delta H_{\text{required}} = [6 \times 414 + 2 \times 348 + 580 + 2 \times 610] \\ - [3 \times 414 + 348 + 580 + 354 + 462] \\ - [118 + 2 \times 580 + 140 + 2 \times 462]$$

$$= -348 \text{ KJ}$$

$$50. \Delta H = 50 - 70 = -20 \text{ kJ}$$

$$51. \Delta H = (\text{B.E.}_{\pi\text{bond in C=C}}) - (\text{B.E.}_{\sigma\text{bond in C-C}}) \\ = (835 - 610) - (348) = -123 \text{ kJ}$$



$$\Delta H = -72 = n \times (-134) - (-732) \Rightarrow n = 6$$

$$\therefore \text{Molecular formula} = (\text{HCHO})_6 = \text{C}_6\text{H}_{12}\text{O}_6$$

53. There is 2.5 B-B bond per B atom. Hence, $\Delta H = -2.5 \times 300 = -750 \text{ kJ/mole of Boron.}$

54. Let the enthalpy of combustion of gauche form be $-x \text{ kcal/mol.}$

Now,

$$690 = 0.7 \times (x - 2) + 0.2 \times x + 0.06$$

$$\times (x + 3) + 0.04 \times (x + 5.5)$$

$$\therefore x = 691$$

55. $\text{M(s)} + \text{X}_2(\text{g}) \rightarrow \text{MX}_2(\text{s}); \Delta H = 1.5 \times \Delta_{\text{eg}} H_{\text{X(g)}}$

From Born-Hafer Cycle, we get:

$$\Delta H = \Delta_{\text{sub}} H_{\text{M(s)}} + \Delta_{\text{li}} H_{\text{M(g)}} + \Delta_{\text{i}_2} H_{\text{M(g)}} + \Delta_{\text{Bond}} H_{\text{X}_2(\text{g})} \\ + 2 \times \Delta_{\text{eg}} H_{\text{X(g)}} + \Delta_{\text{lattice}} H_{\text{MX}_2(\text{s})}$$

$$\text{or, } 1.5 \times (-96) = \Delta_{\text{sub}} H_{\text{M(s)}} + 1.2 \times \Delta_{\text{sub}} H_{\text{M(s)}}$$

$$+ 2.8 \times \Delta_{\text{sub}} H_{\text{M(s)}} + 0.8 \times [1.2 \times \Delta_{\text{sub}} H_{\text{M(s)}}]$$

$$+ 2(-96) + 5 \times [-0.8 \times 1.2 \times \Delta_{\text{sub}} H_{\text{M(s)}}]$$

$$\Delta_{\text{sub}} H_{\text{M(s)}} = 41.38 \text{ kcal/mol}$$

Section B (One or More than one Correct)

- Combustion is exothermic. Decomposition or elimination are endothermic. Graphite is more stable form.
- Conversion of liquid into gas is endothermic.
- $\Delta_f H^\circ = 0$ for elements in their reference state.
- Endothermic compounds have +ve $\Delta_f H^\circ$.
- For $\Delta H = \Delta E$, $\Delta n_g = 0$
- One mole of the substance should burn completely.
- $\Delta_f H_{\text{NO(g)}} = +ve$
- Heat released in reaction = Heat gained by calorimeter system
 $= 1.5 \times 1.4 = 2.1 \text{ kJ}$

$$n_{\text{eq}}(\text{H}_2\text{SO}_4) = \frac{100 \times 0.5}{1000} = 0.05$$

$$n_{\text{eq}}(\text{NH}_4\text{OH}) = \frac{200 \times 0.2}{1000} = 0.04 \quad (\text{Limiting reagent})$$

$$\Delta_{\text{neut}} H_{\text{NH}_4\text{OH}} (\text{By strong acid}) = -\frac{2.1}{0.04} = -52.5 \text{ kJ/eq}$$

$$= -52.5 \text{ kJ/mole}$$

$$\Delta_{\text{diss}} H_{\text{NH}_4\text{OH}} = (-52.5) - (-57) = 4.5 \text{ kJ/mol}$$

$$\Delta_{\text{diss}} H_{\text{CH}_3\text{COOH}} = (57 - 48.1) - 4.5 = 4.4 \text{ kJ/mol}$$

- $\Delta_r H = \left(436 + \frac{1}{2} \times 495 \right) - (-242) = 925.5 \text{ kJ}$
 - $\Delta_r H = \left(\frac{1}{2} \times 436 + \frac{1}{2} \times 495 \right) - (-42) = 423.5 \text{ kJ}$
 - $\Delta_f H_{\text{H(g)}} = \frac{1}{2} \times 436 = 218 \text{ kJ/mol}$
 - $\Delta_f H_{\text{OH(g)}} = 42 \text{ kJ/mol}$

- Resonance occurs in 1, 3-Butadiene and N_2O .
- Resonance occurs in product but not in reactant.

