THERMOCHEMISTRY

PROBLEM 144 The specific heat capacity of water is $4.18\ \mathrm{J(°C)^{-1}\ g^{-1}}$ and that of copper is $0.38\ \mathrm{J(°C)^{-1}\ g^{-1}}$. Calculate the heat that must be supplied to a 500 g copper kettel containing 450 g of water to raise its temperature from 25°C to the boiling point of water. What percentage of heat is used to raise the temperature of the water?

PROBLEM 145 How much heat can be produced from a reaction mixture of 50 g of iron (III) oxide and 25 g of aluminium in the thermite reaction:

$$\mathrm{Fe_2O_3}(s) + 2\mathrm{Al}(s) \longrightarrow \mathrm{Al_2O_3}(s) + 2\mathrm{Fe}(s);\ \Delta H = -851.5\ \mathrm{kJ/mol}$$

PROBLEM 146 Calculate the reaction enthalpy for the hydrogenation of ethyne to ethane, given standard enthalpy of combustion of ethyne, ethane and hydrogen; – 1300, – 1560 and – 286 kJ/mol respectively.

PROBLEM 147 Calculate the reaction enthalpy for the synthesis of HCl(g) from the following data:

$$\begin{aligned}\mathrm{NH_3}(g) + \mathrm{HCl}(g) &\longrightarrow \mathrm{NH_4Cl}(s) \quad \Delta H = -176\ \mathrm{kJ}\\ \mathrm{N_2}(g) + 3\mathrm{H_2}(g) &\longrightarrow 2\mathrm{NH_3}(g) \quad \Delta H = -92.22\ \mathrm{kJ}\\ \mathrm{N_2}(g) + 4\mathrm{H_2}(g) + \mathrm{Cl_2}(g) &\longrightarrow 2\mathrm{NH_4Cl}(s)\ \ \Delta H = -628.86\ \mathrm{kJ}\end{aligned}$$

PROBLEM 148 An important reaction that occurs in the atmosphere is

$$\mathrm{NO_2}(g) \longrightarrow \mathrm{NO}(g) + \mathrm{O}(g)$$

Which is brought about by the sunlight. How mucy energy the sun to cause it must supply? Given, dissociation energy of oxygen = 498 kJ/mol and

$$\begin{aligned}\mathrm{NO}(g) + \mathrm{O_3}(g) &\longrightarrow \mathrm{NO_3}(g) + \mathrm{O_2}(g) \quad \Delta H = -200\ \mathrm{kJ}\\ 3\mathrm{O_2}(g) &\longrightarrow 2\mathrm{O_3}(g) \qquad\qquad\quad \Delta H = 285.4\ \mathrm{kJ}\end{aligned}$$

PROBLEM 149 Using reaction a, b and c determine the enthalpy change of this reaction:

$$\mathrm{CH_4}(g) + \frac{3}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g) + 2\mathrm{H_2O}(g)$$

(a) $\mathrm{CH_4}(g) + 2\mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g) + 2\mathrm{H_2O}(g) \qquad \Delta H° = -802\ \mathrm{kJ/mol}$

(b) $\mathrm{CH_4}(g) + \mathrm{CO_2}(g) \longrightarrow 2\mathrm{CO}(g) + 2\mathrm{H_2}(g) \qquad \Delta H° = +206\ \mathrm{kJ/mol}$

(c) $\mathrm{CH_4}(g) + \mathrm{H_2O}(g) \longrightarrow \mathrm{CO}(g) + 3\mathrm{H_2}(g) \qquad \Delta H° = +247\ \mathrm{kJ/mol}$

PROBLEM 150 The bond energy of $\mathrm{H_2}(g)$ is 436 kJ/mol and that of $\mathrm{N_2}(g)$ is 941.3 kJ/mol. Calculate the average bond energy of an N—H bond in ammonia if $\Delta H°_f$ of ammonia is – 46 kJ/mol.

Problem 151 The heat of formation of PCl_3 and PH_3 are 306 kJ/mol and 8 kJ/mol respectively, and the heats of atomization of phosphorus, chlorine and hydrogen are 314, 121 and 216.5 kJ/mol respectively. Calculate P-Cl and P-H bond energy.

Problem 152 At 25°C, the molar heat of formation of SO_2 and H_2O are – 296.81 and – 285.83 kJ respectively. Using the information from the following reactions,

$$2H_2S(g) + Fe(s) \longrightarrow FeS_2 + 2H_2(g) \qquad \Delta H^\circ = -137\ \text{kJ/mol}$$

$$H_2S(g) + \frac{3}{2}O_2(g) \longrightarrow H_2O(l) + SO_2(g) \qquad \Delta H^\circ = -562\ \text{kJ/mol}$$

Calculate heat of formation of $H_2S(g)$ and $FeS_2(s)$ at 25°C.

Problem 153 The standard molar enthalpy of formation of cyclohexane (l) and benzene (l) at 25°C are – 156 and + 49 kJ/mol respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25°C is – 119 kJ/mol. Use this data to estimate the magnitude of the resonance energy of benzene.

Problem 154 For the reaction *cis*-2-butene → *trans*-2-butene and *cis*-2-butene → 1-butene, $\Delta H = -950$ and $+1771$ cal/mol respectively. The heat of combustion of 1-butene is – 649.8 kcal/mol. Determine the heat of combustion of *trans*-2-butene. Also calculate the bond energy of C═C bond in *trans*-2-butene. Given *B.E* of C═O = 196, O—H = 110, O═O = 118, C—C = 80 and C—H = 98 kcal/mol respectively. $\Delta H_v(H_2O) = 11$ kcal / mol.

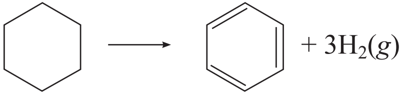
Problem 155 Using the data (all values are in kJ/mol at 25°C) given below:

(i) Enthalpy of polymerization of ethylene = – 72.
(ii) Enthalpy of formation of benzene(l) = 49
(iii) Enthalpy of vaporization of benzene(l) = 30
(iv) Resonance energy of benzene(l) = – 152
(v) Heat of formation of gaseous atoms from the elements in their standard states H = 218, C = 715.

Average bond energy of C—H = 415. Calculate the *B.E.* of C—C and C═C. [*A* : 331 and 590 kJ/mol]

Problem 156 Calculate energy of aromatization of cyclohexane according to the following reaction, both cyclohexane and benzene are in liquid state:

Given, bond energies: C—C = 348, C—H = 415, C═C = 600, H—H = 436 kJ/mol respectively, sublimation energy of C(gr) is 717 kJ/mol, resonance energy of $C_6H_6(l) = -152$ kJ/mol, ΔH_v° of benzene = 30.8 and of cyclohexane is 33 kJ/mol.



