Date: 16/10/2021

Q1. The volume of a gas is reduced to half from its original volume. Predict the change in specific heat.

Q2. Comment on the validity of the following statement:

"Thermodynamically, an exotheric reaction is sometimes not spontaneous."

Q3. When 36 g of liquid water evaporates at 373 K ($\Delta_{vap}H = 40.63$ kJ mol^{-1}), find out the change in entropy.

Q4. (a) For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, what are the signs of ΔH and ΔS?

(b) What would be the heat capacity for 1 mole of water?

[Specific heat of water is 4.18 J g^{-1} K^{-1}]

Q5. (a) Although heat is path function but heat absorbed by the system under certain specific conditions is independent of path. What are those conditions? Explain.

(b) Heat capacity (C_p) is an extensive property but specific heat (C) is an intensive property. What will be the relation between C_p and C for 1 mole of water?

Q6. (a) Enthalpy of combustion of carbon to CO_2 is –393.5 kJ mol^{-1}. Calculate the heat released upon formation of 35.2 g of CO_2 from carbon and dioxygen gas.

(b) The enthalpy of a vaporisation of CCl_4 is 30.5 kJ mol^{-1}. Calculate the heat required for the vaporisation of 284 g of CCl_4 at constant pressure. (Molar mass of CCl_4 = 154 g mol^{-1})

Q7. The enthalpy of neutralisation for the first proton of $H_2S\,(aq)$ is – 33.7 kJ mol^{-1}. Calculate the first acid ionisation energy for $H_2S\,(aq)$

Q8. Two solutions initially at 25.08°C were mixed in an insulated bottle. One contains 400 mL of 0.2 M weak monoprotic acidic solution. The other contains 100 mL of 0.8 M NaOH. After mixing temperature rise to 26.25°C. How much heat is evolved in the neutralisation of 1 mole of acid? Density of the heat capacity of the calorimeter.

Q9. The first and second ionisation enthalpies (in kJ mol^{-1}) and the electron gain enthalpy (in kJ mol^{-1}) of a few elemtnets are given below:

Element	$\Delta_i H_1$	$\Delta_i H_2$	$\Delta_i H_3$
I	520	7300	– 60
II	419	3051	– 48
III	1681	3374	– 328
IV	1008	1846	– 295
V	2372	5251	+ 48
VI	738	1451	– 40

Which of the above element is likely to be

(a) the least reactive metal

(b) the most reactive metal

(c) the most reactive non-metal

(d) the least reactive non-metal

(e) the metal which can form a stable binary halide of the formula MX_2 (X = halogen)?

(f) the metal which can form predominantly stable covalent halide of the formula MX (X = halogen)?

Q10. (a) The first ionisation enthalpy ($\Delta_f H$) values of the third period elements, Na, Mg and Si are respectively 496, 737 and 786 kJ mol^{-1}. Predict the $\Delta_i H_i$ value for Al.

(b) Predict the formula of the stable binary compound that would be formed by the combination of element with atomic number 71 and fluorine.

(c) Electron affinity is positive when O^- changes into O^{2-}. Explain.

Q11. Using the data (all values are in kilocalories per mole at 25°C) given below, calculate the bond energy of C — C and C — H bonds.

(a) $\Delta H°$ combustion (ethane) = – 372.0

(b) $\Delta H°$ combustion (propane) = – 530.0

(c) $\Delta H°$ for C (graphite) $\longrightarrow$ C (g) = 172.0

(d) Bond energy of H — H = 104.0

(e) $\Delta_f H°$ of H_2O (l) = – 68.0

(f) $\Delta H°$ for CO_2 (g) = – 94.0

Q12. Calculate the enthalpy change on freezing of 1 mol of water at 10.0°C to ice at – 10.0°C, Δ_{fus} H = 6.03 kJ mol^{-1} at 0°C.

$$C_p [H_2O(l)] = 75.3 \text{ J mol}^{-1} \text{ K}^{-1}; \quad C_p [H_2O(s)] = 36.8 \text{ J mol}^{-1} \text{ K}^{-1}$$

Q13. The combustion of one mole of benzene produces CO_2 (g), H_2O (l) and 3267 kJ of heat. Calculate the standard enthalpy of formation, $\Delta_f H$ of benzene. (Standard enthalpies of formation of CO_2 (g) and H_2O (l) are – 393.5 kJ mo^{-1} and – 285.83 kJ mol^{-1}, respectively)

Q14. (a) A sample of sucrose $C_{12}H_{22}O_{11}$ weighing 0.1265 g, is burnt in a calorimeter. After the reaction is over, it is found that to produce an equal temperature increment, electrically 2082.3 joule must be used.

(i) Calculate heat of combustion of sucrose.

(ii) If ΔH_t^0 of CO_2 (g) and H_2O (l) are – 393.51 kJ mol^{-1} and – 285.83 kJ mol^{-1} respectively, calculate the heat of formation of sucrose.

(b) The enthalpy change (ΔH) for the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$ is – 92.38 kJ at 298 K. Calculate the internal energy change (ΔU) at 298 K.

Q15. (a) Calculate the standard free energy change for the formation of methane at 298 K. The value of $\Delta_f H^\circ$ for $CH_4\,(g)$ is – 74.81 kJ mol^{-1} and *S* values for C (graphite), $H_2\,(g)$ and $CH_4\,(g)$ are 5.7, 130.7 and 186.3 JK^{-1} mol^{-1} respectively.

(b) The value of enthalpy change (ΔH) for the reaction,

$$C_2H_5OH\,(l) + 3O_2\,(g) \longrightarrow 2CO_2\,(g) + 3H_2O\,(l) \text{ at } 27°C, \text{ is } -1366.5 \text{ kJ mol}^{-1}.$$

What will be the value of internal energy change for the above reaction at this temperature?

(c) The enthalpy changes for the following processes are listed below:

$$Cl_2\,(g) \longrightarrow 2Cl\,(g), \quad 242.3 \text{ kJ mol}^{-1}$$
$$I_2\,(g) \longrightarrow 2I\,(g), \quad 151.0 \text{ kJ mol}^{-1}$$
$$ICl\,(g) \longrightarrow I\,(g) + Cl\,(g), \quad 211.3 \text{ kJ mol}^{-1}$$
$$I_2\,(g) \longrightarrow I_2\,(g), \quad 62.76 \text{ kJ mol}^{-1}$$

Given that the standard states for iodine and chlorine are $I_2\,(s)$ and $Cl_2\,(g)$ respectively. What will be the standard enthalpy for the formation of ICl (g)?

Q16. (a) On the basis of the following reactions,

$$H_2O\,(l) \longrightarrow H^+\,(aq) + OH^-\,(aq); \quad \Delta H = 57.32 \text{ kJ}$$

$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l); \quad \Delta H = -286.2 \text{ kJ} \quad [\Delta_f G^\circ H^+\,(aq) = 0]$$

What is the value of enthalpy for the formation of OH^- ion at 25°C?

(b) An athelete takes 20 breathes per minute at room temperature. The air inhaled in each breathe is 200 mL which contains 20% oxygen by volume, while exhaled air contains 10% oxyen by volume. Assuming that all the oxygen consumed is used for converting glucose into $CO_2\,(g)$ and $H_2O\,(l)$. How much glucose will be burnt in the body in one hour?

Q17. (a) The heat of atomisation of $PH_3\,(g)$ is 228 kcal mol^{-1} and that of $P_2H_4\,(g)$ is 335 kcal mol^{-1}. What is the energy of P — P bond?