- $\Delta_r H = [2 \times (-1263)] - [(-2238) + (-285)] = -3 \text{ kJ}$
 - $-3 \text{ kJ} = \Delta_C H_{\alpha\text{-maltose}} - 2 \times \Delta_C H_{\text{glucose}}$

- $n_{\text{C(s)}} = \frac{1.2 \times 1000}{12} = 100$
 \therefore Maximum obtainable heat = $100 \times 94 = 9400 \text{ cal}$
 - Heat released = $100 \times 68 + 100 \times 68 = 13600 \text{ cal}$
 - Heat released = $\frac{13600}{100} \times \left(\frac{1200}{30} \right) = 5440 \text{ cal}$

- $$\text{C}_6\text{H}_5\text{COOH(s)} + \frac{15}{2} \text{O}_2(\text{g}) \rightarrow 7\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(l)}$$

$$\Delta H = [7(-393) + 3(-286)] - [-408]$$

$$= -3201 \text{ kJ/mol}$$

and $\Delta U = \Delta H - \Delta n_g \cdot RT$

$$= (-3201) - \left(7 - \frac{15}{2} \right) \times \frac{8.314}{1000} \times 300$$

$$= -3199.75 \text{ kJ/mol}$$

- $$\Delta H = q = 3 \times (-35) = -105 \text{ kcal}$$

$$\Delta U = \Delta H - \Delta n_g \cdot RT$$

$$= \left[(-35) - (2 - 3) \times \frac{2}{1000} \times 300 \right] \times 3$$

$$= -103.2 \text{ kcal}$$

and $w = u - q = (-103.2) - (105) = 1.8 \text{ kcal}$

Section C (Comprehensions)

Comprehension I

- From $-\frac{3}{4} \times a - \frac{1}{4} \times b + \frac{1}{4} \times c - \frac{9}{4} \times d$,

$$\Delta H_{\text{required}} = -\frac{3}{4} \times (-76) - \frac{1}{4} \times (240) + \frac{1}{4} \times (36) - \frac{9}{4} \times (68)$$

$$= -147 \text{ kcal}$$

- From $\frac{3}{4} \times a + \frac{1}{4} \times b - \frac{1}{4} \times c + \frac{1}{4} \times d$,

$$\Delta H_{\text{required}} = \frac{3}{4} \times (-76) + \frac{1}{4} \times (240) - \frac{1}{4} \times (36) + \frac{1}{4} \times (68)$$

$$= 11 \text{ kcal/mol}$$

- Given data based

Comprehension II

$$4. \quad \Delta H = -\frac{75 \times 5}{5 + 1.8} = -55.15 \text{ kJ}$$

$$5. \quad \Delta H = -\frac{75 \times 10}{10 + 1.8} = -63.56 \text{ kJ}$$

$$6. \quad \Delta H = -\frac{75}{1 + \frac{1.8}{n}} = -\frac{75}{1 + \frac{1.8}{\infty}} = -75 \text{ kJ}$$

$$7. \quad \Delta H = (-63.56) - (-55.15) = -8.41 \text{ kJ}$$

$$8. \quad \Delta H = (-75) - (-63.56) = -11.44 \text{ kJ}$$

Comprehension III

$$9. \quad \Delta H_1 = -\frac{483 \cdot 636}{2} = -241.818 \text{ kJ/mol H}_2$$

$$\Delta H_2 = -\frac{868 \cdot 2}{3} = -289.4 \text{ kJ/mol H}_2$$

$$\Delta H_3 = -347.33 \text{ kJ/mol H}_2$$

$$10. \quad \Delta H_1 = -\frac{483 \cdot 636}{32} = -15.11 \text{ kJ/gm O}_2$$

$$\Delta H_2 = -\frac{868 \cdot 2}{48} = -18.09 \text{ kJ/gm O}_3$$

$$\Delta H_3 = -\frac{347 \cdot 33}{34} = -10.22 \text{ kJ/gm H}_2\text{O}_2$$

$$11. \quad \Delta H_1 = -\frac{483 \cdot 636}{36} = -13.43 \text{ kJ/gm reactant}$$

