विध्न विचारत भीरु जन, नहीं आरम्भे काम, विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक, 'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

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EXERCISE I

Heat of reaction & it's type

Q.1 When 2 moles of C_2H_6 are completely burnt 3120 kJ of heat is liberated . Calculate the heat of formation, ΔH_f^o for C_2H_6 . Given ΔH_f^o for $CO_2(g)$ & $H_2O(l)$ are – 395 & – 286 kJ respectively.

Q.2 The standard heats of formation of CH_4 (g) , CO_2 (g) and H_2O (*l*) are – 76.2 , – 398.8 , – 241.6 kJ mol^{-1} . Calculate amount of heat evolved by burning 1 m^3 of methane measured under normal (STP) conditions.

Q.3 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 mixed $\Delta H_f°$ for Ca^{2+}(aq), CO_3^{2-} (aq) and $CaCO_3$ (s) are – 129.80, – 161.65, – 288.5 kcal mol^{-1} repectively.

Q.4 The enthalpies of neutralization of NaOH & NH_4OH by HCl are – 13680 calories and – 12270 cal respectively . What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl in solution ? Assume that NH_4OH and NaCl are quantitatively obtained.

Q.5 The heat of solution of anhydrous $CuSO_4$ is – 15.9 kcal and that of $CuSO_4.5H_2O$ is 2.8 kcal. Calculate the heat of hydration of $CuSO_4$.

Q.6 The heat of reaction $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ at 27°C is – 22.1 k cal . Calculate the heat of reaction at 77° C . The molar heat capacities at constant pressure at 27°C for hydrogen , chlorine & HCl are 6.82, 7.70 & 6.80 cal mol^{-1} respectively.

Q.7 Calculate standard heats of formation of carbon–di–sulphide (*l*) . Given the standard heat of combustion of carbon (s) , sulphur (s) & carbon–di–sulphide (*l*) are : – 393.3, – 293.72 and – 1108.76 kJ mol^{-1} respectively.

Q.8 A cylinder of gas supplied by a company contains 14 kg of butane . The heat of combustion of butane is 2658 kJ/mol . A normal family requires 20 MJ of energy per day of cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to inefficient combustion.

Q.9 The enthalpy change for the reaction $C_3H_8 + H_2(g) \longrightarrow C_2H_6(g) + CH_4(g)$ at 25º C is – 55.7 kJ/mol. Calculate the heat of combustion of $C_2H_6(g)$. The heats of combustion of H_2, CH_4 & $C_{graphite}$ are – 285.8, – 890.0 & – 393.5 kJ/mole respectively. Heat of combustion of propane is –2220 kJ mol^{-1}.

Q.10 The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is – 2480 cal . g eq^{-1} and – 13.68 kcal . g eq^{-1} respectively . Find the enthalpy of dissociation of HCN at the same temperature.

Q.11 At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, CO_2 (g) & H_2O (*l*) are ; – 408, – 393 & –286 KJ mol^{-1} respectively . Calculate the heat of combustion of benzoic acid at:(i) constant pressure & (ii) constant volume.

Q.12 The heat liberated on complete combustion of 7.8 g of benzene is 327 kJ . This heat has been measured at constant volume & at 27° C . Calculate the heat of combustion of benzene at constant pressure.

Q.13 A cylinder of gas is assumed to contains 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2658$ kJ/mole for butane.

Q.14 The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 kJmol^{-1} What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point ?

Q.15 When 12.0 g of carbon reacted with oxygen to form CO & CO_2 at 25° C & constant pressure, 75.0 kcal of heat was liberated and no carbon remained . Calculate the mass of oxygen which reacted. $\Delta H_f^\circ (CO_2) = -95$ kcal mol^{-1}, $\Delta H_f^\circ (CO) = -24$kcal mol^{-1}.

Q.16 If the enthalpy of formation of HCl (g) and Cl^- (aq) are –92.3 kJ/mole and – 167.44 kJ/mol, find the enthalpy of solution of hydrogen chloride gas.

Calorimeter

Q.17 0.16 g of methane was subjected to combustion at 27° C in a bomb calorimeter . The temperature of calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure .
The thermal capacity of calorimeter system is 17.7 kJ K^{-1} . (R = 8.313 mol^{-1} K^{-1})

Q.18 1.00 *l* sample of a mixture of CH_4(g) & O_2(g) measured at 25° C & 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO_2 & H_2O caused a temperature rise in the calorimeter of 0.667 K. What was the mole percent of CH_4 in the original mixture?
$\Delta H^\circ_{comb} (CH_4) = -215$ k cal mol^{-1} .

Q.19 Two solutions initially at 25°C were mixed in a adiabatic constant pressure calorimeter. One contains 400 ml of 0.2 M weak monoprotic acid solution. The other contain 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2 °C. How much heat is evolved in the neutralization of 1 mole of acid? Assume density of solution 1.0 g/cm^3, and specific heat of solution 4.2 J/g-K. Neglect heat capacity of the calorimeter.