Problem 157 Enthalpy of polymerization of ethylene and acetylene into corresponding polymers are – 86 kJ/mol and – 148 kJ/mol respectively. Enthalpy of hydrogenation of ethylene is – 132 kJ/mol, determine C═C bond energy. *B.E.* of $H_2(g)$ is 436 kJ/mol and of C—H = 415 kJ/mol.

Problem 158 ΔH_{Comb} of methane and ethane are – 210 kcal/mol and – 368 kcal/mol respectively. Determine ΔH_{Comb} of decane.

Problem 159 Determine resonance energy of benzene [$C_6H_6(l)$] from the following information :

$$\Delta H^\circ_f \text{ of } C_6H_6(l) = +49\ \text{kJ};$$

$$\Delta H^\circ_f \text{ of } C_2H_2(g) = +75\ \text{kJ} \quad \Delta H^\circ_v \text{ of } C_6H_6(l) = +45\ \text{kJ}$$

B.E. C≡C = 930 kJ/mol; C═C = 615 kJ/mol; C—C = 348 kJ/mol

PROBLEM 160 Consider the following thermodynamic data:

Enthalpy of formation of $CaC_2(s) = -60$ kJ/mol;
Enthalpy of sublimation of $Ca(s) = 179$ kJ/mol;
Enthalpy of sublimation of $C(s) = 718$ kJ/mol;
First ionization energy of $Ca(g) = 590$ kJ/mol;
Second ionization energy of $Ca(g)$ 1143 kJ/mol;
Bond energy of $C_2(g) = 614$ kJ/mol;
First electron affinity of $C_2(g) = -315$ kJ/mol;
Second electron affinity of $C_2(g) = +410$ kJ/mol.
Draw a clear Born-Haber cycle and determine lattice energy of $CaC_2(s)$.

PROBLEM 161 Normal L.P.G. contains 90% propane and 10% methane by weight. If combustion of L.P.G. produces acetylene, $CO(g)$ and $H_2O(l)$, calculate the heat evolved by combustion of 100 g of L.P.G.

Given: enthalpy of combustion of methane $= -890$ kJ/mol, $C_3H_8 = -2220$ kJ/mol, $C_2H_2 = -1300$ kJ/mol and $CO(g) = -285$ kJ/mol.

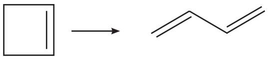
PROBLEM 162 A swimmer breaths 20 times in one minute when swimming and inhale 200 mL of air in one breath. Inhaled air contain 20% O_2 by volume and exhaled air contain 10% O_2 by volume. If all oxygen are consumed in combustion of glucose in the body and 25% of energy obtained from combustion is available for muscular work. Determine the maximum distance this swimmer can swim in one hour if 100 kJ energy is required for 1.0 km swimming. Standard molar enthalpy of combustion of glucose is – 2880 kJ/mol and body temperature is 37°C.

PROBLEM 163 Standard molar enthalpies of formation of $H_2O(l)$ and $H_2O_2(l)$ are – 285 and – 200 kJ/mol respectively and their molar enthalpies of vaporization are 41 and 60 kJ respectively. If enthalpy of atomization of $O_2(g)$ is 298 kJ/mol, determine bond energy of O—O bond.

PROBLEM 164 Determine resonance energy of 1,3-butadiene using the following information:

Enthalpy of combustion : 1,3-butadiene $= -2841$ kJ/mol, $C(gr) = -394$ kJ/mol, $H_2(g) = -285$ kJ/mol

Bond enthalpy : C—C = 348 kJ/mol, C═C = 615 kJ/mol. Also standard enthalpy of formation of cyclobutene = 130 kJ/mol,



PROBLEM 165 Standard molar enthalpy of formation of hydrazine liquid (N_2H_4) is 50 kJ/mol, $NH_3(g) = -46$ kJ/mol. Average N—H and H—H bond energies are 393 and 436 kJ/mol respectively. If enthalpy of vaporization of N_2H_4 is 18 kJ/mol, determine N—N bond energy in N_2H_4.

PROBLEM 166 Using following standard enthalpies:

$\Delta H^\circ_f\ HF(aq) = -329$ kJ/mol $\Delta H^\circ_f\ H_2O(l) = -285$ kJ/mol,
$\Delta H^\circ_f\ F^-(aq) = -320$ kJ/mol and

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l),\ \Delta H = -56$ kJ/mol.

Determine enthalpy of neutralization of HF against a strong base.

PROBLEM 167 From the following reactions and thermal information at 25°C:

$$2Fe(s) + \frac{3}{2}O_2 \longrightarrow Fe_2O_3(s) \qquad \Delta H^\circ = -821.4\ \text{kJ}$$

$$2FeO(s)+\frac{1}{2}O_2 \longrightarrow Fe_2O_3(s) \qquad \Delta H^\circ = -284\ \text{kJ/mol}$$

$$Fe(s)+2H^+(aq.) \longrightarrow Fe^{2+}(aq.)+H_2(g) \qquad \Delta H^\circ = -87.8\ \text{kJ}$$

$$\frac{1}{2}H_2(g) \longrightarrow H^+(aq.) \qquad \Delta H^\circ = 0$$

$$H_2(g)+\frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285\ \text{kJ}$$

Calculate ΔH° for the reaction :

$$FeO(s)+2H^+(aq) \longrightarrow H_2O(l)+Fe^{2+}(aq)$$

PROBLEM 168 A 150 cc portion of 0.4 N HCl is neutralized with excess of NH_4OH in a bomb calorimeter which results in a temperature rise of 2.36°C. If the heat capacity of calorimeter content is 1316.7 J/°C, calculate heat of neutralization of HCl Vs NH_4OH.

PROBLEM 169 Determine S—S bond energy;
Given ΔH°_f of $(C_2H_5)_2S(g) = -147$ kJ/mol,
ΔH°_f of $(C_2H_5)_2S_2(g) = -202$ kJ/mol and $\Delta H^\circ_{\text{Sublimation}}$ of $S(s) = 223$ kJ/mol.

PROBLEM 170 Given the following standard molar enthalpies:
ΔH°_f of $CH_3CN(g) = 88$ kJ/mol, ΔH°_f of $C_2H_6 = -84$ kJ/mol, $\Delta H^\circ_{\text{Sublimation}}$ of C(gr) = 717 kJ/mol, bond dissociation energy of $N_2(g)$ and $H_2(g)$ are 946 and 436 kJ/mol respectively, *B.E.* (C—H) = 410 kJ/mol. Determine C—C and C≡N bond energies.