$$\Delta H_2 = -\frac{868 \cdot 2}{54} = -16.08 \text{ kJ/gm reactant}$$

$$\Delta H_3 = -\frac{347 \cdot 33}{36} = -9.65 \text{ kJ/gm reactant}$$

Comprehension IV

$$12. \quad \text{Heat released} = 0.25 \times 320 = 80 \text{ cal}$$

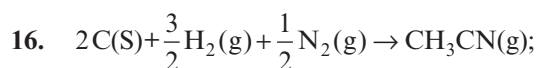
\therefore Molar enthalpy of solution

$$= -\frac{80}{0.98} \times 98 = -8000 \text{ cal}$$

$$13. \quad \text{Heat released} = 0.80 \times 320 = 256 \text{ cal}$$

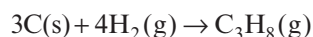
$$\therefore \Delta_r H = -\frac{256}{0.49} \times 98 = -51200 \text{ cal}$$

Comprehension V



$$\Delta H = 88 = [2 \times 719 + \frac{3}{2} \times 435 + \frac{1}{2} \times 948]$$

$$- [3 \times 414 + \text{B.E.}_{\text{C-C}} + \text{B.E.}_{\text{C}\equiv\text{N}}] \rightarrow 1$$



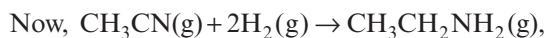
$$\Delta H = -85 = [3 \times 719 + 4 \times 435]$$

$$- [2 \times \text{B.E.}_{\text{C-C}} + 8 \times 414] \rightarrow 2$$

From (1) and (2), we get:

$$\text{B.E.}_{\text{C-C}} = 335 \text{ kJ/mol and}$$

$$\text{B.E.}_{\text{C}\equiv\text{N}} = 899.5 \text{ kJ/mol}$$



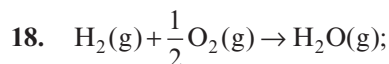
$$\Delta H = [3 \times 414 + 335 + 899.5 + 2 \times 435]$$

$$- [5 \times 414 + 335 + 378 + 2 \times 426]$$

$$= -288.5 \text{ kJ/mol}$$

Comprehension VI

17. $C_{p,m,N_2(g)} < C_{p,m,H_2O(g)}$



$$\Delta H = -55.85 \text{ kcal}$$

$$\Delta U = -56.0 \text{ kcal}$$

Let x mole H_2 be burnt. $\frac{x}{2}$ mol $O_2(g)$ is needed

and hence, $\frac{x}{2} \times 4 = 2 \times \text{mol } N_2$ is also present.

Now,

Heat released from reaction = Heat gained by $H_2O(g)$ and $N_2(g)$

$$56.0 \times 10^3 = x \times 6.2 \times (T_2 - 300) + 2x \times 4.9 \times (T_2 - 300)$$

$$\therefore T_2 = 3800 \text{ K}$$

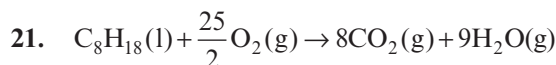
19.
$$\frac{p_1}{n_1 T_1} = \frac{p_2}{n_2 T_2} \Rightarrow \frac{1}{x + \left(\frac{x}{2} + 2x\right) \times 300}$$

$$= \frac{p_2}{(x + 2x) \times 3800}$$

$$\therefore p_2 = 10.86 \text{ atm}$$

20. $q = 0, w = 0 \Rightarrow \Delta E = 0$

Comprehension VII



$$\Delta_c H = [8 \times (-94) + 9 \times (-58)] - [-74]$$
$$= -1200 \text{ kcal/mol}$$

22. $\Delta H_{\text{required}} = [8 \times (-26.5) + 9 \times (-58)] - [-74]$
$$= -660 \text{ kcal/mol}$$

23. Let x mole of C_8H_{18} be converted into CO_2 . As temperature is increased, some heat is absorbed by product gases.