Q.20 When 1.0 g of fructose $C_6H_{12}O_6$(s) is burned in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56 °C. If the heat capacity of the calorimeter and its contents is 10.0 kJ/°C. Calculate the enthalpy of combustion of fructose at 298 K.

Q.21 A quantity of 1.92 g of methanol was burnt in a constant pressure calorimeter. The temperature of water increased by 4.2 °C. If the quantity of water surrounding the inner vessel was 2000 ml and the heat capacity of the inner vessel was 2.02 kJ/°C. Calculate the heat of combustion of methanol. [Specific heat of capacity of H_2O = 4.18 J/g°C]

Bond energy

Q.22 The enthalpy of dissociation of PH_3 is 954 kJ/mol and that of P_2H_4 is 1.485 M J mol^{-1}. What is the bond enthalpy of the P–P bond?

Q.23 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.
$C_2H_4(g) + H_2(g) \rightarrow C_2H_6\,(g)$

Data:

Bond	C–C	C = C	C–H	H–H
Bond Enthalpy	336.81 KJ/mol	606.68 KJ/mol	410.87 KJ/mol	431.79 KJ/mol

Q.24 The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows:
$CH_4(g) \longrightarrow C(g) + 4H(g) \quad \Delta_rH = 396$ kcal/mole
$C_2H_6(g) \longrightarrow 2C(g) + 6H(g) \quad \Delta_rH = 676$ kcal/mole
Calculate C–C bond energy in C_2H_6 & heat of formation of $C_2H_6(g)$
Given: $\Delta_{sub}C(s) = 171.8$ kcal/mole
B.E. (H–H) = 104.1 kcal/mole

Q.25 The polymerisation of ethylene to linear polyethylene is represented by the reaction $n\,CH_2 = CH_2 \rightarrow (-CH_2-CH_2)_n$ where n has a large integral value . Given that the average enthalpies of bond dissociation for C=C & C–C at 298 K are + 590 & + 331 KJ mol^{-1} respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Q.26 From the following data :
Enthalpy of formation of CH_3CN = 87.86 KJ/mol ,Enthalpy of formation of C_2H_6 = – 83.68 KJ/mol
Enthalpy of sublimation of graphite = 719.65 KJ/mol
Enthalpy of dissociation of nitrogen = 945.58 KJ/mol ; Enthalpy of dissociation of H_2 = 435.14 KJ/mol
C–H bond enthalpy = 414.22 KJ/mol
Calculate the (i) $\in_{C-C}$; (ii) $\in_{C\equiv N}$

Q.27 The heat of combustion of acetylene is 312 kcal . If heat of formation of CO_2 & H_2O are –94.38 & –68.38 kcal respectively, calculate C ≡ C bond energy . Given that heat of atomisation of C & H are 150.0 & 51.5 k cal respectively and C — H bond energy is 93.64 k cal.

Q.28 Using the given data calculate enthalpy of formation of acetone (g) . [All values in kJ mol^{-1}]
binding energy of : C — H = 413.4 ; C — C = 347.0 ; C = O = 728.0 ;
O = O = 495.0 ; H — H = 435.8 ; ΔH_{sub} of C = 718.4.

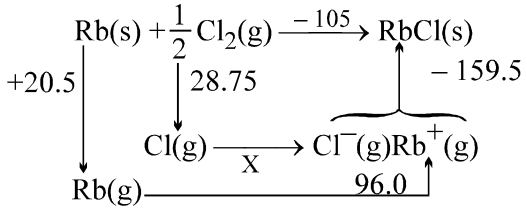
Q.29 Find the enthalpy of S–S bond from the following data.
(i) $C_2H_5 - S - C_2H_5\,(g) \qquad \Delta H_f^{\circ} = -147.2$ kJ/mol
(ii) $C_2H_5 - S - S - C_2H_5\,(g) \qquad \Delta H_f^{\circ} = -201.9$ kJ/mol
(iii) S (g) $\qquad \Delta H_f^{\circ} = 222.8$ kJ/mol

Born Haber cycle

Q.30 Calculate the electron affinity of fluorine atom using the following data . Make Born–Haber's cycle. All the values are in kJ mol^{-1} at 25° C . $\Delta H_{diss}\,(F_2) = 160$, ΔH_f° (NaF(s)) = – 571, I.E. [Na(g)] = 494, ΔH_{vap} [Na(s)] = 101 . Lattice energy of NaF(s) = – 894.

Q.31 Cesium chloride is formed according to the following equation
$Cs(s) + 0.5Cl_2(g) \longrightarrow CsCl(s)$.
The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron affinity of chlorine are 81.2, 243.0, 375.7 and – 348.3 kJ mol^{-1} . The energy change involved in the formation of CsCl is – 388.6 kJ mol^{-1} . Calculate the lattice energy of CsCl.