PROBLEM 171 Determine standard state enthalpy of the following reaction:

$$CH_3COOH(l) \longrightarrow CH_4(g)+CO_2(g)$$

Given $\Delta H^\circ_{\text{Combustion}}$ $CH_4 = -860$ kJ/mol. Bond energies in kJ/mol. C—H = 410, C—C = 348, C═O = 728, C—O = 352, O—H = 463, O═O = 498. $\Delta H^\circ_{\text{Vaporization}}$ of acetic acid and water are 52 and 41 kJ/mol respectively.

PROBLEM 172 ΔH°_f of $C_2H_5OH(l) = -66$ kcal/mol, enthalpy of combustion of $CH_3OCH_3(g) = -348$ kcal/mol, ΔH°_f of water is – 68 kcal/mol and ΔH°_f of $CO_2(g) = -94$ kcal/mol. Determine enthalpy of the following isomerization reaction:

$$C_2H_5OH(l) \longrightarrow CH_3OCH_3(g)$$

PROBLEM 173 The standard enthalpies of formation of $BH_3(g)$ and $B_2H_6(g)$ are 100 kJ and 36 kJ per mol respectively and the enthalpies of formation of B(*g*) and H(*g*) are 563 kJ mol^{-1} and 218 kJ mol^{-1} respectively. Determine mean B—H bond enthalpies in each case. Assume terminal B—H bonds have same strengths, estimate enthalpies of the three centre B—H—B bonds in B_2H_6. Which bonds would you expect to be longer-terminal or bridged one?

PROBLEM 174 Enthalpy of combustion of $C_6H_6(l)$, $C_6H_{12}(l)$ (cyclohexane) $H_2(g)$ are –3268, –3920 and –289 kJ/mol respectively. If enthalpy of hydrogenation of cyclohexane is –120 kJ/mol, determine resonance energy of benzene(*l*).

PROBLEM 175 Assuming that mileage of an automobile gets is directly proportional to the heat of combustion of fuel, calculate how many times farther an automobile could be expected to go on one litre gasoline than on 1.0 litre ethanol.

Assume gasoline to be pure *n*-octane ($\rho = 0.7025\ \text{gmL}^{-1}$). Density of ethanol is $0.7893\ \text{gmL}^{-1}$. ΔH_f° of ethanol and octane are $-278\ \text{kJ mol}^{-1}$ and $-208.4\ \text{kJ mol}^{-1}$. ΔH_f° of $CO_2(g)$ and $H_2O(l)$ are $-394\ \text{kJ mol}^{-1}$ and $-286\ \text{kJ mol}^{-1}$ respectively.

PROBLEM 176 10 g of propane was burnt in air at 30°C and 1.0 atm pressure. Assume air to be 21.00% O_2, determine volume of air required for combustion process. If all the heat produced from combustion of 10 g of propane was transferred to 8.00 kg of water at 30°C, determine final temperature of water. C_P of water is $4.18\ \text{Jg}^{-1}\text{K}^{-1}$. Also, ΔH_f° of propane, CO_2 and H_2O are: $-104\ \text{kJ mol}^{-1}$, $-394\ \text{kJ mol}^{-1}$ and $-286\ \text{kJ mol}^{-1}$ respectively.

PROBLEM 177 With the following informations, determine standard state Gibb's free energy of formation of $N_2O_4(g)$.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO(g) \qquad \Delta G^\circ = 86.6\ \text{kJ} \qquad \ldots\text{(i)}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \longrightarrow NO_2(g) \qquad \Delta G^\circ = -34.82\ \text{kJ} \qquad \ldots\text{(ii)}$$

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta G^\circ = -5.77\ \text{kJ} \qquad \ldots\text{(iii)}$$

PROBLEM 178 Standard state enthalpy of formations of CO(g) and $CO_2(g)$ are $-111\ \text{kJ mol}^{-1}$ and $-394\ \text{kJ mol}^{-1}$ respectively. Bond dissociation energies of $O_2(g)$ and C═O(g) are $498\ \text{kJ mol}^{-1}$ and $743\ \text{kJ mol}^{-1}$ respectively. Supposing that there is a double bond in CO as two double bond in CO_2, determine the enthalpy of combustion of CO(g) and compare it with actual value. Also, explain the difference in calculate and observed value of enthalpies.

PROBLEM 179 One mole of $N_2(g)$ and 3.0 mole of $H_2(g)$ taken in a flask at 25°C and heated to 450°C. Now pressure was applied on the gaseous mixture which results in conversion of 0.1 mole of N_2 into NH_3. The gases are then cooled rapidly back to 25°C. Determine the net heat change in this process given the following bond enthalpies:

$N_2(g) = 944\ \text{kJ mol}^{-1}$; $H_2 = 436\ \text{kJ mol}^{-1}$ and average N—H bond energy $= 388\ \text{kJ mol}^{-1}$.

PROBLEM 180 A 150 cc portion of 0.4 NHCl is neutralized with an excess of NH_4OH in a Dewar vessel with a resulting rise in temperature of 2.36°C. If the heat capacity of Dewar and its contents after the reaction is 1316.7 J/°C, calculate heat of neutralization.

PROBLEM 181 At 25°C, the heat of solution of anhydrous $CuSO_4$ in a large volume of water is $-66.044\ \text{kJ mol}^{-1}$, while that of $CuSO_4\cdot 5H_2O$ is -11.495 kJ. Determine heat of reaction:

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4\cdot 5H_2O(s)$$

PROBLEM 182 The integral heats of solution at 25°C, for the various solid modification of $CaCl_2$ in the indicated quantities of water are shown below:

$$CaCl_2(s) + 400\ H_2O(l) \longrightarrow CaCl_2(400\ H_2O) \qquad \Delta H_1^\circ = -4.3\ \text{kJ} \qquad \ldots\text{(i)}$$

$$CaCl_2\cdot 2H_2O + 398\ H_2O(l) \longrightarrow CaCl_2(400\ H_2O) \qquad \Delta H_2^\circ = -41.925\ \text{kJ} \qquad \ldots\text{(ii)}$$

$$CaCl_2\cdot 4H_2O + 396\ H_2O \longrightarrow CaCl_2(400\ H_2O) \qquad \Delta H_3^\circ = -7.65\ \text{kJ} \qquad \ldots\text{(iii)}$$

$$CaCl_2\cdot 6H_2O + 394\ H_2O \longrightarrow CaCl_2(400\ H_2O) \qquad \Delta H_4^\circ = +19.06\ \text{kJ} \qquad \ldots\text{(iv)}$$