(b) The free energy change for the following reactions are given below:

$$C_2H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2CO_2\,(g) + H_2O\,(l), \quad \Delta G^\circ = -1234 \text{ kJ}$$
$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g), \quad \Delta G^\circ = -394 \text{ kJ}$$
$$H_2\,(g) + \frac{1}{2}O_2\,(g) \longrightarrow H_2O\,(l), \quad \Delta G^\circ = -237 \text{ kJ}$$

What is the standard free energy change for the following reaction?

$$H_2\,(g) + 2C\,(s) \longrightarrow C_2H_2\,(g)$$

(c) What is the value of $\log_{10} K$ for a reaction, $A \rightleftharpoons B$?

Given, $\Delta_r H^\circ_{(298\,K)} = -54.07 \text{ kJ mol}^{-1}$

$\Delta_r S^\circ_{(298\,K)} = 10 \text{ kJ K}^{-1} \text{ mol}^{-1}$

and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$.

Q18. (a) The enthalpy ($\Delta H°$) for the following reaction at 25°C are given below:

$$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow OH(g), \quad \Delta H° = -10.06 \text{ kcal}$$

$$H_2(g) \longrightarrow 2H(g), \quad \Delta H° = 104.18 \text{ kcal}$$

$$O_2(g) \longrightarrow 2O(g), \quad \Delta H° = 118.32 \text{ kcal}$$

Calculate the O — H bond energy in the hydroxyl radical.

(b) Using the data (all values are in k cal mol^{-1} at 25°C) given below, calculate the bond energy of C — C and C — H bonds in ethane and propane.

$$C(s) \longrightarrow C(g), \quad \Delta H = 172$$

$$H_2(s) \longrightarrow 2H(g), \quad \Delta H = 104$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta H = -68.0$$

$$C(s) \longrightarrow CO_2(g), \quad \Delta H = 94.0$$

Heat of combustion of $C_2H_6 = -321.0$

Heat of combustion of $C_3H_8 = -530.0$

Q19. (a) A gaseous mixture of 3.67 L of ethylene and methane on complete combustion at 25°C produces 6.11 L of CO_2. Find out the amount of heat evolved on burning 1 L. of the gaseous mixture. The heat of combustion of ethylene and methane are -1423 kJ mol^{-1} and -891 kJ mol^{-1} respectively, at 25°C.

(b) How much energy is released when 6 mol of octane are burnt in air? Given, $\Delta H_f°$ for $CO_2(g)$, $H_2O(g)$ and $C_8H_{18}(l)$ respectively are -490, -240 and $+160$ J mol^{-1}.

Q20. (a) Consider the following data:

H — H bond energy = 431.37 kJ mol^{-1}

C ═ C bond energy = 606.10 kJ mol^{-1}

C — C bond energy = 336.49 kJ mol^{-1}

C — H bond energy = 410.50 kJ mol^{-1}

Calculate the enthalpy for the following reaction:

(b) If 16 g of oxygen gas expands isothermally and reversibly at 300 K from 10 dm^3 to 100 dm^3, calculate the work done (in J).

(c) Calculate the heat of the reaction when steam is passed over coke as

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

The enthalpy of formation of carbon monoxide and steam are -110.5 and -243 kJ respectively.

Q21. (a) Calculate the enthalpy change for the process,

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

and calculate the bond enthalpy of C — Cl in $CCl_4(g)$.

$$\Delta_{vap}H^\circ(CCl_4) = 30.5 \text{ kJ mol}^{-1}$$
$$\Delta_f H^\circ(CCl_4) = -135.5 \text{ kJ mol}^{-1}$$
$$\Delta_a H^\circ(C) = 715.0 \text{ kJ mol}^{-1}$$
$$\Delta_a H^\circ(Cl_2) = 242 \text{ kJ mol}^{-1}$$

where, $\Delta_a H^\circ$ is enthalpy of atomisation.

(b) For the reaction at 298 K, $2A + B \longrightarrow C$

$$\Delta H = 400 \text{ kJ mol}^{-1} \quad \text{and} \quad \Delta S = 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

At what temperature, will the reaction become spontaneous? Considering ΔH and ΔS to be constant over the temperature range.

Q22. (a) If BE of Cl — Cl bond, H — H bond and H — Cl bond are 243, 435 and 431 kJ mol^{-1}, then calculate ΔH_f° of HCl.

(b) When 1 mol of ice melts at 0°C and a constant pressure of 1 atm, 1440 cal of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 L and 0.0180 L, respectively. Calculate ΔH and ΔE.

Q23. (a) Water is brought to boil under a pressure of 1.0 atm. When an electric current of 0.5 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporised. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K)

(b) Gaseous ozone is bubbled through a water-ice mixture at 0°C. As the $O_3(g)$ decomposes to form $O_2(g)$, the enthalpy of reaction is absorbed by the resulting ice. Given that the heat of fusion of ice is 6.0095 kJ mol^{-1}, determine the mass of ice that melts for each gram of $O_3(g)$ that decomposes.

$$2O_3(g) \longrightarrow 3O_2(g); \quad \Delta H^\circ = -285.4 \text{ kJ}$$

Q24. (a) A sample of 4.5 g of methane occupies 12.7 L at 310 K.

(i) Calculate the work done when the gas expands isothermally against a constant external pressure of 200 torr until its volume has increased by 3.3 L.

(ii) Calculate the work that would be done, if the same expansion occurred reversibly.

(b) For the reaction, C (graphite) + $\frac{1}{2}O_2(g) \longrightarrow CO(g)$, at 298 K and 1 atm,

$$\Delta H = -26.4 \text{ kcal.}$$

What is ΔE, if the molar volume of graphite is 0.0053 L? ($R = 0.002$ kcal mol^{-1} K^{-1})

Q25. 5 mol of an ideal gas at 293 K is expanded isothermally from an initial pressure 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa.

(a) Calculate q, W, ΔU and ΔH.

(b) Calculate the corresponding values of q, W, ΔU and ΔH, if this process is carried out reversibly.

Q26. (a) Find out the work done when 11.2 g of iron dissolves in hydrochloric acid in

(i) an open beaker at 25°C (ii) a closed vessel. [Atomic mass of Fe = 56 u]

(b) On the basis of the following thermochemical data [$\Delta_f G^\circ$ (H^+, *aq*) = 0]

$$H_2O\,(l) \longrightarrow H^+\,(aq) + OH^-\,(aq); \quad \Delta H = 57.32 \text{ kJ}]$$

$$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l); \quad \Delta H = 286.20 \text{ kJ}$$

calculate the value of enthalpy of formation of OH^- ion at 25°C.

Q27. (a) (i) Calculate the value of $\Delta_f H^\circ$ for the following reaction:

$$2H_2S\,(g) + 3O_2\,(g) \longrightarrow 2H_2O\,(l) + 2SO_2$$

Given,

$$H_2\,(g) + S\,(s) \longrightarrow H_2S\,(g); \quad \Delta_f H^\circ\,(H_2S) = -20.1 \text{ kJ mol}^{-1}$$

$$H_2\,(g) + {}^*\,O_2\,(g) \longrightarrow H_2O\,(l); \quad \Delta_f H^\circ\,(H_2O) = -285.8 \text{ kJ mol}^{-1}$$

$$S\,(s) + O_2\,(g) \longrightarrow SO_2\,(g); \quad \Delta_f H^\circ\,(SO_2) = -296.9 \text{ kJ mol}^{-1}$$

(ii) The bond dissociation energies of H_2, Cl_2, and HCl are 104, 58 and 103 kcal mol^{-1}, respectively. Calculate the enthalpy of formation of HCl.