Q.32 The Born–Haber cycle for rubidium chloride (RbCl) is given below (the energies are in k cal mol^{-1})



Find out the electron affinity of chlorine in kJ mol^{-1} .

Resonance Energy

Q.33 The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are –2839.2, –2275.2 and –5506 KJmol^{-1} respectively. Calculate the resonance energy of benzene. The bond enthalpy of C–H bond is given as equal to + 410.87 KJ/mol.

Q.34 Calculate the heat of combustion of methyl alcohol at 298 K from the following data

Bond	C – H	C – O	O – H	O = O	C = O
Energy kJ mol^{-1}	414	351.5	464.5	494	711

Resonance energy of CO_2 = – 143 kJ mol^{-1}

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

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

Q.35 Calculate the enthalpy of combustion of benzene (l) on the basis of the following data :

(i) Resonance energy of benzene(l) = – 152 kJ/mol

(ii) Enthalpy of hydrogenation of cyclohexene(l) = – 119 kJ/mol

(iii) ΔH^o_f of $C_6H_{12}(l)$ = – 156 kJ/mol

(iv) ΔH^o_f of $H_2O(l)$ = – 285.8 kJ/mol

(v) ΔH^o_f of $CO_2(g)$ = – 393.5 kJ/mol

PROFICIENCY TEST

Q.1 Fill in the blanks with appropriate items:

1. The combustion of a substance is always__________.

2. If heat content of X is smaller than that of Y then the process $X \longrightarrow Y$ is __________.

3. C (Diamond) $\longrightarrow$ C (Graphite) + x kJ. The heat change in this process is called__________.

4. For any reaction, $\Delta H° =$ _________.

5. As per reaction, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) - 66$ kJ the value of ΔH_f of NO_2 is __________.

6. Heats of combustion of methane, carbon and hydrogen are –212, –94, –68 kcal mol^{-1}. The heat of formation of CH_4 is __________.

7. The heat of neutralisation of 1 mole of $HClO_4$ with 1 gm-equivalent of NaOH in aqueous solutions is _____kJ mol^{-1}.

8. The heat of combustion of graphite and carbon monoxide respectively are – 393.5 kJ mol^{-1} and – 283 kJ mol^{-1}. Thus, heat of formation of carbon monoxide in kJ mol^{-1} is_____________.

9. At 298 K, the bond energies of C–H, C–C, C = C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol^{-1}. The value of enthalpy change for the reactions
$H_2C = CH_2(g) + H_2(g) \longrightarrow H_3C - CH_3(g)$ at 298 K will be_____________.

10. For the reaction,
$C_3H_8\,(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O\,(l)$
at constant temperature, $\Delta H - \Delta U$ is__________.

Q.2 Mark the following statements as True or False:

1. The ΔH of a reaction is independent of temperature.

2. The enthalpies of elements are always taken to be zero.

3. Integral heat of solution is same as heat of hydration of substance.

4. Heat of neutralisation of weak acid-strong base is not constant.

5. Combustion reactions are always exothermic.

6. Resonance energy is always negative.

7. $\Delta E = 0$ Combustion of benzene in a sealed container that is immersed in a water bath at 25°C and has rigid, thermally conducting walls.

8. For reaction $2A(g) + B(g) \longrightarrow 3\,C(g)$ $\Delta H = -\,x$ kJ

   then for reactiion $\frac{3}{2}C\,(g) \longrightarrow A(g) + \frac{B}{2}\,(g)$ $\Delta H = \frac{x}{2}$ kJ.

9. ΔH_f° (C, diamond) $\neq 0$.

10. For a particular reaction $\Delta E = \Delta H + P.\,\Delta V$

EXERCISE II

Q.1 Calculate the mass of mercury which can be liberated from HgO at 25° C by the treatment of excess HgO with 41.84 kJ of heat at
(a) constant pressure (b) constant volume conditions .
Given : ΔH_f^{o} (HgO, s) = – 90.8 kJ mol^{-1} & M (Hg) = 200.6 g mol^{-1} .

Q.2 For reduction of ferric oxide by hydrogen, $Fe_2O_3(s) + 3\,H_2(g) \longrightarrow 2\,Fe(s) + 3\,H_2O(l)$; $\Delta H^{o}_{298} = -35.1$ kJ . The reaction was found to be too exothermic to be convenient . It is desirable that ΔH^{o} should be at the most – 26 kJ . At what temperature is it possible ?
$C_P[Fe_2O_3] = 104.5$, $C_P[Fe(s)] = 25.5$, $C_P[H_2O(l)] = 75.3$, $C_P[H_2(g)] = 28.9$ (all in J/mol)

Q.3 From the following data of ΔH of the following reactions
$C(s) + 1/2O_2(g) \longrightarrow CO(g)$; ΔH = –110 KJ
and $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$; ΔH = 132 KJ
Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K, keeping the reaction temperature constant.