Determine enthalpies of the following hydration reactions:

(a) $CaCl_2(s) + 2H_2O \longrightarrow CaCl_2 \cdot 2H_2O$

(b) $CaCl_2 \cdot 2H_2O + 2H_2O \longrightarrow CaCl_2 \cdot 4H_2O$

(c) $CaCl_2(s) + 6H_2O \longrightarrow CaCl_2 \cdot 6H_2O$

PROBLEM 183 The enthalpy of following reactions at 25°C are:

(i) $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$ $\Delta H^\circ = -410.6$ kJ

(ii) $H_2(g) + S(s) + 2O_2(g) \longrightarrow H_2SO_4(l)$ $\Delta H^\circ = -810.54$ kJ

(iii) $2Na(s) + S(s) + 2O_2(g) \longrightarrow Na_2SO_4(s)$ $\Delta H^\circ = -1381.5$ kJ

(iv) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ $\Delta H^\circ = -92.21$ kJ

From the above thermal data, determine enthalpy of the following reaction:

$$2NaCl(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(s) + 2HCl(g).$$

PROBLEM 184 Given the following standard state enthalpies of reaction, calculate the standard molar heat of formation of AgCl.

(i) $Ag_2O(s) + 2HCl(g) \longrightarrow 2AgCl(g) + H_2O(l)$ $\Delta H^\circ = -324.4$ kJ

(ii) $2Ag(s) + \frac{1}{2}O_2(g) \longrightarrow Ag_2O(s)$ $\Delta H^\circ = -30.56$ kJ

(iii) $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$ $\Delta H^\circ = -92.21$ kJ

(iv) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H^\circ = -394$ kJ

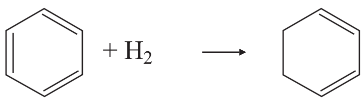
PROBLEM 185 Draw Lewis structures of hypothetical molecule $N_6(g)$ consisting of a six membered ring of nitrogen atom. If its standard enthalpy of formation is 1072 kJ mol^{-1}, predict the most likely structure. Given:

B.E. $N_2 = 944$ kJ mol^{-1}, N—N = 163 kJ mol^{-1} and N═N = 409 kJ mol^{-1}.

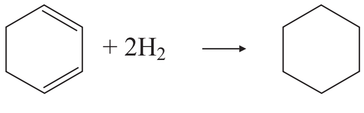
PROBLEM 186 A male burns 2000 kJ of energy while jogging for 1.0 hour. If the standard heat of combustion of a typical fat is 38 kJ g^{-1} and only 70% energy is available for muscular activity. What minimum hours would he need to jog if he wished to lose 0.5 g fat?

PROBLEM 187 Strong sunshine bombards the Earth with about 1 kJ m^{-2}s^{-1}. If a beaker containing ethanol, is placed in sunlight for 10 minutes, 3.24 g of liquid was vaporized. Assuming that all the heat is used for vaporization, not to increase temperature, determine surface area of beaker. Enthalpy of vaporization is 42.6 kJ mol^{-1}.

PROBLEM 188 From the following enthalpies values, determine resonance energy of $C_6H_6(l)$ "Benzene".

(i)


$\Delta H^\circ = -38$ kJ

(ii)


$\Delta H^\circ = -170$ kJ

Also, given the resonance energy of 1,3-cyclohexadiene is 70 kJ mol^{-1}.

Solutions

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144. Heat consumed by water $= 450 \times 4.18 \times 75 = 141.075$ kJ

Heat consumed by copper $= 500 \times 0.38 \times 75 = 14.25$ kJ

Total heat required = **155.325 kJ**

% heat used to raise temperature of $H_2O = \frac{141.075}{155.325} \times 100 = \mathbf{90.82}$

145.

$$\underset{50\text{ g}}{Fe_2O_3} + \underset{25\text{ g}}{2Al} \longrightarrow Al_2O_3 + 2Fe; \qquad \Delta H = -851.5\text{ kJ/mol}$$

Here, Fe_2O_3 is limiting reagent.

Hence,
$$Q = \frac{-851.5}{160} \times 50 = \mathbf{-266.1\ kJ}$$

146.

$$\Delta H = \Sigma\Delta H_{\text{comb}}\text{ (reactants)} - \Sigma\Delta H_{\text{comb}}\text{ (products)}$$

$$= -1300 - 2 \times 286 + 1560 = \mathbf{-312\ kJ}$$

147. Writing the reactions given as follows :

$$2NH_4Cl(s) \longrightarrow 2NH_3(g) + 2HCl(g) \qquad \Delta H = 352\text{ kJ}$$

$$2NH_3 \longrightarrow N_2 + 3H_2 \qquad \Delta H = 92.22\text{ kJ}$$

$$N_2 + 4H_2 + Cl_2 \longrightarrow 2NH_4Cl(s) \qquad \Delta H = -628.86\text{ kJ}$$

Now add the above equations :

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -184.64\text{ kJ}$$

$$\Rightarrow \qquad \mathbf{\Delta H_f^\circ HCl(g) = -92.32\ kJ/mol.}$$

148. Writing the given reactions as follows :

$$NO_2 + O_2 \longrightarrow NO + O_3 \qquad \Delta H = +200 \text{ kJ}$$

$$O_3 \longrightarrow \tfrac{3}{2}O_2 \qquad \Delta H = -142.7 \text{ kJ}$$

$$\tfrac{1}{2}O_2 \longrightarrow O(g) \qquad \Delta H = +249 \text{ kJ}$$

Adding above reactions gives :

$$NO_2 \longrightarrow NO + O(g) \qquad \mathbf{\Delta H = 306.3 \text{ kJ}}$$

149. Performing $a + b - 2c$ gives :

$$4H_2 + 2O_2 \longrightarrow 4H_2O \qquad \Delta H = -1090$$

$$\Rightarrow \quad H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -272.5 \text{ kJ} \quad \ldots\text{(i)}$$

Also $a + b + c$ gives :

$$3CH_4 + 2O_2 \longrightarrow H_2O + 3CO + 5H_2 \qquad \Delta H = -349 \text{ kJ}$$

and

$$5H_2 + \tfrac{5}{2}O_2 \longrightarrow 5H_2O \qquad \Delta H = -1362.5 \text{ kJ}$$

Adding the above two equations gives :

$$3CH_4 + \tfrac{9}{2}O_2 \longrightarrow 6H_2O + 3CO \qquad \Delta H = -1711.5 \text{ kJ}$$

$$\Rightarrow \quad CH_4 + \tfrac{3}{2}O_2 \longrightarrow 2H_2O + CO \qquad \mathbf{\Delta H = -570.5 \text{ kJ}}$$

150. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$

$$-92 = 941.3 + 3 \times 436 - 6 \text{ B.E.}(N-H) \Rightarrow \text{B.E. }(N—H) = \mathbf{390.25 \text{ kJ}}$$

151.

$$306 = 314 + 3 \times 121 - 3 \text{ B.E.}(P-Cl) \Rightarrow \text{B.E.}(P—Cl) = \mathbf{123.67 \text{ kJ}}$$

$$8 = 314 + 3 \times 216.5 - 3 \text{ B.E.}(P-H) \Rightarrow \text{B.E.}(P-H) = \mathbf{318.5 \text{ kJ}}$$

152. Multiply the 2nd reaction by 2 and subtract from 1st :

$$Fe(s) + 2H_2O(l) + 2SO_2(g) \longrightarrow FeS_2 + 2H_2 + 3O_2 \qquad \Delta H = 987$$

$$987 = \Delta H^\circ_f\ (FeS_2) + 2 \times 285.83 + 2 \times 296.81$$

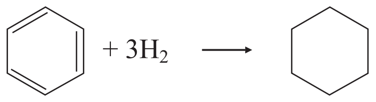
$$\Rightarrow \quad \Delta H^\circ_f\ FeS_2 = \mathbf{-178.28 \text{ kJ / mol}}$$

Also,

$$-137 = -178.28 - 2H^\circ_f\ (H_2S)$$

$$\Rightarrow \quad \Delta H^\circ_f\ (H_2S) = \mathbf{-20.64 \text{ kJ / mol}}$$

153.



$$; \quad \Delta H = -119 \times 3 = -357$$

$$-357 = -156 - \Delta H^\circ_f\ (\text{benzene}) \Rightarrow \Delta H_f{}^\circ(\text{benzene}) = 201$$

$$\text{R.E.} = \Delta H^\circ_f\ (\text{exp}) - \Delta H^\circ_f\ (\text{theoretical}) = -152 \text{ kJ/mol}$$

154.

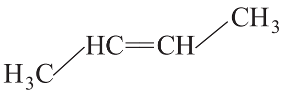
$$trans\text{-2-butene} \longrightarrow cis\text{-2-butene} \qquad \Delta H = +0.95 \text{ kcal}$$

$$cis\text{-2-butene} \longrightarrow \text{1-butene} \qquad \Delta H = +1.771 \text{ kcal}$$

$$\text{1-butene} + 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H = -649.8 \text{ kcal}$$

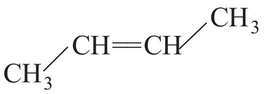
Adding above three equation gives:

$$\textit{trans}\text{-2-butene} + 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H = -647.079 \text{ kcal}$$



$$+\ 6O_2 \longrightarrow 4CO_2 + 4H_2O(l)$$

$$H_2O(l) \longrightarrow H_2O(v) \qquad \Delta H^\circ_V = +11 \text{ kcal}$$



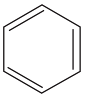
$$+6O_2 \longrightarrow 4CO_2 + 4H_2O(v) \qquad \Delta H = -636.079 \text{ kcal}$$

$$-636.079 = 8\times 98 + 2\times 80 + \text{B.E.}(C{=}C) + 6\times 118 - 8\times 196 - 8\times 110$$

$$\text{B.E.}(C{=}C) = \mathbf{159.921\ kcal.}$$

155. Let $\text{B.E.}(C{=}C) = x, \text{B.E.}(C{-}C) = y \Rightarrow x - 2y = -72$ ...(i)

$$6C(gr) + 3H_2(g) \longrightarrow$$



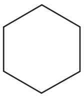
$$(g)$$

$$\Delta H = 79 = 6\times 715 + 6\times 218 - 3\,(x+y) - 6\times 415 - 152$$

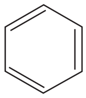
$\Rightarrow$ $x + y = 959$ ...(ii)

From, Eqs. (i) and (ii) $\boldsymbol{x = 615.33}$**,** $\boldsymbol{y = 343.67}$ **kJ.**

156.



$$(g) \longrightarrow$$



$$(g) + 3H_2(g)$$

$$\Delta H = 6\times 415 + 3\times 348 - 3\times 600 - 3\times 436 = 426 \text{ kJ}$$

$$C_6H_6(g) \longrightarrow C_6H_6(l) \qquad \Delta H = -30.8 \text{ kJ}$$

$$C_6H_{12}(l) \longrightarrow C_6H_{12}(g) \qquad \Delta H = 33.0 \text{ kJ}$$

$$C_6H_6(l)_{\text{Theo.}} \longrightarrow C_6H_6(l)_{\text{Exp.}} \qquad \Delta H = -152 \text{ kJ}$$

Adding the above equations yields :

$$\text{Cyclohexane}\ (l) \longrightarrow C_6H_6(l) + 3H_2 \qquad \Delta H = 276.2 \text{ kJ}$$

157. Let B.E. of $C{-}C = x, C{=}C = y$ and $C{\equiv}C = z$

$\Rightarrow$ $y - 2x = -86$ ...(i)

$z - x - y = -148$ ...(ii)

$y + 436 - x - 2\times 415 = -132$

$\Rightarrow$ $y - x = 262$ ...(iii)

From Eqs. (i) and (iii) $\boldsymbol{x = 348}$ **kJ,** $\boldsymbol{y = 610}$ **kJ,**

Substituting in Eq. (ii) gives, $z = \mathbf{810\ kJ}$

158. Heat evolved on combustion of one unit of $CH_2 = -158$

$$\Rightarrow \Delta H_{\text{comb}}\,(C_{10}H_{22}) = \Delta H_{\text{comb}}(CH_4) + 9\times \Delta H_{\text{comb}}\,(CH_2) = -210 - 9\times 158 = \mathbf{-1632\ kcal}$$

159. $3C_2H_2(g) \longrightarrow C_6H_6(g) \qquad \Delta H = 3\times 930 - 3(615+348) = -99\text{ kJ}$

$C_6H_6(g) \longrightarrow C_6H_6(l) \qquad \Delta H = 45\text{ kJ}$

$\Rightarrow \quad 3C_2H_2(g) \longrightarrow C_6H_6(l) \qquad \Delta H = -54\text{ kJ} = \Delta H^\circ_f\ C_6H_6(l) - 3\times 75$

$\Rightarrow \quad \Delta H^\circ_f\ C_6H_6\ (l) = 171\text{ kJ}$

$\Rightarrow \quad \text{R.E.} = 49 - 171 = \mathbf{-122\ kJ\ /\ mol}$

160.