(b) For the reaction, $2x(g) + Y(g) \longrightarrow 2X(g)$; $\Delta U^\circ = -10.5$ kJ and $\Delta S^\circ = -44\ JK^{-1}$.

Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously. (Given, $R = 8.314\ JK^{-1}\ mol^{-1}$, $T = 298$ K)

Q28. (a) Calculate the standard enthalpy of formation of $CH_3OH\,(l)$ from the following data:

$$CH_3OH\,(l) + \frac{3}{2}\,O_2\,(g) \longrightarrow CO_2\,(g) + H_2O\,(l); \quad \Delta_r H^\circ = -726 \text{ kJ mol}^{-1}$$

$$C\,(\text{graphite}) + O_2\,(g) \longrightarrow CO_2\,(g); \quad \Delta_c H^\circ = -393 \text{ kJ mol}^{-1}$$

$$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l); \quad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1}$$

(b) Calculate the work done when 1 mole of an ideal gas is compressed reversibly from 1 bar to 4 bar at a constant temperature of 300 K.

Q29. (a) A gas expands isothermally against a constant external pressures of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. It absorbs 800 J of thermal energy from its surroundings. Calculate the change in internal energy (ΔE).

(b) ΔH for the reaction, C (graphite) + $2H_2\,(g) \longrightarrow CH_4\,(g)$ at 298 K and 1 atm is – 17900 cal. Calculate ΔE for the above conversion.

(c) ΔG for a reaction at 300 K is – 16 k cal and ΔH is – 10 k cal. What is the entropy of the reaction?

Q30. (a) Calculate reasonance energy of N_2O from the following data:

$$\Delta H_f^\circ\,(N_2O) = 82 \text{ kJ mol}^{-1};$$

BE of $N \equiv N$ = 946 kJ mol^{-1}	Be of $N \equiv N$ = 418 kJ mol^{-1}
BE of $O = O$ = 498 kJ mol^{-1}	Be of $N = O$ = 607 kJ mol^{-1}

(b) The enthalpy change for the reaction of 50 mL of ethlene with 50 mL of H_2 at 1.5 atm pressure is $\Delta H = -0.31$ kJ. What is the value of ΔE?

Q31. (a) Assume $\Delta H°$ and $\Delta S°$ to be independent of temperature, at what temperature, will the reaction given below become spontaneous?

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

	$N_2(g)$	$O_2(g)$	$2NO(g)$
$S°$ (in KJ^{-1} mol^{-1})	191.4	204.9	210.5

$$\Delta H° = 180.8 \ JK^{-1} \ mol^{-1}.$$

(b) For the reactions,

I. $2Na(s) + \frac{1}{2}O_2(g) \longrightarrow Na_2O, \quad \Delta H = x$

II. $Na_2O + H_2O \longrightarrow 2NaOH, \quad \Delta H = -56$ kcal

III. $2Na + 2H_2O \longrightarrow 2NaOH + H_2, \quad \Delta H = -88$ kcal

IV. $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O, \quad \Delta H = -68$ kcal

From these values, calculate the value of x.

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S1. Specific heat is an intensive property depending only on the nature of the gas. SO, on reducing the volume half form original volume, specific heat will remain constant.

S2. As we know that, $\Delta G = \Delta H - T\Delta S$.

The given statement is true because for exothermic reaction, ΔH is negative If $T\Delta S$ is positive (*i.e.*, entropy factor opposes the process) and $T\Delta S > \Delta H$ in magnitude, ΔG will be positive and process will not be spontaneous.

S3. Given, $\Delta_{vap} H = 40.63 \text{ kJ mol}^{-1}$

$T_b = 373 \text{ K}$

$$\therefore \quad \Delta_{vap} S = \frac{\Delta_{vap} H}{T_b} = \frac{40.63 \times 1000 \text{ J mol}^{-1}}{373 \text{ K}}$$

$$= 109 \text{ JK}^{-1} \text{ mol}^{-1}$$

$\therefore$ Entropy change for evaporation of 36 g of water

$$= \frac{109}{18} \times 36 = 218 \text{ JK}^{-1}.$$

S4. (a) The given reaction represents the formation of bonds. Hence, energy is released, *i.e.*, ΔH is – ve. Further, 2 moles of atoms have greater randomness than 1 mole of molecules. Hence, randomness decreases, *i.e.*, ΔS is – ve.

(b) For water, heat capacity, $C_p = 18 \times \text{specific heat}$

$\therefore \quad = 18 \times c$

But specific heat of water, $(c) = 4.18 \text{ Jg}^{-1} \text{ K}^{-1}$

$\therefore$ Heat capacity, $C_p = 18 \;\; 4.18 \text{ JK}^{-1} \text{ mol}^{-1}$

$= 75.3 \text{ JK}^{-1} \text{ mol}^{-1}$

S5. (a) The two conditions under which heat becomes independent of path are:

(i) When volume remains constant. (ii) When pressure remains constant.

A constant volume By first law of thermodynamics,

$$\Delta U = q + W$$

or $q = \Delta U - W$ $[\because \; W = -p\Delta V]$

Hence, $q = \Delta U + p\Delta V$

But as volume remains constant,

$$\Delta V = 0$$

$\therefore \quad q_V = \Delta U$

Since, ΔU is a state function. Hence, q_V also is a state function.

At constant pressure: $q_p = \Delta U + p\Delta V$

But $\Delta U + p\Delta V = \Delta H$

$\therefore$ $qp = \Delta H$

As ΔH is a state function, therefore, q_p is a state function.

(b) For water, molar heat capacity,

$$C_p = 18 \times \text{Specific heat} \qquad [\because \text{ Molecular weight of } H_2O = 18]$$
$$= 18 \times C$$

Specific heat, C for water $= 4.18\ \text{Jg}^{-1}\ \text{K}^{-1}$

$$= 18 \times 4.18\ \text{JK}^{-1}\ \text{mol}^{-1} = 75.3\ \text{JK}^{-1}\ \text{mol}^{-1}.$$

S6. (a) $$C(s) + O_2(g) \longrightarrow CO_2(g); \qquad \Delta H = -393.5\ \text{kJ mol}^{-1}$$

$$1\ \text{mol of } CO_2 = 44\ \text{g}$$

$\because$ Heat released when 44 g of CO_2 is formed = 393.5 kJ

$\therefore$ Heat released when 35.2 g of CO_2 is formed = $\dfrac{393.5}{44} \times 35.2\ \text{kJ} = 314.8\ \text{kJ}$

(b) $$1\ \text{mol of } CCl_4 = 154\ \text{g}$$

Heat required for vaporising 154 g CCl_4 = 30.5 kJ

$\therefore$ Heat required for vaporising 284 g CCl_4 = $\dfrac{30.5 \times 284}{154}\ \text{kJ} = 46.25\ \text{kJ}$

S7. Thinking process:

I. $$H_2S(aq) + OH^-(aq) \longrightarrow HS^-(aq) + H_2O(l)$$

II. $$H_2S(aq) \longrightarrow HS^-(aq) + H^+(aq)$$

ΔH° of reaction I has been given, ΔH° of reaction II is to be calculate. For this, we have to consider ΔH° of reaction of strong and (H^+) and strong base (OH^-) which is constant.