Q.4 Although C_P is usually assumed to be constant, for more accurate calculations we must consider its variation with temperature as well . This relation is given by ;
$C_P = a + bT + cT^2 + dT^3$ cal mol^{-1} K^{-1}.
(a) Find the expression for the amount of heat required to raise the temperature of 1 mole of gas from T_1K to T_2K, while
(i) keeping the first term [i.e. $C_P = a$] (ii) keeping the first two terms .
(iii) keeping all the terms . of the above expression . Note that each successive term introduces higher accuracy.
(b) For CO_2, a = 5.0 , b = 15 x 10^{-5} . Find the heat required to raise its temperature from 300 K to 500 K in case (i) and case (ii) . (number of moles = 1) . Case (ii) gives a more accurate value . Find the percent error in case (i) .

Q.5 An intimate mix of ferric oxide & Al is used as solid rocket fuel . Calculate the fuel value per gm & fuel value per CC of the mix . Heats of formation & densities are :
ΔH_f^{o} (Al_2O_3) = – 399 k cal/mole ; ΔH_f^{o} (Fe_2O_3) = – 199 kcal / mole,
density of Fe_2O_3 = 5.2 g/cc ; density of Al = 2.7 g/cc.

Q.6 A person takes 15 breaths per minute . The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume . The exhaled air contains 16% of oxygen by volume . If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day & how much heat is evolved . ΔH_{com} of sucrose is = – 6000 kJ mol^{-1} . Take temperature to be 300 K throughout.

Q.7 The enthalpies of neutralization of a strong acid HA & a weaker acid HB by NaOH are – 13680 cal/equivalent & – 2900 cal/equivalent respectively . When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was – 6900 calories . In what ratio is the base distributed between HA & HB ?

Q.8 Calculate the heat produced when 3.785 litre of octane (C_8H_{18}) reacts with oxygen to form CO & water vapour at 25° C. The density of octane is 0.7025 gm/ml. Heat of combustion of C_8H_{18} is – 1302.7 k cal/mol .
ΔH_f^{o} $CO_2(g)$ = – 94.05 k cal mol^{-1} ; ΔH_f^{o} CO(g) = – 26.41 k cal mol^{-1} ;
ΔH_f^{o} $H_2O(l)$ = – 68.32 k cal mol^{-1} ; ΔH_f^{o} $H_2O(g)$ = – 57.79 k cal mol^{-1}

Q.9 Using the data (all values are in kJ/mol at 25° C) given below :

$\Delta H^\circ_{\text{combustion}}$ (ethane) $= -1559.8$; $\Delta H^\circ_{\text{combustion}}$ (ethene) $= -1410.9$

$\Delta H^\circ_{\text{combustion}}$ (acetylene) $= -1299.7$; $\Delta H^\circ_{\text{combustion}}$ (acetaldehyde) $= -1192.3$

ΔH°_f $CO_2(g) = -393.5$; ΔH°_f of $H_2O(l) = -285.8$

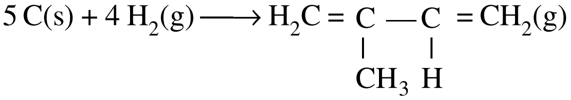
ΔH° for $C_{(s)}$ (graphite) $\rightarrow C_{(g)} = +716.68$; Bond energy of $H-H = 435.94$

Bond energy of $O=O = 498.94$

Calculate the following bond energies :

(i) $C-C$ (ii) $C-H$ (iii) $C=O$ (iv) $C=C$ (v) $C\equiv C$

Q.10 Using bond energy data, calculate heat of formation of isoprene .



$$5\,C(s) + 4\,H_2(g) \longrightarrow H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - \underset{\displaystyle H}{\underset{|}{C}} = CH_2(g)$$

Given : $C - H = 98.8$ k cal ; $H - H = 104$ k cal ;

$C - C = 83$ k cal ; $C = C = 147$ k cal &

$C(s) \rightarrow C(g) = 171$ k cal .

Q.11 Use the following data to calculate the enthalpy of formation of As_2O_3 .

(i) $As_2O_3(s) + [(3\,H_2O + aq)] \rightarrow 2\,H_3AsO_3\,(aq)$; $\Delta H = +7550$ cal

(ii) $As(s) + \frac{3}{2}Cl_2(g) \rightarrow AsCl_3\,(l)$; $\Delta H = -71390$ cal

(iii) $AsCl_3(l) + (3\,H_2O + aq) \rightarrow H_3AsO_3\,(aq) + 3\,HCl(aq)$; $\Delta H = -17580$ cal

(iv) $HCl(g) + aq \rightarrow HCl\,(aq)$; $\Delta H = -17315$ cal

(v) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)$; $\Delta H = -22000$ cal

(vi) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O\,(l)$; $\Delta H = -68360$ cal

Q.12 Calculate the enthalpy change for the reaction $XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$.
The average Xe–F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol.