Now, $[x \times 1200 + (0.1 - x) \times 660] - \frac{1}{1000}$
$$\times [8x \times 8 \times 500 + 8(0.1 - x) \times 7.0$$
$$\times 500 + 0.9 \times 6.0 \times 500] = 87.3$$

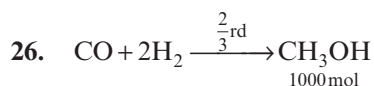
$$\therefore x = 0.05$$

$$\text{Moles of } CO_2 \text{ formed} = 0.05 \times 8 = 0.4$$

24. Moles of H_2O formed = $9x + (0.1 - x) \times 9 = 0.9$

25. $w = -p(v_2 - v_1) = -p\left(\frac{n_2 RT_2}{p} - \frac{n_1 RT_1}{p}\right)$
$$= -R(n_2 T_2 - n_1 T_1)$$
$$= -2 \times \{0.05 \times 8 + (0.1 - 0.05) \times 8 + 0.9\} \times 800$$
$$- \left\{0.05 \times \frac{25}{2} + (0.1 - 0.05) \times \frac{17}{2}\right\} \times 300]$$
$$= -2090 \text{ cal}$$

Comprehension VIII



$$= \frac{3}{2} \times 1000$$

$$= 1500 \text{ mol}$$

In reformer, CO and H_2 is forming in 1 : 3 ratio.

27. $CO = 1500 - 1000 = 500 \text{ mole}$

$$H_2 = 4500 - 2000 = 2500 \text{ mole}$$

28. Heat produced in 1 min = $1000 \times 100 \text{ R} \times 60$
$$= 1.2 \times 10^7 \text{ cal}$$

Comprehension IX

29. Let x mole C be converted into CO. Hence,
 $x \times 26 + (1 - x) \times 94 = 53.2 \Rightarrow x = 0.6$
 Hence, moles of C formed = 0.6

30. $O_2 \text{ consumed} = \left[\frac{x}{2} + (1 - x) \right] 32 = 22.4 \text{ gm}$

Comprehension X

Given thermochemical equations are

- (a) $H_2S(g) \rightarrow H(g) + H S(g); \Delta H = 376.0 \text{ kcal}$
 (b) $H_2(g) + S(s) \rightarrow H_2 S(g); \Delta H = -20.0 \text{ kcal}$
 (c) $S(s) \rightarrow S(g); \Delta H = 277.0 \text{ kcal}$
 (d) $H_2(g) \rightarrow 2H(g); \Delta H = 436.0 \text{ kcal}$

31. $\frac{1}{2}H_2(g) + S(s) \rightarrow HS(g)$

From $a + b - \frac{1}{2} \times d$, we get:

$$\Delta H_{\text{required}} = 376 + (-20) - \frac{1}{2} \times 436 = 138 \text{ kJ/mol}$$

32. $HS(g) \rightarrow H(g) + S(g)$

From (d) - (a) - (b) + (c)

$$\Delta H_{\text{required}} = 436 - 376 - (-20) + 277 = 357 \text{ kJ/mol}$$

Comprehension XI

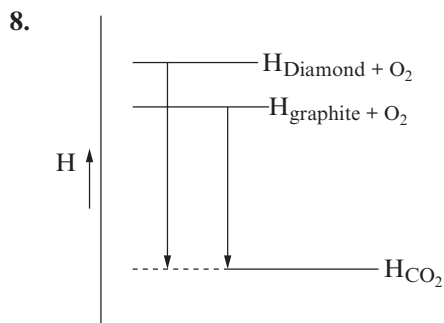
33. $\Delta H^\circ = \Delta E^\circ + \Delta n_g \cdot RT = 2.1 + 2 \times \frac{2}{1000} \times 298$
 $= 3.292 \text{ kcal}$

Now, $\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ = 3.292 - \frac{298}{1000} \times 20$
 $= -2.668 \text{ kcal}$

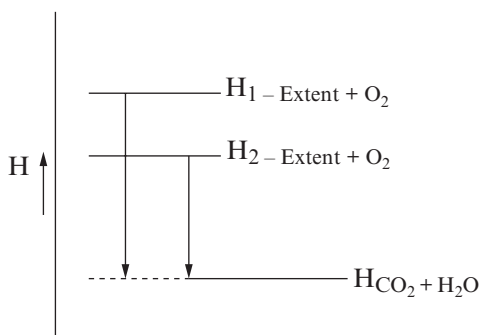
34. Spontaneous as $\Delta G^\circ = -ve$

Section D (Assertion – Reason)

1. Theory based
2. Theory based
3. H_2SO_4 is dibasic but HCl is monobasic.
4. Information based
5. Heat liberated will be four times but as quantity is also four times, the change in the temperature will be same.
6. Solubility is exothermic but all gases are not highly soluble in all liquid.
7. If $|\Delta_{\text{Hydration}} H| < |\Delta_{\text{lattice}} H|$, the salt dissolves partially and the extent depends on the difference in two values.



9.