$$\begin{tikzcd}
Ca^{2+}(g) & + & C_2^{2-}(g) \arrow[r, dash] & {} \arrow[ddd, "U_0"] \\
 & & C_2(g) \arrow[u, "\Delta H = 95"'] & \\
Ca(g) \arrow[uu, "\Delta H = 1733"] & & 2C(g) \arrow[u, "\Delta H = -614"'] & \\
Ca(s) \arrow[u, "\Delta H = 179"'] & + & 2\,C(gr) \arrow[u, "\Delta H = 1436"'] \arrow[r, "\Delta H = -60\text{ kJ}"] & CaC_2(s)
\end{tikzcd}$$

$$179 + 1733 + 1436 - 614 + 95 + U_0 = -60 \quad \Rightarrow \quad \mathbf{U_0 = -2889\ kJ}$$

161. Required combustion reactions are :

$$C_3H_8 + 2O_2 \longrightarrow C_2H_2 + CO + 3H_2O \qquad \Delta H = -2220 + 1300 + 285 = -635\text{ kJ}$$

$$CH_4 + \frac{3}{2}O_2 \longrightarrow CO + 2H_2O \qquad \Delta H = -890 + 285 = -605\text{ kJ}$$

For 100 g L.P.G., $Q = \dfrac{90}{44}(-635) + \dfrac{10}{16}(-605) = \mathbf{-1676.98\ kJ}$

162. Total O_2 consumed in 1.0 hour = $400 \times 60 = 24000$ mL = 24 L.

$$n(O_2) = \frac{1\times 24}{0.082\times 310} = 0.944; \quad C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$

Energy produced = 453.12 kJ, available energy = 113.28 kJ,
distance travelled = **1.1328 km.**

164. From combustion data : ΔH°_f (1, 3-butadiene) $= -4\times 394 - 4\times 285 + 2841 = +125$

From bond enthalpies : $2\times 348 - 615 = 81\text{ kJ} = \Delta H^\circ_f$ (1,3-butadiene)–130

$\Rightarrow \quad \Delta H^\circ_f$ (1,3-butadiene) = 211

$\text{R.E.} = 125 - 211 = \mathbf{-86\ kJ\ /\ mol}$

165. $2NH_3(g) \longrightarrow N_2H_4(l) + H_2(g) \qquad \Delta H = 142\text{ kJ}$

$N_2H_4(l) \longrightarrow N_2H_4(g) \qquad \Delta H = 18\text{ kJ}$

Adding the above two equations yields :

$$2NH_3(g) \longrightarrow N_2H_4(g) + H_2(g) \qquad \Delta H = 160$$

$\Rightarrow \quad 160 = 2\times 393 - \text{B.E.}(N{-}N) - 436$

$\Rightarrow \quad \text{B.E.}(N - N) = 190\text{ kJ/mol}$

166. $-56 = -285 - \Delta H^\circ_f\ (\mathrm{OH^-}) \Rightarrow \Delta H^\circ_f\ (\mathrm{OH^-}) = -229$

Also for $\qquad \mathrm{HF + OH^- \longrightarrow F^- + H_2O}$

$$\Delta H = -320 - 285 + 229 + 329 = \mathbf{-\ 47\ kJ}$$

167. Writing the given reactions as follows :

$$\mathrm{2FeO}(s) + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{Fe_2O_3}(s) \qquad \Delta H = -284\ \mathrm{kJ}$$

$$\mathrm{2Fe}(s) + \mathrm{4H^+} \longrightarrow \mathrm{2Fe^{2+} + 2H_2} \qquad \Delta H = -175.6$$

$$\mathrm{Fe_2O_3}(s) \longrightarrow \mathrm{2Fe}(s) + \tfrac{3}{2}\mathrm{O_2} \qquad \Delta H = 821.4$$

$$\mathrm{2H_2 + O_2 \longrightarrow 2H_2O} \qquad \Delta H = -570$$

Adding the above equations yields :

$$\mathrm{2FeO}(s) + \mathrm{4H^+} \longrightarrow \mathrm{2Fe^{2+} + 2H_2O} \qquad \Delta H = -208.2$$

$$\Rightarrow \qquad \mathrm{FeO}(s) + \mathrm{2H^+} \longrightarrow \mathrm{Fe^{2+} + 2H_2O} \qquad \boldsymbol{\Delta H = -\ 104.1\ \mathrm{kJ}}$$

168. $Q = 1316.7 \times 2.36 = 3107.412\ \mathrm{J}$

$$\Delta H_{\mathrm{Neut}} = -\frac{3107.412}{60} \times 1000\ \mathrm{J} = \mathbf{-\ 51.79\ kJ\ /\ mol}$$

169. For $\qquad (\mathrm{C_2H_5})_2\mathrm{S}(g) + \mathrm{S}(g) \longrightarrow (\mathrm{C_2H_5})_2\mathrm{S_2}(g) \qquad \Delta H = -202 + 147 - 223 = -278\ \mathrm{kJ}$

$$\mathrm{B.E.\,(S-S)} = \mathbf{+\ 278\ kJ\ /\ mol}$$

170. Let B.E. $\mathrm{C-C} = x,\ \mathrm{C \equiv N} = y$ and $\mathrm{C-H} = z$

$$\Rightarrow \qquad \mathrm{2C(gr) + 2H_2} + \tfrac{1}{2}\mathrm{N_2} \longrightarrow \mathrm{CH_3CN}(g)$$

$$\Delta H = 88 = 2 \times 717 + 2 \times 436 + \tfrac{1}{2} \times 946 - (x + y + 3z)$$

or $\qquad x + y + 3z = 2691\ \mathrm{kJ} \qquad \ldots\text{(i)}$

$$\mathrm{2C(gr) + 3H_2 \longrightarrow C_2H_6} \quad \Delta H = -84 = 2 \times 717 + 3 \times 436 - (x + 6z)$$

or $\qquad x + 6z = 2826\ \mathrm{kJ}$

$\Rightarrow \qquad x = 2826 - 6 \times 410 = \mathbf{366\ kJ\ /\ mol}$

$$y = 2691 - 366 - 3 \times 410 = \mathbf{1095\ kJ/mol}$$

171. $\mathrm{CH_3COOH}(g) + \mathrm{2O_2} \longrightarrow \mathrm{2CO_2} + \mathrm{2H_2O}(g)$

$$\Delta H = 3 \times 410 + 348 + 728 + 352 + 463 + 2 \times 498 - (4 \times 728 + 4 \times 463) = -647\ \mathrm{kJ}$$