Q.13 By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion.
Comment on the difference in their values.

* enthalpy change of solution of NaCl(s) = – 2 kJ/mol.
* enthalpy change of solution of NaI(s) = + 2 kJ/mol.
* enthalpy change of hydration of $Na^+(g) = -390$ kJ/mol.
* lattice energy of NaCl = – 772 kJ/mol.
* lattice energy of NaI = – 699 kJ/mol.

Q.14 The standard enthalpy of combustion of sucrose is -5645 kJ mol^{-1} . What is the advantage (in kJ mol^{-1} of energy released as heat) of complete aerobic oxidation compared to anaerobic hydrolysis of sucrose to lactic acid ? ΔH_f° for lactic acid, CO_2 and H_2O is –694, –395.0 and –286.0 respectively.

Q.15 In the combustion of solid naphthalene ($C_{10}H_8$) at 298 K and atmospheric pressure 5157 kJ/mol of heat are evolved. Calculate resonance energy of naphthalene.Given

Latent heat of sublimation of naphthalene = 72.0 kJ/mol
Enthalpy of formation of $H_2O = -286.0\ kJ\ mol^{-1}$
Enthalpy of formation of $CO_2 = -393.5\ kJ\ mol^{-1}$
Enthalpy of atomization of C = $715.5\ kJ\ mol^{-1}$
B.E. for C– C bond = $345.5\ kJ\ mol^{-1}$
C = C bond = $617.0\ kJ\ mol^{-1}$
C – H bond = $413.0\ kJ\ mol^{-1}$
H–H bond = 436 kJ/mol

Q.16 Calculate the proton affinity of $NH_3(g)$ from the following data (in kJ/mole)

$\Delta H^\circ_{dissociation} : H_2(g) = 218$; $\Delta H^\circ_{dissociation} : Cl_2(g) = 124$
$\Delta H^\circ_{formation} : NH_3(g) = -46$; $\Delta H^\circ_f : NH_4Cl(s) = -314$
Lattice energy of NH_4Cl (s) = – 683
Ionization energy of H = 1310
Electron affinity of Cl = 348

Q.17 The standard enthalpy of formation of FeO & Fe_2O_3 is – 65 kcal mol^{-1} and –197kcalmol^{-1} respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2 : 1 . If by oxidation, it is changed into a 1 : 2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture ?

Q.18 The enthalpy of formation of $C_2H_5OH(l)$ is – 66 k cal/mol . The enthalpy of combustion of $CH_3–O–CH_3$ is – 348 k cal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are –94 k cal/mol & – 68 k cal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at 25° C.

Q.19 During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition to O_2 and N_2. Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sucked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.

An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.

(i) If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?

(ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling–exhaling take?

$\Delta H_{comb}(CO) = -280 kJ.mol^{-1}$. Neglect any use of Graham's Law.

Q.20 Fe_xO_4 a mixed oxide of iron consists of only Fe^{+2} & Fe^{+3} ions, with the ratio of $Fe^{+2} : Fe^{+3} = 1:2$ in the mixed oxide. From the data given below,

Enthalpy of formation, $\Delta H_f(Fe_xO_4) = -1092$ kJ/mol.
Enthalpy of sublimation, ΔH_{sub} (Fe) = 390 kJ/mol.
B.D.E of O_2 = 490 kJ/mol.
$I.E_1$ of Fe = 760 kJ/ mol.
$I.E_2$ of Fe = 1560 kJ/mol.
$I.E_3$ of Fe = 2960 kJ/mol.
$I.E_1$ of O^{2-} = –844 kJ/mol.
$I.E_2$ of O^{2-} = 142 kJ/mol.
Lattice Energy of Fe_xO_4 = 18930 kJ/mol.
Prove that value of x is 3 with the help of given data.

EXERCISE III

Q.1 For which of the following change $\Delta H \neq \Delta E$?

(A) $H_2\,(g) + I_2\,(g) \longrightarrow 2HI\,(g)$ (B) $HCl\,(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$

(C) $C(s) + O_2(g) \longrightarrow CO_2(g)$ (D) $N_2\,(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

Q.2 $\Delta_r H$ of which of the following reactions is zero?

(A) $H_2(g) \longrightarrow 2H^+\,(g) + 2e^-$ (B) $2H(g) + aq \longrightarrow 2H^+(aq) + 2e^-$

(C) $2H(g) \longrightarrow 2H^+(g) + 2e^-$ (D) $H_2(g) + aq \longrightarrow 2H^+(aq) + 2e^-$

Q.3 ΔH_f^0 of water is – 285.8 kJ mol^{-1}. If enthalpy of neutralisation of monoacid strong base is –57.3 kJ mol^{-1}, ΔH_f^0 of OH^- ion will be

(A) – 228.5 kJ mol^{-1} (B) 228.5 kJ mol^{-1} (C) 114.25 kJ mol^{-1} (D) –114.25 kJ mol^{-1}

Q.4 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C. Calculate the enthalpy of neutralization per mole of HCl.