Reaction involving neutralisation of first proton of $H_2S(aq)$ is

I. $$H_2S(aq) + OH^-(aq) \longrightarrow HS^-(aq) + H_2O(l); \qquad \Delta H^\circ = -33.7\ \text{kJ mol}^{-1}$$

Reaction involving neutralistion of strong acid and strong base is

II. $$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l); \qquad \Delta H^\circ = -57.3\ \text{kJ mol}^{-1}$$

Thus, reaction of ionisation

$$H_2S(aq) \longrightarrow H^+(aq) + HS^-(aq)$$

is obtained by subtract (II) from (I)

$\therefore$ $$\Delta H^\circ = -33.7 - (-57.3) = 23.6\ \text{kJ mol}^{-1}.$$

S8. Moles of monobasic acid in 400 mL = $\frac{0.2}{1000} \times 400 = 0.08$ mol

Moles of NaOH in 100 mL = $\frac{0.800}{1000} \times 100 = 0.08$ mol

Thus, acid is completely neutralised

$$m = 500 \text{ mL solution} = 500\text{ g}, \quad (d = 1 \text{ g cm}^{-3})$$

$$\Delta t = \text{rise in temperature} = 26.25 - 25.08 = 1.17$$

$$s = \text{specific heat} = 4.2 \text{ J g}^{-1}\text{ K}^{-1}$$

$\therefore$ $$\text{Heat} = ms\Delta t = 500 \times 4.2 \times 1.17 = 2.457 \times 10^3 \text{ J}$$

Heat evolved in the neutralisation of one mole acid

$$= \frac{2.457 \times 10^3}{0.08} \text{ J} = \frac{2.457}{0.08} \text{ kJ} = 30.71 \text{ kJ mol}^{-1}.$$

S9. (a) The element V, has the highest first ionisation enthalpy ($\Delta_i H_1$) and positive electron gain enthalpy ($\Delta e_g H$). Hence, it is the least reactive metal.

(b) The element II, which has the least first ionisation enthalpy ($\Delta_i H_1$) and a low negative electron gain enthalpy ($\Delta e_g H$). Hence, it is the most reactive metal.

(c) The element III which has high first ionisation enthalpy ($\Delta_i H_1$) and a very high negative electron gain enthalpy ($\Delta e_g H$). Hence, it is the most reactive non-metal.

(d) The element IV has a high negative electron gain enthalpy ($\Delta e_g H$) but not, so high first ioisation enthalpy ($\Delta_i H_1$). Therefore, it is the least reactive non-metal.

(e) The element VI has low first ionisation enthalpy but higher than that of alkali metal. Therefore, it seems that the element is an alkaline earth metal, hence will form binary halide of the formula MX_2.

(f) The element I has low first ionisation enthalpy ($\Delta_i H_1$) but a very high second ionisatin enthalpy ($\Delta_i H_2$), therefore it must be an alkali metal. As the metal forms a predominantly stable covalent halide of the formula *MX*. therefore alkali metal must be least reactive, *i.e.*, Li.

S10. (a) Arranging the elements, Na, Mg, Al and Si into different groups in order of their increasing atomic numbers,

	1	2	13	14
Group	Na	Mg	Al	Si

In case of Al, a 3*p*-electron is to be lost while in Mg, a 2*s*-electron to be lost. Therefore, $\Delta_i H_i$ of Al will be lower than that of Mg due to the effective shielding of the 3*p*-electron from the nucleus by 3*s*-electrons. Therefore, $\Delta_i H_i$ for Al will be lower than that of 737 kJ/mol.

(b) Element with atomic numbe 71 is a lanthanoid called lutetium (Lu). Its most common valency is 3. Fluorine has a valency equal to 1. Thus, formula of the compound would be LuF_3.

(c) When O^- changes into O^{2-}, the change is endothermic. The reson is that O^- repels the incoming electron due to similar charge, it needs energy to accept the electron. Hence, electron affinity is positive.

S11. We are given,

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O; \quad \Delta H^\circ = -372.0 \text{ kcal/mol} \qquad \text{... (i)}$$

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O; \quad \Delta H^\circ = -530.0 \text{ kcal/mol} \qquad \text{... (ii)}$$

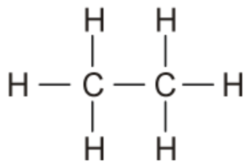
$$C(s) \longrightarrow C(g); \quad \Delta H^\circ = 172.0 \text{ kcal/mol} \qquad \text{... (iii)}$$

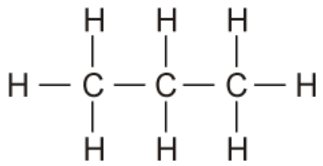
$$H_2(g) \longrightarrow 2H(g); \quad \Delta H^\circ = 104.0 \text{ kcal/mol} \qquad \text{... (iv)}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g); \quad \Delta H^\circ = -68.0 \text{ kcal/mol} \qquad \text{... (v)}$$

$$C(g) + O_2(g) \longrightarrow CO_2(g); \quad \Delta H^\circ = -94.0 \text{ kcal/mol} \qquad \text{... (vi)}$$

Suppose the bond energy of C — C bond = x kcal mol^{-1} and that of C — H bond = y kcal mol^{-1}.

Then for $C_2H_6(g)$, *i.e.*,  $\longrightarrow 2C(g) + 6H; \quad \Delta H = x + 6y$ ... (vii)

and for $C_3H_8(g)$, *i.e.*,  $\longrightarrow 3C(g) + 8H(g); \quad \Delta H = 2x + 8y$ ... (viii)

To get Eq. (vii), operate Eq. (i) + 2 × Eg. (iii) + 3 × Eq. (iv) – 3 × Eq. (v) – 2 × Eq. (vi)

It gives ΔH = 676 kcal/mol

To get Eq. (viii), operate Eq. (ii) + 3 × Eg. (iii) + 4 × Eq. (iv) – 4 × Eq. (v) – 3 × Eq. (vi)

It gives ΔH = 956 kcal/mol

Thus, $\quad x + 6y = 676, \quad 3x + 8y = 956$

On solving these equations, we get $x = 82$, $y = 99$

Hence, C — C bond energy = 82 kcal mol^{-1} and C — H bond energy = 99 kcal mol^{-1}.

S12. Conversion of 1 mol of water at 10°C to ice at – 10°C involves the following steps

1 mol H_2O (l) at 10°C $\longrightarrow$ 1 mol H_2O (l) at 0°C; $\quad \Delta H_1 = C_p[H_2O(l)] \times \Delta T$

1 mol H_2O (l) at 0°C $\longrightarrow$ 1 mol H_2O (s) (*i.e.*, ice) at 0°C; $\quad \Delta H_2 = \Delta H_{freezing}$

1 mol H_2O (s) at 0°C $\longrightarrow$ 1 mol H_2O (s) at – 10°C; $\quad \Delta H_3 = C_p[H_2O(s)] \times \Delta T$

ΔT = 10 K and we know that according to Hess's law, total enthalpy change, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$, so first calculate ΔH_1, ΔH_2, ΔH_3 and then ΔH.