$\Rightarrow \mathrm{CH_3COOH}(l) + \mathrm{2O_2} \longrightarrow \mathrm{2CO_2} + \mathrm{2H_2O}(l) \qquad \Delta H = -647 + 52 - 82 = -677\ \mathrm{kJ}$

$\Rightarrow \qquad \Delta H_{\mathrm{reaction}} = -677 + 860 = \mathbf{183\ kJ}$

172. For $\mathrm{CH_3OCH_3}(g)$: $-348 = -2 \times 94 - 3 \times 68 - \Delta H^\circ_f \Rightarrow \Delta H^\circ_f = -44\ \mathrm{kcal/mol}$

$\Rightarrow$ For $\qquad \mathrm{C_2H_5OH}(l) \longrightarrow \mathrm{CH_3OCH_3}(g) \qquad \Delta H = -44 + 66 = \mathbf{+\ 22\ kcal\ /\ mol}$

173.

$$\mathrm{BH_3}(g) \longrightarrow \mathrm{B}(g) + \mathrm{3H}(g) \qquad \Delta H_1^\circ$$

$$\mathrm{B_2H_6}(g) \longrightarrow \mathrm{2B}(g) + \mathrm{6H}(g) \qquad \Delta H_2^\circ$$

$$\Delta H_1^\circ = \Delta H_f^\circ\ \text{B}(g) + 3\Delta H_f^\circ\ \text{H}(g) - \Delta H_f^\circ\ \text{BH}_3(g) = 563 + 3 \times 218 - 100 = 1117\ \text{kJ}$$

$$\Delta H_2^\circ = 2\Delta H_f^\circ\ \text{B}(g) + 6\Delta H_f^\circ\ \text{H}(g) - \Delta H_f^\circ\ \text{B}_2\text{H}_6(g) = 2 \times 563 + 6 \times 218 - 36 = 2398\ \text{kJ}$$

⇒ mean B—H bond energy in BH_3

$$= \frac{\Delta H_1^\circ}{3} = 372.33\ \text{kJ/mol}$$

mean B—H bond energy in B_2H_6

$$= \frac{\Delta H_2^\circ}{6} = 399.67\ \text{kJ/mol}$$

Also, B_2H_6 has four terminal B—H sigma covalent bond and two 3-centered 2-electron bond.

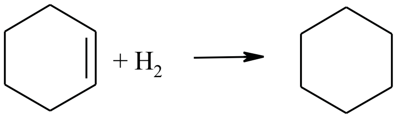
$$\Rightarrow \qquad 2398 = 4 \times 372.33 + 2x \quad \Rightarrow \quad x = 454.34\ \text{kJ/mol.}$$

Therefore, average B—H bond energy of the bridged B—H—B bond

$$= \frac{454.34}{2} = 227.17\ \text{kJ/mol}$$

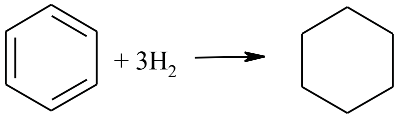
Also, $\text{BE} \propto \frac{1}{\text{Bond length}}$; Hence, terminal B—H bonds are shorter than bridged B—H bond.

174. Given:



$\Delta H^\circ = -120$ kJ

⇒



$\Delta H^\circ = -120 \times 3 = -360$ kJ

Using combustion data: $\Delta H^\circ = \Delta H^\circ_{\text{combustion}}$ [Benzene + $3H_2$ – Cyclohexane] = – 215 kJ

Resonance energy = ΔH° (from bond energy) – ΔH° (combustion) = – 145 kJ

175. moles of ethanol in 1.0 L $= \frac{7893}{46} = 171.587$

moles of octane in 1.0 L $= \frac{7025}{114} = 61.62$

Also: $$C_2H_5OH + \tfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$\Delta H = -(2 \times 394 + 3 \times 286) + 278 = -1368\ \text{kJ mol}^{-1}$$

$$C_8H_{18} + \tfrac{25}{2}O_2 \longrightarrow 8CO_2 + 9H_2O$$

$$\Delta H = -(8 \times 394 + 9 \times 286) + 208.4 = -5067.6\ \text{kJ mol}^{-1}$$

⇒ Heat produced from 171.587 mol ethanol $= -171.587 \times 1368 = -234.731 \times 10^3$ kJ

Heat produced from 61.62 mol octane $= -61.62 \times 5067.6 = -312.26 \times 10^3$ kJ

$$\Rightarrow \qquad \text{factor} = \frac{312.26 \times 10^3}{234.731 \times 10^3} = 1.33$$

i.e., automobile running on gasoline will gas 1.33 times farther than the automobile running in ethanol, on combustion of 1.0 litre of fuel.

176. The combustion reaction is:

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$$

i.e., for $\frac{10}{44}$ mol of propane, $\frac{50}{44}$ mole of O_2 would be required.

Therefore, $\quad \text{vol of } O_2 \text{ required} = \frac{50}{44} \times 0.082 \times 303 = 28.234 \text{ L.}$

$$\Rightarrow \qquad \text{Vol. of air required} = \frac{100}{21} \times 28.234 = 134.45 \text{ L.}$$

Heat produced in the combustion reaction $= \frac{10}{44} \times (-394 \times 3 - 4 \times 286 + 104) = -2222 \text{ kJ}$

Since, $\quad Q = ms\Delta T$

$$\Rightarrow \qquad 2222 \times 10^3 = 8000 \times 4.18\, \Delta T$$

$$\Rightarrow \qquad \Delta T = 66.45 \quad \Rightarrow \quad T_2 = 96.45^\circ\text{C.}$$

177. Multiplying both Eqs (i) and (ii) by 2 and finally adding them yields

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta G^\circ = 103.56 \text{ kJ}$$

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta G^\circ = -5.77 \text{ kJ} \qquad \ldots\text{(iii)}$$

Adding: $\quad N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g) \qquad \Delta G^\circ = \mathbf{97.79 \text{ kJ}}$

178. The combustion reaction is:

$$CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$$

$$\Delta H^\circ \text{ (from bond enthalpies)} = 743 + \frac{1}{2} \times 498 - 2 \times 743 = -494 \text{ kJ}$$

$$\Delta H^\circ \text{ (from formation enthalpies)} = -394 + 111 = -283 \text{ kJ}$$

The above values of enthalpy indicates that in carbonmonoxide, the bond between carbon and oxygen is stronger than the same in CO_2.