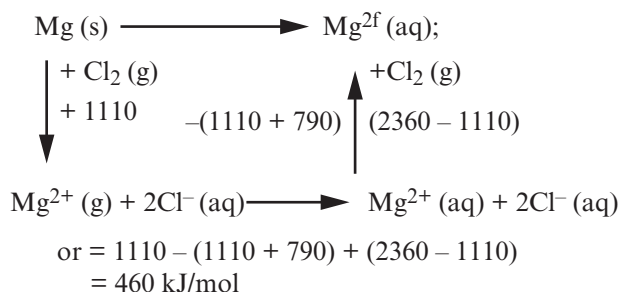


10. Theory based

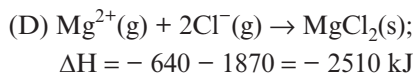
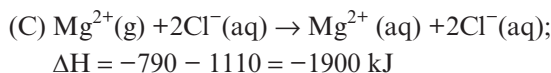
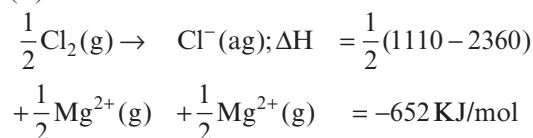
Section E (Column Match)

1. $C \rightarrow CO, \Delta H \neq \Delta H_{\text{combustion}}$
2. (A) $\Delta n_g = 0$ (B) $\Delta n_g = -1$ (C) $\Delta n_g = 1$ (D) $\Delta n_g = -2$
3. (A) $\Delta H = (-57.3) + 15 = -42.3 \text{ kJ}$
(B) $\Delta H = -42.3 - 70.7 + 20 = -93.0 \text{ kJ}$
(C) $\Delta H = -70.7 + 15 = -55.7 \text{ kJ}$
(D) $\Delta H = 0$

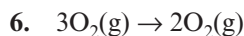
4. (A)



(B)



5. Definition based



7. Theory based

8. $\Delta n_g = 0 \Rightarrow \Delta H = \Delta U$

$\Delta n_g = +ve \Rightarrow \Delta H > \Delta U$

$\Rightarrow \text{If } \Delta H = -ve, \text{ then } |\Delta H| < |\Delta U|$

$\Rightarrow \text{If } \Delta H = +ve, \text{ then } |\Delta H| > |\Delta U|$

$\Delta n_g = -ve \Rightarrow \Delta H < \Delta U$

$\Rightarrow \text{If } \Delta H = -ve, \text{ then } |\Delta H| > |\Delta U|$

$\Rightarrow \text{If } \Delta H = +ve, \text{ then } |\Delta H| < |\Delta U|$

9. Definition based

(10) (A) $\Delta H_{400} = \Delta H_{300} + [c_{p,A_3(g)} - c_{p,A_3(l)}] \times [T_2 - T_1]$
 $= 25 + (20 - 40) \times \frac{1}{1000} \times (400 - 300)$
 $= +23 \text{ kJ/mol}$

(B) $\Delta H_{300} = \Delta H_{400} + [c_{p,A_3(g)} - c_{p,A_3(l)}] \times [T_2 - T_1]$
 $= 50 + (30 - 50) \times \frac{1}{1000} \times (300 - 400)$
 $= +52 \text{ kJ/mol}$

(C) $\Delta H_{300} = 3 \times 25 - 100 - 52 = -77 \text{ kJ/mol}$

(D)

$\Delta H_{400} = \Delta H_{300} + [c_{p,A_3(l)} - 3 \times c_{p,A_3(l)}] \times [T_2 - T_1]$
 $= (-77) + (50 - 3 \times 40) \times \frac{1}{1000} \times (400 - 300)$
 $= -84 \text{ kcal/mol}$

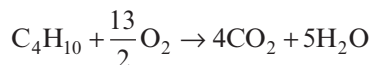
Section F (Subjective)

Single-digit Integer Type

1. For HCl : $13.7 \times 0.05 = c \times 411$ (1)
 For HCOOH : $q \times 0.05 = c \times 321$ (2)
 From (2) \div (1) $\Rightarrow q = 10.7 \text{ kcal}$
 \therefore Enthalpy of ionisation of $\text{HCOOH} = 13.7 - 10.7 = 3.0 \text{ kcal/mol}$
2. $(\text{C}_6\text{H}_{10}\text{O}_5)_x + 6x \text{ O}_2 \text{ (g)} \rightarrow 6x \text{ CO}_2 \text{ (g)} + 5x \text{ H}_2\text{O (l)}$
 $\Delta H = -4.6 \times 162x = [6x(-94.2) + 5x(-68.4)] - [\Delta_f H_{(\text{C}_6\text{H}_{10}\text{O}_5)_x} + 0]$