Enthalpy change for the conversion of 1 mol liquid water at 10°C into 1 mol liquid ater at 0°C,

$$\Delta H_1 = C_p[H_2O(l)] \times \Delta T = 75.3 \text{ J mol}^{-1}\text{ K}^{-1} \ (0 - 10) \text{ K}$$

$$= -753 \text{ J mol}^{-1} = -0.753 \text{ kJ mol}^{-1}$$

Enthalpy of fusion, $\Delta H_2 = \Delta H_{freezing} = -\Delta H_{fus} = -6.03 \text{ kJ mol}^{-1}$

Enthalpy change for the conversion of 1 mol of ice at 0°C to 1 mol of ice at – 10°C,

$$\Delta H_3 = C_p[H_2O(s)] \times \Delta T = 36.8 \text{ J mol}^{-1} \text{ K}^{-1} \times (-10 \text{ K})$$
$$= -368 \text{ J mol}^{-1} = -0.368 \text{ kJ mol}^{-1}$$

$$\Delta H_{total} = -(0.753 + 6.03 + 0.368) \text{ kJ mol}^{-1} = -7.151 \text{ kJ mol}^{-1}$$

Note: As heat is evolved in the process of cooling (freezing), so each step will have a negative sign with ΔH.

S13. The formation reaction of benzene is given by

$$6C\,(\text{graphite}) + 3H_2(g) \longrightarrow C_6H_6(l),\ \Delta_f H^\circ = ? \quad \text{... (i)}$$

The enthalpy of combustion of 1 mol of benzene is

$$C_6H_6(l) + \frac{15}{2}O_2 \longrightarrow 6CO_2(g) + 3H_2O(l),\ \Delta_f H^\circ = -3267 \text{ kJ mol}^{-1} \quad \text{... (ii)}$$

The enthalpy of formation of 1 mol of $CO_2(g)$

$$C\,(\text{graphite}) + O_2(g) \longrightarrow CO_2(g),\ \Delta_f H^\circ = -393.5 \text{ kJ mol}^{-1} \quad \text{... (iii)}$$

The enthalpy of formation of 1 mol of $H_2O(l)$

$$H_2(g) + \frac{1}{2}O_2 \longrightarrow H_2O(l),\ \Delta_f H^\circ = -285.83 \text{ kJ mol}^{-1} \quad \text{... (iv)}$$

On multiplying Eq. (iii) by 6 and Eq. (iv) by 3, we get

$$6C\,(\text{graphite}) + 6O_2(g) \longrightarrow 6CO_2(g),\ \Delta_f H^\circ = -2361 \text{ kJ mol}^{-1} \quad \text{... (v)}$$

$$3H_2(g) + \frac{3}{2}O_2 \longrightarrow 3H_2O(l),\ \Delta_f H^\circ = -857.49 \text{ kJ mol}^{-1} \quad \text{... (vi)}$$

On adding Eq. (v) and Eq. (vi), we get

$$6C\,(\text{graphite}) + 3H_2(g) + \frac{15}{2}O_2 \longrightarrow 6CO_2(g) + 3H_2O(l),\ \Delta_f H^\circ = -3218.49 \text{ kJ mol}^{-1} \quad \text{... (vii)}$$

Eq. (ii) is reversed, we get

$$6CO_2(g) + 3H_2O(l) \longrightarrow C_6H_6(l) + \frac{15}{2}O_2,\ \Delta_f H^\circ = 3267 \text{ kJ mol}^{-1} \quad \text{... (viii)}$$

Adding Eq. (vii) and Eq. (viii), we get

$$6C\,(\text{graphite}) + 3H_2(g) \longrightarrow C_6H_6(l),\ \Delta_f H^\circ = 48.51 \text{ kJ mol}^{-1}$$

S14. (a) (i) Heat of combustion is the enthalpy decrease when one mole of the substance is completely burnt. Enthalpy decreases when 0.1265 g of sucrose burnt

$$= 2082.3 \text{ J} = 2.0823 \text{ kJ}$$

Hence, for one mole sucrose (342.0 g mol^{-1}), enthalpy decrease

$$= \frac{2.0823}{0.1265} \times 342 = 5629.62 \text{ kJ mol}^{-1}$$

Hence, heat of combustion of sucrose

$$= -5629.62 \text{ kJ mol}^{-1}.$$

(ii) $C_{12}H_{22}O_{11}(s) + 12O_2(g) \longrightarrow 12CO_2(g) + 11H_2O(l)$

$$\Delta H = -5692.62\, T\Delta S^\circ$$

$$= [12\Delta H_t^0(CO_2) + 11\Delta H_t^0(H_2O)] - [\Delta H_t^0(C_{12}H_{22}O_{11}) + 12\Delta H_t^0(O_2)]$$

$$-5692.62 = -12 \times 393.51 - 11 \times 285.83 - \Delta H_t^0(C_{12}H_{22}O_{11})$$

$$\therefore \Delta H_t^0(C_{12}H_{22}O_{11}) = -2236.63 \text{ kJ mol}^{-1}$$

(b) $\Delta H = \Delta E - p\Delta V$

or $\Delta H = \Delta E + \Delta nRT$

or $\Delta E = \Delta H - \Delta nRT$

$$= -92.38 - (-2)(8.34) \times 10^{-3} \times (298)$$

$$\Delta E = -92.38 + 4.955 = -87.425 \text{ kJ}.$$

S15. (a) For the reaction: $C + 2H_2 \longrightarrow CH_4$

Given, $\Delta H^\circ = -74.81 \text{ kJ mol}^{-1}$

ΔS° can be calculated as

$$\Delta S^\circ = S^\circ_{(product)} - S^\circ_{(reactant)}$$

$$= S^\circ CH_4(g) - [S^\circ C_{(graphite)} + 2S^\circ_m H_2(g)]$$

$$= [186.3 - (5.7 + 2\ \ 130.7)] \text{ JK}^{-1} \text{ mol}^{-1}$$

$$= -80.8\ \ 10-3 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Since, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$= -74.81 - [(298) \text{ K} \times (-80.8 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})]$$

$$= [-74.81 + 24.07] \text{ kJ mol}^{-1}$$

$$= -50.74 \text{ kJ mol}^{-1}.$$

(b) Relation between ΔH and ΔE can be written as

$$\Delta H = \Delta E + \Delta n_g RT$$

where, Δn_g = moles of gaseous products – moles of gaseous reactants

$$= 2 - 3 = 1$$

$\Rightarrow$ $-1366.5 = \Delta E - 1 \times 8.314 \times 10^{-3} \times 300$

$\therefore$ $\Delta E = -1364.0 \text{ kJ mol}^{-1}.$

(c) $\frac{1}{2} I_2(s) + \frac{1}{2} Cl_2(g) \longrightarrow ICl(g)$

$$\Delta H^\circ = \left[\frac{1}{2}\Delta H_{\text{sublimation}}(I_2) + \frac{1}{2}\Delta H_{\text{diss}}(Cl_2) + \frac{1}{2}\Delta H_{\text{diss}}(I_2)\right] - \Delta H_{Cl}$$

$$= \left(\frac{1}{2}\times 62.76 + \frac{1}{2}\times 242.3 + \frac{1}{2}\times 151.0\right) \text{kJ mol}^{-1} - 211.3 \text{ kJ mol}^{-1}$$

$$= 228.03 - 211.3 = 16.73 \text{ kJ mol}^{-1}$$

S16. (a) Consider the heat of formation of H_2O

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \quad \Delta H = -286.2 \text{ kJ}$$

$$\Delta H_r = \Delta H_f(H_2O, l) - [\Delta H_f(H_2, g) - \frac{1}{2}\Delta H_f(O_2, g)]$$

$$-286.2 = \Delta H_f(H_2O, l) - 0 - 0$$

$$\Delta H_f(H_2O, l) = -286.2 \text{ kJ}$$

Now, consider the ionisation of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq); \quad \Delta H = 57.32 \text{ kJ}$$

$$\Delta H_r = \Delta H_f(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f(H_2O, l)$$

$$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.2) = -228.88 \text{ kJ}$$

Thus, $\Delta H_f(OH^-, aq) = 57.32 - 286.2 = -228.88$ kJ

(b) O_2 inhaled in one breathe = $\frac{200\times 20}{100} = 20$ mL

O_2 exhaled in one breathe = $\frac{200\times 10}{100} = 20$ mL

$\therefore$ O_2 used in one breathe = 40 – 20 = 20 mL

$\therefore$ Volume of O_2 used in 1200 breathe taken in one hour at 27°C = 1200 × 20 = 24000 mL.