(A) -2.5×10^2 kJ (B) -1.3×10^2 kJ (C) -8.4×10^1 kJ (D) -6.3×10^1 kJ

Q.5 The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is – 56.1 kJ mol^{-1}. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is – 57.3 kJ equiv^{-1}, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

(A) 10 (B) 15 (C) 20 (D) 25

Q.6 For the allotropic change represented by the equation C (graphite) $\longrightarrow$ C (diamond), ΔH = 1.9 kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2, the heat liberated in first case is

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

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

Q.7 If x_1, x_2 and x_3 are enthalpies of H–H, O=O and O–H bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

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

Q.8 $NH_3(g) + 3Cl_2(g)$ 1 $NCl_3(g) + 3HCl\,(g); -\Delta H_1$

$N_2(g) + 3H_2(g)$ 1 $2NH_3(g); \Delta H_2$

$H_2(g) + Cl_2(g)$ 1 $2HCl\,(g)\,; \Delta H_3$

The heat of formation of NCl_3 (g) in the terms of ΔH_1, ΔH_2 and ΔH_3 is

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

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

Q.9 Ethanol can undergoes decomposition to form two sets of products

$$C_2H_5OH\,(g) \longrightarrow \begin{cases} \xrightarrow{1} C_2H_4(g) + H_2O\,(g) & \Delta H^\circ = 45.54 \text{ kJ} \\ \xrightarrow{2} CH_3CHO(g) + H_2\,(g) & \Delta H^\circ = 68.91 \text{ kJ} \end{cases}$$

if the molar ratio of C_2H_4 to CH_3CHO is 8 : 1 in a set of product gases, then the energy involved in the decomposition of 1 mole of ethano*l* is

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

Q.10 Reactions involving gold have been of particular interest to a chemist . Consider the following reactions,

$Au(OH)_3 + 4\,HCl \longrightarrow HAuCl_4 + 3\,H_2O$, $\Delta H = -28$ kcal

$Au(OH)_3 + 4\,HBr \longrightarrow HAuBr_4 + 3\,H_2O$, $\Delta H = -36.8$ kcal

In an experiment there was an 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 %

Q.11 (i) Cis–2 – butene → trans – 2 – butene, ΔH_1

(ii) Cis – 2– butene → 1 – butene, ΔH_2

(iii) Trans – 2 – butene is more stable than cis – 2 – butene.

(iv) Enthalpy of combustion of 1–butene, $\Delta H = -649.8$ kcal/mol

(v) $9\Delta H_1 + 5\,\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans 2 – butene, $\Delta H = -647.0$ kcal/mol.

The value of ΔH_1 & ΔH_2 in Kcal/mole are

(A) –1.0 , 1.8 (B) 1.8, -1.0 (C) –5, 9 (D) –2, 3.6

Q.12 The reaction $CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$ has $\Delta H = -25$ kCal.

Bond	Bond Energy kCal
ε_{C-Cl}	84
ε_{H-Cl}	103
ε_{C-H}	x
ε_{Cl-Cl}	y
x : y = 9 : 5	

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

(A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Q.13 From the following data at 25°C

Reaction	**$\Delta_r H°$ kJ/mol**
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g)$	42
$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$	–242
$H_2(g) \longrightarrow 2H(g)$	436
$O_2(g) \longrightarrow 2O(g)$	495

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

Statement (a) : $\Delta_r H°$ for the reaction $H_2O(g) \longrightarrow 2H(g) + O(g)$ is 925.5 kJ/mol

Statement (b) : $\Delta_r H°$ for the reaction $OH(g) \longrightarrow H(g) + O(g)$ is 502 kJ/mol

Statement (c) : Enthalpy of formation of H(g) is –218 kJ/mol

Statement (d) : Enthalpy of formation of OH(g) is 42 kJ/mol

(A) Statement c (B) Statement a, b, d (C) Statement b, c (D) Statement a, d

Q.14 A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm, is exploded in a **closed rigid vessel**. If the process occurs under **adiabatic condition** then using the given datas answer the questions that follow :

Given (i) $C_P = 8.3$ cal deg^{-1} mol^{-1}; (ii) $C_P = 11.3$ cal deg^{-1} mol^{-1} ; $\Delta H_f [H_2O(g)] = –57.8$ Kcal

[Take air as 80% N_2, 20% O_2 by volume]

(i) The value of C_P of N_2 & H_2O in the order N_2, H_2O will be (in cal. deg.$^{-1}$ mol^{-1})

(A) 8.3, 8.3 (B) 8.3, 11.3 (C) 11.3, 11.3 (D) 11.3, 8.3

(ii) What will be the maximum temperature attained if the process occurs in adiabatic container.