$\therefore \Delta_f H_{(\text{C}_6\text{H}_{10}\text{O}_5)_x} = -162 \text{ kcal/mol} = -1 \text{ kcal/gm}$

3. $1 \times 800 = a \times 3120 \Rightarrow a = \frac{800}{3120} \text{ L/hr Butane}$



$\therefore \text{Rate of Oxygen Supply} = \frac{800}{3120} \times \frac{13}{2} \times 3 = 5 \text{ L/hr}$

4. $\Delta H_{\text{required}} = \frac{100}{75} \times (13.7 - 12.2) = 2 \text{ kcal/mol}$

$$5. \text{ Total moles of gases} = \frac{1.192 \times 1.642}{0.0821 \times 298} = 0.08$$

Now,

$$n_{\text{CH}_4} \times 210 \times 10^3 = 1260 \times 0.667 \Rightarrow n_{\text{CH}_4} = 0.004$$

$$\therefore \text{Volume per cent of CH}_4 = \frac{0.004}{0.08} \times 100 = 5\%$$

$$6. \text{ Heat released by } \frac{6.3}{64000} \text{ mole haemoglobin} \\ = 25 \times 4.2 \times 0.03 = 3.15 \text{ J}$$

$$\therefore \text{Heat released per mole haemoglobin} \\ = \frac{3.15 \times 64000}{6.3} = 32000 \text{ J}$$

$$\therefore \text{Heat released per mole O}_2 = \frac{32000}{4} = 8000 \text{ J}$$

$$7. \text{ Heat released} = 300 \times 1.0 \times 1.0 \times (26 - 25) = 300 \text{ cal}$$

Now,

$$n_{\text{HA}} = \frac{200 \times 0.4}{1000} = 0.08$$

$$n_{\text{NaOH}} = \frac{100 \times 0.5}{1000} = 0.05$$

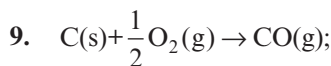
Hence, NaOH is a limiting reagent.

$$\therefore \Delta_{\text{neut}} H = -\frac{300}{0.05} \times 1 = -6000 \text{ cal/mol}$$

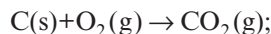
8. There is 3 H-bond per NH_3 molecule because for each bond two NH_3 molecules are required.

\therefore Strength of H-bond

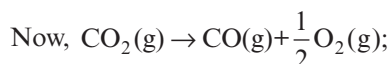
$$= \frac{30.4 - 15.4}{3} = 5.0 \text{ kcal/mol}$$



$$\Delta H_1 = -\frac{7.5}{3} \times 12 = -30 \text{ kcal/mol}$$



$$\Delta H_2 = -\frac{32}{4} \times 12 = -96 \text{ kcal/mol}$$



$$\Delta H = \Delta H_1 - \Delta H_2 = +66 \text{ kcal/mol}$$

$$\text{For } 4.0 \text{ gm CO}_2, \Delta H = \frac{66}{44} \times 4 = 6 \text{ kcal}$$

$$10. (1-a) \times 6900 + a \times 2900 = 3900 \Rightarrow a = \frac{3}{4}$$

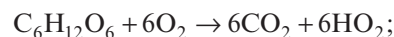
$$\therefore n_{\text{eq(HA)}} : n_{\text{eq(HB)}} = (1-a) : a = \frac{1}{4} : \frac{3}{4} = 1 : 3$$

Four-digit Integer Type

1. $\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2 \text{CH}_4$; $\Delta H = -65.2 \text{ kJ}$
 $\text{C}_3\text{H}_8 + 2\text{H}_2 \rightarrow 3 \text{CH}_4$; $\Delta H = -87.4 \text{ kJ}$
Hence, for $\text{CH}_4(\text{g}) + \text{C}_3\text{H}_8(\text{g}) \rightarrow 2 \text{C}_2\text{H}_6(\text{g})$;
 $\Delta H = (-87.4) - 2 \times (-65.2) = +43 \text{ kJ}$

2. Moles of O_2 consumed

$$= \frac{\left\{ \frac{164.2}{1000} \times \left(\frac{20-10}{100} \right) \times 20 \times 60 \right\} \times 1}{0.0821 \times 310} = \frac{24}{31}$$



$$\Delta H = -3100 \text{ kJ}$$

\therefore Heat produced in body per hr

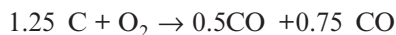
$$= \frac{3100}{6} \times \frac{24}{31} = 400 \text{ kJ}$$