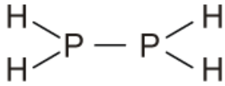
$\because$ 6 × 22400 mL O_2 is used during the burning of 180 g glucose.

$\therefore$ 24000 mL O_2 is used during the burning of $\left(\frac{180\times 24000}{6\times 22400}\right)$ g glucose = 32.14 g.

S17. (a) **Step I:** P — H bond energy from bond dissociation energy of $PH_3(g)$ containing 3P — H bonds

$$= \frac{228}{3} = 76 \text{ k cal mol}^{-1}$$

Step II: The structure of P_2H_4 is



i.e., it contains four P — H bonds and one P — P bond, so P — P bond energy can be calculated as $4 \times$ (P — H) (P — P) bond dissociation energy of P_2H_4.

$\therefore$ P — P bond energy = 335 – 4 (76) = 31 kcal mol^{-1}.

(b)

$$C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l), \quad \Delta G^\circ = -1234 \text{ kJ} \quad \text{... (i)}$$

$$C(s) + O_2(g) \longrightarrow CO_2(g), \quad \Delta G^\circ = -394 \text{ kJ} \quad \text{... (ii)}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta G^\circ = -237 \text{ kJ} \quad \text{... (iii)}$$

On multiply Eq. (ii) by 2 and adding Eq. (iii), then subtract Eq. (i), we get

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g)$$

$$\Delta G^\circ = 2(-394) + (-237) - (-1234)$$

$$\Delta G^\circ = 209 \text{ kJ.}$$

(c) Given reaction is $A \rightleftharpoons B$

We know that, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = -2.303\, RT \log K$$

On equating Eqs. (i) and (ii), we get

$$\log K = \frac{\Delta H^\circ - T\Delta S^\circ}{-2.303\, RT}$$

Here, $\Delta H^\circ = -54.07 \text{ kJ mol}^{-1}$

$$T = 298 \text{ K}$$

$$\Delta S = 10 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

and $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

Putting these values in Eq. (iii), we get

$$= \frac{-54.07 \times 10^3 - 298 \times 10}{-2.303 \times 8.314 \times 298} = 10\,.$$

S18. (a) $\Delta H^\circ = \sum BE_{(reactants)} - \sum BE_{(products)}$

$\Rightarrow$ $-10.06 = \frac{1}{2}(104.18) + \frac{1}{2}(118.32) - BE(O — H)$

BE (O — H) = 121.31 kcal

(b) Let x kcal be the C — C bond energy and y kcal be the C — H bond energy per mole.

$\Rightarrow$ $2C(g) + 3H_2(g) \longrightarrow C_2H_6(g)$

$$\Delta H^\circ = -2 \times 94 - 3 \times 68 + 372 = -20 \text{ kcal}$$

$\Rightarrow$ $$-20 \text{ kcal} = 2 \times 172 + 3 \times 104 - \text{BE}(C_2H_6)$$

$$\text{BE}(C_2H_6) = 676 \text{ kcal}$$

Similarly, $$3C(g) + 4H_2(g) \longrightarrow C_3H_8(g)$$

$$\Delta H^\circ = -3 \times 94 - 4 \times 68 + 530 = -24 \text{ kcal}$$

$$-24 \text{ kcal} = 3 \times 172 + 4 \times 104 - \text{BE}(C_3H_8)$$

$\Rightarrow$ $$\text{BE}(C_3H_8) = 956 \text{ kcal}$$

Also, $$\text{BE}(C_2H_6) = 676 \text{ kcal} = x + 6y \qquad \text{... (i)}$$

$$\text{BE}(C_3H_8) = 956 \text{ kcal} = 2x + 8y \qquad \text{... (ii)}$$

On solving Eqs. (i) and (ii), we have

$$y = 99 \text{ kcal (C — H) BE}$$

$$x = 82 \text{ kcal (C — C) BE}$$

S19. (a) Let the mixture contains x litre of CH_4 and $(3.67 - x)$ litre of ethylene

$$\underset{x}{CH_4} + 2O_2 \longrightarrow \underset{x}{CO_2} + 2H_2O$$

$$\underset{3.67 - x}{C_2H_4} + 3O_2 \longrightarrow \underset{2(3.67 - x)}{2CO_2} + 2H_2O$$

Given, $$x + 2(3.67 - x) = 6.11 \text{ L}$$

$\Rightarrow$ $$x = 1.23 \text{ L}$$

$$\text{Volume of ethylene} = 2.44 \text{ L}$$

$$\text{Total moles of gas in 1 L} = \frac{pV}{RT} = \frac{1 \times 1}{0.082 \times 298} = 0.04$$

Also, CH_4 and ethylene are in 1 : 2 volume (or mole) ratio. Moles of $CH_4 = \frac{0.04}{3}$ and moles of ethylene = $\frac{2 \times 0.04}{3}$

$\Rightarrow$ Heat evolved due to methane = $\frac{0.04}{3} \times 891 = 11.88$ kJ

Heat evolved due to ethylene = $\frac{2 \times 0.04}{3} \times 1423 = 37.94$ kJ

$\Rightarrow$ Total heat evolved on combustion of 1.0 L gaseous mixture at 25°C

$$= 11.88 + 37.94 = 49.83 \text{ kJ.}$$

(b) $$C + O_2 \longrightarrow CO_2; \quad \Delta H = -490 \text{ J} \qquad \text{... (i)}$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \quad \Delta H = -240 \text{ J} \qquad \text{... (ii)}$$

$$8C + 9H_2 \longrightarrow C_8H_{18}; \quad \Delta H = +160 \text{ J} \qquad \text{... (iii)}$$

Reverse Eq. (iii) and then 8 × Eq. (i) + 9 × Eq. (ii) – Eq (iii), we have

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

$$\Delta H = 8 \ (-490) + 9 \ (-240 + 160$$
$$= -3920 - 2160 + 160 \text{ J mol}^{-1}$$
$$= -5920 \text{ K mol}^{-1}.$$

S20. (a) $\Delta H_{\text{reaction}} = \sum BE_{(\text{reactants})} - \sum BE_{(\text{products})}$

$$= [BE4 (C — H) + BE (C = C) + BE (H — H)] - [BE6 (C — H) + BE (C — C)]$$
$$= [BE (C = C) + BE (H — H)] - [BE2 (C — H) - BE (C — C)]$$

$$= 606.10 + 431.37 - 2 \times 410.50 - 336.49$$
$$= 1037.47 - 1157.49$$
$$= -120.02 = -120 \text{ kJ mol}^{-1}$$