(A) ≅ 2940 K (B) ≅ 2665 K (C) ≅ 1900 K (D) ≅ 298 K

(iii) What will be the final pressure in atm.

(A) ≅ 8.5 (B) ≅ 7.6 (C) ≅ 5.46 (D) ≅ 0.85

(iv) If at initial temperature $T_1 E_1$ is initial internal energy & at higher final temperature. $T_2 E_2$ is the final internal energy, then which option is true

(A) $E_1 > E_2$ (B) $E_2 > E_1$

(C) $E_1 = E_2$ (D) can't be compared from the given data

Q.15 The commerical production of "Water gas" utilises the endothermic reaction $C(s) + H_2O(g) \longrightarrow H_2(g) + CO(g)$. The heat required for this reaction is generated by combustion of coal to CO_2 using stoichiometric amount of air.(79% N_2 by volume and 21% O_2 by volume). The superheated steam undergoes 75% conversion. Using the following data, answer the question that follows :

$\Delta H_f [CO(g)] = –110.53$ kJ/mol ; $\Delta H_f [H_2O(g)] = –241.81$ kJ/mol ; $\Delta H_f [CO_2(g)] = –314.0$ kJ/mol

(i) The amount of heat liberated when one litre of product gases are burnt at 373 K and one atm is

(A) ≅ 3.6 kJ (B) ≅ 3.9 kJ (C) ≅ 4.43 kJ (D) ≅ 5.34 kJ

(ii) Match the gas and percentage of each gas in one litre product gases.

	Gas		**Percentage**
(I)	N_2	(a)	≈ 23.1
(II)	CO_2	(b)	≈ 36.4
(III)	H_2	(c)	≈ 7.7
(IV)	H_2O	(d)	≈ 9.7

(A) (I-a), (II-b), (III-c), (IV-d) (B) (I-b), (II-a), (III-d), (IV-c)

(C) (I-c), (II-d), (III-a), (IV-c) (D) (I-b), (II-d), (III-a), (IV-c)

EXERCISE IV

OBJECTIVE

Q.1 Which of the following reactions defines ΔH_f° ?

(A) $C_{(diamond)} + C_2(g) \longrightarrow CO_2(g)$ (B) $1/2\, H_2(g) + 1/2\, F_2(g) \longrightarrow HF(g)$

(C) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3$ (D) $CO(g) + 1/2O_2(g) \longrightarrow CO_2(g)$ **[JEE 2003]**

Q.2 ΔH_f° for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and –241.8 kJ mol^{-1} respectively. The standard enthalpy change (in kJ) for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O\,(g) \text{ is}$$

(A) 524.1 (B) 41.2 (C) –262.5 (D) – 41.2 **[JEE 2000]**

Q.3 Which of the following is not an endothermic reaction?

(A) Combustion of methane

(B) Decomposition of water

(C) Dehydrogenation of ethene to ethylene

(D) Conversion of graphite to diamond **[JEE 1999]**

Q.4 Standard molar enthalpy of formation of CO_2 is equal to

(A) zero

(B) standard molar enthalpy of combustion of carbon (graphite)

(C) standard molar enthalpy of combustion of gaseous carbon

(D) sum of molar enthalpies of formation of CO and O_2 **[JEE 1997]**

SUBJECTIVE

Q.5 Diborane is a potential rocket fuel which undergoes combustion according to the reaction,

$$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

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

$$2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s)\,; \qquad \Delta H = -1273 \text{ kJ}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\,; \qquad \Delta H = -286 \text{ kJ}$$

$$H_2O(l) \longrightarrow H_2O(g)\,; \qquad \Delta H = 44 \text{ kJ}$$

$$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)\,; \qquad \Delta H = 36 \text{ kJ}$$

[JEE 2000]

Q.6 Estimate the average S–F bond energy in SF_6. The ΔH_f° values of SF_6 (g), S(g), and F (g) are – 1100 , 275 and 80 kJ/mol respectively. **[JEE 99, 5]**

Q.7 From the following data, calculate the enthalpy change for the combustion of cyclopropane at 298 k. The enthalpy of formation of CO_2 (g), H_2O (*l*) and propene (g) are – 393.5, – 285.8 & 20.42 kJ/mol respectively. The enthalpy of isomerisation of cyclopropane to propene is – 33.0 kJ/mol. **[JEE '98, 5]**

Q.8 Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1}, using the following data. Heat of vaporisation of liquid CH_3OH = 38 kJ/mol . Heat of formation of gaseous atoms from the elements in their standard states ; H , 218 KJ / mol ; C, 715 KJ / mol ; O, 249 KJ / mol.
Average Bond energies C – H, 415 KJ / mol ;
C – O , 356 KJ / mol ; O – H , 463 KJ / mol **[JEE '97, 5]**