179. The formation reaction is:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

For reaction of 0.1 mol N_2, 0.3 mol H_2 is also reacted and 0.2 mol NH_3 formed.

$$\Rightarrow \qquad \text{BE (entered)} = 0.1 \times 944 + 0.3 \times 436 = 130.8 \text{ kJ}$$

Energy released on formation of NH_3

$$= 0.2 \times (3 \times 388) = 232.8$$

$\Rightarrow$ Energy transferred to surrounding $= 232.8 - 130.8 = \mathbf{102 \text{ kJ}}$.

180. Heat produced on neutralization $=1316.7\times 2.36=3107.412$ J

moles of HCl neutralized $=0.15\times 0.4=0.06.$

$$\Rightarrow \qquad \Delta H_{(\text{neutralization})}=\frac{3107.412}{0.06}=51.8 \text{ kJ/mol of HCl.}$$

181. Given:

$$\mathrm{CuSO_4}(s)+(aq)\longrightarrow \mathrm{CuSO_4}(aq) \qquad \Delta H^\circ=-66.04 \text{ kJ}$$

$$\mathrm{CuSO_4\cdot 5H_2O}(s)+(aq)\longrightarrow \mathrm{CuSO_4}(aq) \qquad \Delta H^\circ=-11.495 \text{ kJ}$$

Subtracting the second equation from first equation yields:

$$\mathrm{CuSO_4}(s)+\mathrm{5H_2O}\longrightarrow \mathrm{CuSO_4\cdot 5H_2O}(s) \qquad \Delta H^\circ=-54.545 \text{ J}$$

182. (a) For the desired equation: (i)–(ii)

$$\mathrm{CaCl_2}+\mathrm{2H_2O}\longrightarrow \mathrm{CaCl_2\cdot 2H_2O} \qquad \Delta H^\circ=37.628$$

183. Carrying out the following operations and rewriting the equations:
(i) ×2 and reversing (ii) reversing (iii) as such (iv) ×2

$$\mathrm{2NaCl}(s)\longrightarrow \mathrm{2Na}(s)+\mathrm{Cl_2}(g) \qquad \Delta H^\circ=821.2 \text{ kJ}$$

$$\mathrm{H_2SO_4}(l)\longrightarrow \mathrm{H_2}(g)+\mathrm{S}(s)+\mathrm{2O_2}(g) \qquad \Delta H^\circ=810.54 \text{ kJ}$$

$$\mathrm{2Na}(s)+\mathrm{S}(s)+\mathrm{2O_2}(g)\longrightarrow \mathrm{Na_2SO_4}(s) \qquad \Delta H^\circ=-1381.5 \text{ kJ}$$

$$\mathrm{H_2}(g)+\mathrm{Cl_2}(g)\longrightarrow \mathrm{2HCl}(g) \qquad \Delta H^\circ=-184.42 \text{ kJ}$$

Adding the above equations gives the desired equation:

$$\mathrm{2NaCl}(s)+\mathrm{H_2SO_4}(l)\longrightarrow \mathrm{Na_2SO_4}(s)+\mathrm{2HCl}(g) \qquad \Delta H^\circ=65.82 \text{ kJ}$$

184. The required reaction is:

$$\mathrm{Ag}(s)+\tfrac{1}{2}\mathrm{Cl_2}(g)\longrightarrow \mathrm{AgCl}(s) \qquad \Delta H^\circ=?$$

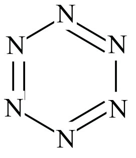
(i) + (ii) + 2 × (iii) – (iv) gives

$$\mathrm{2Ag}+\mathrm{Cl_2}\longrightarrow \mathrm{2AgCl}$$

$$\Delta H^\circ=-324.4-30.56-2\times 92.21+394=-145.38 \text{ kJ}$$

$$\Rightarrow \qquad \mathrm{Ag}(s)+\tfrac{1}{2}\mathrm{Cl_2}(g)\longrightarrow \mathrm{AgCl}(s) \qquad \Delta H^\circ=\mathbf{-72.69\ kJ}.$$

185. Adding the theory of covalent bonding, the structures of $\mathrm{N_6}(g)$ can be predicted as: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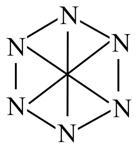
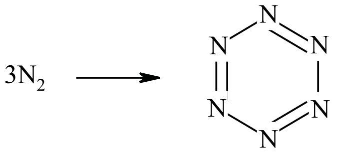

II

Here I has delocalized π-electrons as well as aromaticity.


$\Delta H^\circ = 1072 \text{ kJ mol}^{-1}$

$$\Delta H^\circ \text{ (from bond enthalpies)} = 3 \times 944 - 3\,(163 + 409) = 1116 \text{ kJ mol}^{-1}.$$

The observed ΔH_f° is 44 kJ mol^{-1} less than that calculated from bond enthalpies indicating presence of resonance. Hence, I structure is most probable.

186. If all energy available for muscular activity is consumed in jogging, energy available from 0.5 kg fat for jogging $= 500 \times 38 \times 0.7 = 13300$ kJ

$$\text{minimum jogging hour} = \frac{13300}{2000} = 6.65 \text{ hr.}$$

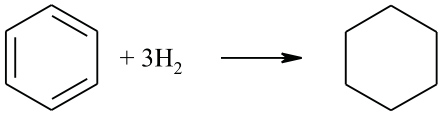
187.

$$\text{Total energy absorbed } = 42.6 \times \frac{3.24}{46} = 3 \text{ kJ}$$

$$\text{Energy absorbed in one second} = \frac{3}{60 \times 10} = \frac{1}{200} \text{ kJ}$$

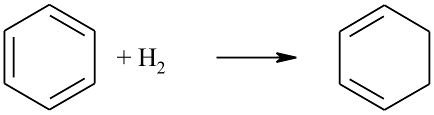
$$\text{Surface area of beaker} = \frac{1}{200} \text{ m}^2 = \mathbf{50\ cm^2}.$$

188. Adding the two given thermochemical equations (i) and (ii) yields



$\Delta H^\circ = -208$ kJ ...(a)

Had there been no resonance energy in cyclohexadiene, the enthalpy of (ii) reaction would have been $-170 - 70 = -240$ kJ. This indicates that independent hydrogenation of one double bond gives off on an average 120 kJ of heat. Therefore, theoretically.



$\Delta H^\circ_{\text{Theoretical}} = -120$ kJ

$$\Rightarrow \qquad \Delta H^\circ_{\text{exp}} - \Delta H^\circ_{\text{Theo}} = 82 = \text{R.E. (benzene)} - \text{R.E. (cyclohexadiene)}$$

$$\Rightarrow \qquad \mathbf{R.\,E.\ (benzene) = 152\ kJ\ mol^{-1}}.$$