(b) $W = -2.303 \, nRT \log \frac{V_2}{V_1}$

$$= -2.303 \times \frac{16}{32} \times 8.314 \times 300 \log \frac{100}{10}$$
$$= -2972 \text{ J}$$

(c) We are given

$$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g); \quad \Delta H = -1105 \text{ kJ} \quad \text{... (i)}$$

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g); \quad \Delta H = -243 \text{ kJ} \quad \text{... (ii)}$$

Subtracting Eq. (ii) from Eq. (i), we get

$$C + H_2O(g) \longrightarrow CO(g) + H_2(g); \quad \Delta H = +132.5 \text{ kJ}$$

S21. (a) **Step I:** Write the balanced equation for all the enthalpy changes.

$$CCl_4(l) \longrightarrow CCl_4(g), \quad \Delta_{vap} H° = +30.5 \text{ kJ mol}^{-1} \quad \text{... (i)}$$
$$C(s) + 2Cl_2(g) \longrightarrow CCl_4(g), \quad \Delta_f H° = -135.5 \text{ kJ mol}^{-1} \quad \text{... (ii)}$$
$$C(s) \longrightarrow C(g), \quad \Delta_a H° = 7150 \text{ kJ mol}^{-1} \quad \text{... (iii)}$$
$$Cl_2(g) \longrightarrow 2Cl(g), \quad \Delta_a H° = 242 \text{ kJ mol}^{-1} \quad \text{... (iv)}$$

Step II: Apply Hess's law to obtain the ΔH for the reaction,

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

On multiply Eq. (iv) by 2

$$2Cl_2(g) \longrightarrow 4Cl(g), \quad \Delta_a H° = 484.0 \text{ kJ mol}^{-1} \quad \text{... (v)}$$

On adding Eq. (iii) and Eq. (v), we get

$$C(s) + 2Cl_2(g) \longrightarrow C(g) + 4Cl(g), \quad \Delta H = 1199 \text{ kJ mol}^{-1} \quad \text{... (vi)}$$

Reverse Eq. (i) and Eq (ii), we get

$$CCl(g) \longrightarrow CCl(l), \qquad \Delta H = -30.5 \text{ kJ mol}^{-1} \qquad \text{... (vii)}$$

$$CCl(l) \longrightarrow C(s) + 2Cl_2(g), \Delta_f H^\circ = 135.5 \text{ kJ mol}^{-1} \qquad \text{... (viii)}$$

On adding Eqs. (vi), (vii) and (viii), we get

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g), \quad \Delta H = 1304 \text{ kJ mol}^{-1}$$

Step III: Since, bond enthalpy is the average of all the bonds.

Bond enthalpy of C — Cl bond in

$$CCl_4 = \frac{1304}{4} = 326 \text{ kJ mol}^{-1}.$$

(b) If $\Delta G < 0$, the process is spontaneous and if $\Delta G > 0$, the process is non-spontaneous.

From Gibb's Helmholtz equation,

$$\Delta G = \Delta H - T\Delta S$$

$$0 = 400 \text{ kJ mol}^{-1} - T \times 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Temperature, $$T = \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 2000 \text{ K}$$

Therefore, above 2000 K, the reaction will become spontaneous.

S22. (a) $$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$

First we calculate ΔH of this reaction using BE values.

$$\underset{\text{Bonds broken}}{H—H + Cl—Cl} \longrightarrow \underset{\text{Bonds formed}}{2H—Cl}$$

$\Delta H = [(BE)_{H—H} + (BE)_{Cl—Cl}] - 2[(BE)_{HCl}] = [435 + 243] - 2[431] = -184$ kJ

Two moles of HCl (s) are formed from its elements, hence

$$\Delta H_f(HCl) = -\frac{184}{2} = -92.0 \text{ kJ mol}^{-1}$$

(b) Since, heat absorbed, $q = 1440$ cal

$\therefore$ $\Delta H = 1440$ cal

Given, $$HeO(s) \rightleftharpoons H_2O(l)$$

$$\Delta V = (0.0180 - 0.0196) = -0.0016 \text{ L}$$

$\therefore$ $$p\Delta V = -1 \text{ atm} \times 0.0016 \text{ L}$$

$$= -0.0016 \text{ L atm} = -0.039 \text{ cal} \qquad [\because 1 \text{ L atm} = 24.20 \text{ cal}]$$

Using, $$\Delta H = \Delta E + p\Delta V$$

$\Rightarrow$ $$\Delta E = \Delta H - p\Delta V = 1440 - (-0.039) = 1440.039 \text{ cal}$$

S23. (a) ΔH = Work done (J) = $i \times V \times t$

where, i = current in ampere, V = volt, t = time in second.

This ΔH vaporises n moles of H_2O (l) thus, ΔH per mole (molar heat of vaporisation) is determined. Thus, ΔE is calculated using

$$\Delta H = \Delta E + \Delta n_g RT$$

Since, the vaporisation occurs at constant pressure, the enthalpy change is equal to the work done on the heater (which enters the water as heat):

$$\Delta H = 0.50\text{ A} \times 12\text{ V} \times 300\text{ s} = 1800\text{ J} = +\,1.8\text{ kJ}$$

$\therefore$ Molar enthalpy of vaporisation,

$$\Delta H_m = \frac{\Delta H}{\text{Moles of } H_2O} = \frac{\Delta H}{n_{H_2O}} = \frac{1.8\text{ kJ}}{\left(\frac{0.798}{18}\right)} = 40.6\text{ kJ mol}^{-1}$$

Also, $\Delta H_m = \Delta E_m + p\Delta V$ $[\because\ H_2O\,(l) \rightleftharpoons H_2O\,(g),\ \Delta n_g = 1)$

$= \Delta E_m + \Delta n_g RT = \Delta E_m + RT$

$\therefore$ ΔE_m = Molar internal energy change = $\Delta H_m - RT$

$= 40.6 - 8.6314 \times 10^{-3} \times 373.15 = 37.5\text{ kJ mol}^{-1}$

(b) $$2O_3(g) \longrightarrow 3O_2(g)$$

$\Delta H = -285.4$ kJ for 2 moles O_3 or for 96 g O_3

$\therefore$ ΔH (per g ozone) = $-\dfrac{285.4}{96} = -2.973$ kJ

6.0095 kJ of heat melts = 18 g ice

$\therefore$ 2.973 kJ of heat melts = $\dfrac{18}{6.0095} \times 2.973$ g ice = 8.905 g ice

S24. (a) (i) Given, $p_{ext} = 200\text{ torr} = \dfrac{200}{760}\text{ atm} = 0.2632\text{ atm}$

$\Delta V = (V_2 - V_1) = 3.3$ L

$\therefore$ Work done = $p_{ext}\,\Delta V = -0.2632 \times 3.3$ L atm

$= -0.8684$ L atm $= -87.99$ J [1 L atm = 1.01325×10^2 J]

(ii) We know that, $W = -2.303\, nRT \log \dfrac{V_2}{V_1}$

$$= -2.303 \times \frac{4.5}{16} \times 8.314 \times 310 \log \frac{16.0}{12.7}\ -167.5\text{ J}$$

(b) Here, $\Delta n_g = 1 - \dfrac{1}{2} = \dfrac{1}{2}$

We can neglect molar volume of graphite, as it is a solid.