Q.9 The Enthalpy change involved in the oxidation of glucose is -2880 KJ mol^{-1} . 25% of this energy is availbale for muscular work . If 100 kJ of muscular work is needed to walk one km. What is the maximum distance a person will be able to walk after eating 120 g of glucose. **[JEE '97, 2]**

ANSWER KEY

EXERCISE I

Q.1 −88kJ/mol Q.2 35.973 MJ Q.3 2.95 kcal Q.4 – 1410 cal

Q.5 – 18.7 kcal Q.6 −22.123 k cal Q.7 128.02 kJ Q.8 18.95 %

Q.9 −1560.1 kJmol^{-1} Q.10 11.2Kcal.

Q.11 **(i)** − 3201 kJ/mol **; (ii)** − 3199.75 kJ/mol Q.12 − 3273.77 kJ/mol Q.13 25.66 days

Q.14 ΔE= 27.91 KJ mol^{-1}, t= 514 sec.

Q.15 27.43 g O_2 Q.16 – 75.14 kJ/mole Q.17 **(i)** − 885 kJ/mol **(ii)** − 889.980 kJ/mol

Q.18 10.0 mol % CH_4 Q.19 –31.5 kJ/mole Q.20 –2808 kJ/mole Q.21 –726.6 kJ/mole

Q.22 213 kJ / mol Q.23 – 120.08 J/ml

Q.24 B.E. (C–C) = 82 kcal/mole; $\Delta_f H[C_2H_6(g)] = -20.1$ kcal/mole

Q.25 − 72 kJ mol^{-1}

Q.26 (i) 343.08 ; (ii) 891.2 Q.27 $E_{C\equiv C}$ = 160.86 k cal

Q.28 – 192.3 kJ mol^{-1} Q.29 277.5 kJ/mol Q.30 E.A. = – 352 kJ mol^{-1}

Q.31 − 618.7 kJ mol^{-1} Q.32 − 90.75 kcal mol^{-1}

Q.33 – 23.68 KJ/mol Q.34 – 669.7 kJ mol^{-1}

Q.35 H_f^o(benzene) = 49 kJ mol^{-1}, H_C^o(benzene) = − 3267.4 kJ mol^{-1}

PROFICIENCY TEST

Q.1 1. exothermic 2. endothermic 3. Heat of transition 4. $\sum \nu_p \Delta H^\circ_{(P)} - \sum \nu_r \Delta H^\circ_{(R)}$

5.+33 kJ mol^{-1} 6. –18 kcal mol^{-1} 7. –57.2 kJ 8.–110.5

9. –125.0 kJ 10. – 3RT

Q.2 1.False 2. False 3. False 4. True 5. True

6. True 7. False 8. True 9. True 10. False

EXERCISE II

Q.1 (a) 92.435 g (b) 93.72 g Q.2 404 K Q.3 mole % $O_2(g) = 37.5$, $H_2O(g) = 62.5$

Q.4 **(a) (i)** $a\Delta T$ **(ii)** $a\Delta T + \frac{b}{2}(T_2^2 - T_1^2)$ **(b)** 1000 cal, 1012 cal, 1.1858 % error

Q.5 0.9346 k cal g^{-1}, 3.94 kcal cm^{-3} Q.6 9.822 MJ/day evolved

Q.7 0.371 : 0.629 Q.8 – 666.81 k cal mol^{-1}, 15.55 Mcal

Q.9 $C-C = 97.81$ kJ, $C-H = 454.64$ kJ, $C{=}O = 804.26$ kJ, $C=C = 434.3$ kJ, $C\equiv C = 733.48$ kJ

Q.10 + 20.6 k cal Q.11 – 154.68 k cal

Q.12 292 kcal/mol Q.13 for Cl^- – 384 kJ mol^{-1}, for I^- – 307 kJ mol^{-1}

Q.14 advantage = 5396 kJ.mol^{-1} Q.15 –287.0 kJ mol^{-1} Q.16 – 718 kJ/mol

Q.17 Heat released= 13.4 kcal. per mol of initial mixture Q.18 22 kcal mol^{-1}

Q.19 (i) 13 times, (ii) 21.53 sec

EXERCISE III

Q.1 D Q.2 D Q.3 A Q.4 A Q.5 C Q.6 C Q.7 B

Q.8 A Q.9 B Q.10 C Q.11 A Q.12 D Q.13 D

Q.14 (i) B (ii) A (iii) A (iv) C Q.15 (i) A (ii) D

EXERCISE IV

Q.1 B Q.2 B Q.3 A Q.4 B Q.5 –2035kJ mol^{-1}

Q.6 309.6 kJ/mol Q.7 – 2091.32 kJ mol^{-1} Q.8 – 266 kJ mol^{-1}

Q.9 4.82 km