3. Number of glycogen units oxidized per day

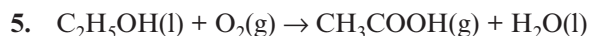
$$= \frac{150 \times 60 \times 60 \times 24}{432 \times 10^3} = 30$$

4. Moles of $\text{C} = \frac{15}{12} = 1.25$

$$\text{Moles of O}_2 = \frac{\left(20 \times \frac{19}{100} \right) \times 8.21}{0.0821 \times 380} = 1$$



$$\therefore \text{Heat produced} = 0.5 \times 26 + 0.75 \times 96 = 85 \text{ kcal}$$

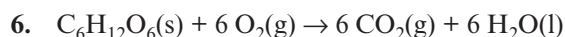


$$\Delta H = [(-118) + (-68)] - [(-66) + 0] = -120 \text{ kcal}$$

Hence, rate of heat removal

$$= \frac{120}{46} \times 2.3 \times 10^3 \times \frac{40}{100}$$

$$= 2400 \text{ kcal/mol}$$



$$\Delta H = [6 \times (-395) + 6 \times (-285)] - [(-1280) + 0] = -2800 \text{ kJ}$$

Moles of CO_2 released per astronaut

$$= \frac{6}{2800} \times 2100 = 4.5$$

$$\therefore \text{Mass of LiOH required} = 4.5 \times 2 \times 24 = 216 \text{ gm}$$

7. $\frac{16.1}{322} \times 100 \times 10^3 = V \times 10000 \Rightarrow V = 0.5 \text{ m}^3 = 500 \text{ L}$

8. Total heat absorbed

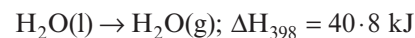
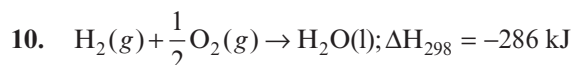
$$= \left(\frac{8}{9} \times 45 + \frac{1}{9} \times 72 \right) \times 2.5 = 120 \text{ KJ}$$

9. For banana: $q = c \times 3.0$ (1)

For benzoic acid: $\frac{800}{122} \times 0.305 = c \times 4.0$ (2)

From (1) and (2), $q = 1.5 \text{ kcal}$ for 2.5 gm banana

$$\therefore \text{Heat obtained per banana} = \frac{1.5}{2.5} \times 125 = 75 \text{ kcal}$$



$$\Delta H_{298} = \Delta H_{398} + \Delta C_p \cdot \Delta T$$

$$= 40.8 + \frac{33.4 - 75.4}{1000} \times (298 - 398)$$

$$= 45 \text{ kJ}$$

$$\therefore \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}); \Delta H_{298} = -[45 - 286]$$

$$= 241 \text{ kJ}$$

11. $\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT$

$$\text{or, } 0 - (-4000) = \int_{300}^T (2 \times 10^{-2} T) dT$$

$$= \frac{2 \times 10^{-2}}{2} (T^2 - 300^2)$$

$$\therefore T = 700 \text{ K}$$



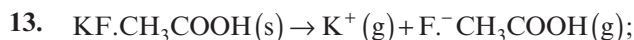
$$\Delta H_{\text{theo}} = (3 \times 715 + 6 \times 218) - (3 \times 356 + 6 \times 408)$$

$$= -63 \text{ kJ}$$

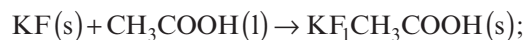
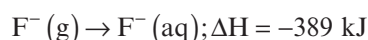
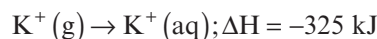
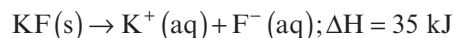
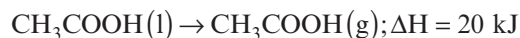
$$\Delta H_{\text{exp}} = [3 \times (-393) + 3 \times (-285)] - [3 \times (-697)]$$

$$= 57 \text{ kJ}$$

$$\therefore \text{Strain energy} = 57 - (-63) = 120 \text{ kJ/mol}$$

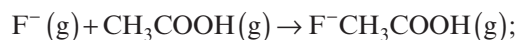


$$\Delta H = 734 \text{ kJ}$$



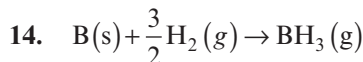
$$\Delta H = -25 \text{ kJ}$$

Required:



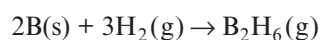
$$\Delta H = (-389) + 734 - 20 - 35 + (-325) + (-25)$$

$$= -60 \text{ kJ/mol}$$



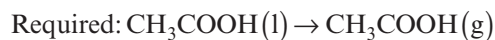
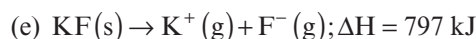
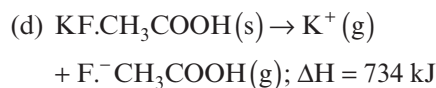
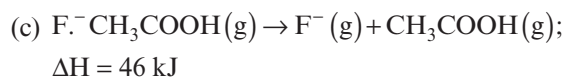
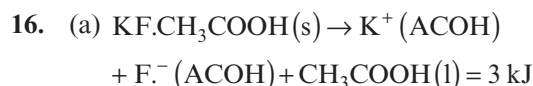
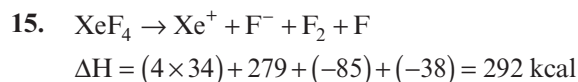
$$\Delta H = 100 = \left(565 + \frac{3}{2} \times 436 \right) - (3 \times \text{B.E.}_{\text{B-H}})$$

$$\therefore \text{B.E.}_{\text{B-H}} = 373 \text{ kJ/mol}$$



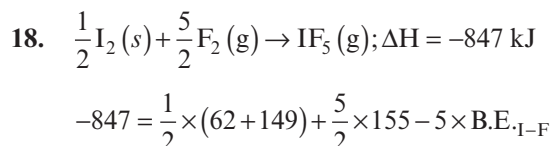
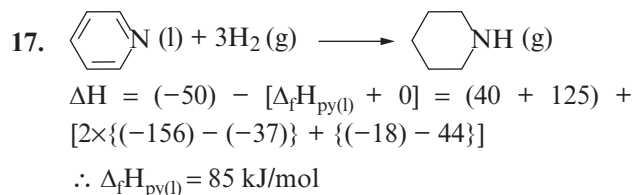
$$\Delta H = 36 = [2 \times 565 + 3 \times 436] - [4 \times 373 + 2 \times \text{B.E.}_{\text{3c-2e}}]$$

$$\therefore \text{B.E.}_{\text{3c-2e}} = 455 \text{ kJ/mol}$$

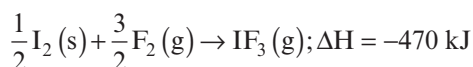


From (c) – (a) + (d) – (e) + (b), we get:

$$\Delta H = 46 - (-3) + 734 - 797 + 35 = 21 \text{ kJ/mol}$$

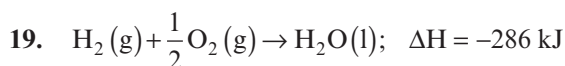


$$\text{B.E.}_{\text{I-F}} = 268 \text{ kJ/mol}$$

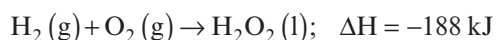


$$-470 = \frac{1}{2} (62 + 149) + \frac{3}{2} \times 155 - \left[2 \times 268 + \text{B.E.}_{\text{I-F(eq)}} \right]$$

$$\text{B.E.}_{\text{I-F(eq)}} = 272 \text{ kJ/mol}$$

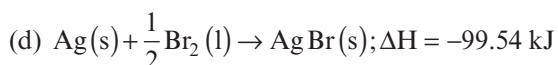
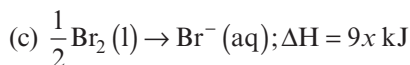
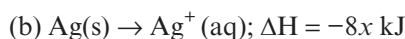
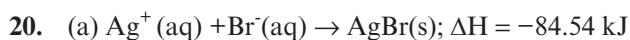


$$-286 = \left(\text{B.E.}_{\text{H-H}} + \frac{1}{2} \times 498 \right) - 2 \times \text{B.E.}_{\text{O-H}} - 44 \quad (1)$$



$$-188 = (\text{B.E.}_{\text{H-H}} + 498) - (2 \times \text{B.E.}_{\text{O-H}} + \text{B.E.}_{\text{O-O}}) - 53 \quad (2)$$

$$\text{From (1) - (2), we get: B.E.}_{\text{O-O}} = 142 \text{ kJ/mol}$$



As (a) + (b) + (c) = (d), we get:

$$(-84.54) + (-8x) + 9x = -99.54$$

$$\Rightarrow x = -15$$

$$\therefore \Delta_f H_{\text{Ag}^+(\text{aq})} = -8x = 120 \text{ kJ/mol}$$