Given, $\Delta H = -24.6 \text{ k cal}$

$$T = 298 \text{ k}$$

$$R = 0.002 \text{ k cal mol}^{-1} \text{ K}^{-1}$$

Using, $\Delta H = \Delta E + \Delta n_g RT$

$$\Delta E = \Delta H - \Delta n_g RT$$

$$= -26.4 - \frac{1}{2} \times 0.002 \times 298 = -26.7 \text{ k cal}$$

S25. (a) For an isothermal expansion against a constant pressure, we have

$$W = -P_{ex} \times (V_2 - V_1)$$

$$= -p_{ex}\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right) = -p_{ex}\, nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

$$= -0.1 \times 5 \times 8.314 \times 293\left(\frac{0.4 - 0.1}{0.04}\right) = -9135 \text{ J}$$

Since, temperature is constant

$$\Delta U = 0, \quad \Delta H = 0, \quad q = -W = 9135 \text{ J}$$

(b) For isothermal reversible expansion,

$$-\text{W} = 2.303 \text{ nRT} \log \frac{p_1}{p_2}$$

$$= 2.303 \;\; 5 \;\; 8.314 \;\; 293 \log \frac{0.4}{0.1}$$

$\Rightarrow$ $\text{W} = -16888\text{J}$

At constant temperature,

$$\Delta U = \Delta H = 0, \quad q = -W = 16888 \text{ J}$$

S26. (a) Iron reacts with HCl acid to produce H_2 gas as

$$Fe\,(s) + 2HCl\,(aq) \longrightarrow FeCl_2\,(aq) + H_2\,(g)$$

Thus, 1 mol of Fe, *i.e.*, 56 g Fe produces H_2 gas = 1 mol

$\therefore$ 11.2 g Fe will produce H_2 gas = $\frac{1}{56} \times 11.2 = 0.2$ mol

(i) If the reaction is carried out in an open beaker (external pressure being 1 atm)

Initial volume = 0 (because no gas is present)

Final volume occupied by 0.2 mol of H_2 at 25°C and 1 atm pressure can be calculated as follows:

$$pV = nRT$$

$\therefore$ $$V = \frac{nRT}{p} = \frac{0.2 \text{ mol} \times 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ atm}} = 4.89 \text{ L}$$

$\therefore$ $$\Delta V = V_{\text{final}} - V_{\text{initial}} = 4.89 \text{ L}$$

$$W = -p_{ext}\Delta V = -2 \text{ atm } 4.89 \text{ L} = -4.89 \text{ L atm}$$
$$= -4.89 \times 101.3 \text{ K} = -495 \text{ J}$$

(ii) If the vessel is closed then volume is fixed.

Hence, $\Delta V = 0$

And, therefore no work is done.

(b) Consider the heat of formation of H2O

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l), \quad \Delta H = -286.20 \text{ kJ}$$

$$\Delta H_f = \Delta H_f(H_2, I) - \Delta H_f(H_2, g) - \frac{1}{2}\Delta H_f(O_2, g)$$

$$-286.20 = \Delta H_f(H_2O, l) - 0 - 0$$
$$\Delta H_f(H_2O, l) = 286.20 \text{ kJ}$$

Now, consider the ionisation of H_2O

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq); \quad \Delta H = 57.32 \text{ kJ}$$
$$\Delta H_f = \Delta H_f(H^+, aq) + \Delta H_f(OH^-, aq) - \Delta H_f(H_2O, l)$$
$$57.32 = 0 + \Delta H_f(OH^-, aq) - (-286.20)$$

Thus, $\Delta H_f(OH^-, aq) = 57.32 - 286.20 = -228.88 \text{ kJ}$

S27. (a) (i) $\Delta_f H° = \sum \Delta_f H° \text{ (products)} - \sum \Delta_f H° \text{ (reactants)}$

$$= [2\Delta_f H° \, H_2O(l) + 2\Delta_f H° \, SO_2(g)] - [2\Delta_f H° \, H_2S(g) - 3\Delta_f H° \, O_2(g)]$$
$$= 2 \times (-285.8 \text{ kJ mol}^{-1}) + 2 \times (-296.9 \text{ kJ mol}^{-1}) - [2 \times (-20.1 \text{ kJ mol}^{-1}) - (3 \times 0)]$$
$$= -1165.5 \text{ kJ mol}^{-1} + 40.2 \text{ kJ mol}^{-1}$$
$$= -1125.2 \text{ kJ mol}^{-1}$$

(ii) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$

$$\text{Enthalpy of formation of HCl(g)} = \frac{(104 + 58) - (2 \times 103)}{2} = \frac{162 - 206}{2}$$
$$= -\frac{44}{2} = -22 \text{ kcal mol}^{-1}$$

(b) $\Delta H = \Delta U + \Delta n_g RT$

$$2X(g) + Y(g) \longrightarrow 2Z(g); \quad \Delta n_g = 2 - (2 + 1) = -1$$

On substituting the values in the equation, we have

$$\Delta H = -10.5 \times 10^3 \text{ J} + (-1) \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K}$$
$$= -10500 \text{ J} - 2477.5 \text{ J} = -12977.57 \text{ J}$$

We have the relation, $\Delta G = \Delta H - T\Delta S$

On substituting the values, we have

$$\Delta G = -12977.57 \text{ J} - 298 \text{ K} \times (-44 \text{ JK}^{-1})$$
$$= -12977.57 \text{ J} + 13112 \text{ J} = +134.43 \text{ J}$$

As ΔG is positive, therefore, the reaction will not occur spontaneously, *i.e.*, the reaction is non-spontaneous.

S28. (a) Required reaction for the formation of methanol is as follows:

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l); \quad \Delta_f H^\circ = ?$$

Given enthalpy for the combustion of methanol.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + H_2O(l); \quad \Delta_r H^\circ = -726 \text{ kJ mol}^{-1} \quad \text{... (i)}$$

Enthalpy for the formation of 1 mole of $CO_2(g)$

$$C(g) + O_2(g) \longrightarrow CO_2(g); \quad \Delta_f H^\circ = -393 \text{ kJ mol}^{-1} \quad \text{... (ii)}$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \quad \Delta_f H^\circ = -286 \text{ kJ mol}^{-1} \quad \text{... (iii)}$$

Multiplying Eq. (iii) by 2 [because 2 moles of $H_2O(l)$ are formed in Eq. (i)] thus, we get

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l); \quad \Delta_f H^\circ = -572 \text{ kJ mol}^{-1} \quad \text{... (iv)}$$

Adding Eq. (ii) and Eq. (iv), we get

$$C(s) + 2H_2(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta_f H^\circ = -965 \text{ kJ mol}^{-1} \quad \text{... (v)}$$

Reversing Eq. (i), we get

$$CO_2(g) + 2H_2O(l) \longrightarrow CH_3OH(l) + \frac{3}{2}O_2(g); \quad \Delta_f H^\circ = +726 \text{ kJ mol}^{-1} \quad \text{... (vi)}$$

Adding Eqs. (v) and (vi), we get the required equation

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(l); \quad \Delta_f H^\circ = -393 \text{ kJ mol}^{-1}.$$

(b)

$$\text{Work done} = -2.303\, nRT \log \frac{p_1}{p_2}$$

$$= -2.303 \times 8.314 \times 300 \log \frac{1}{4}$$

$$= 3458.3 \text{ J} = 3.458 \text{ kJ}.$$

S29. (a)

$$W = \int_{V_1}^{V_2} pdV = -p_2(V_2 - V_1)$$

$$W = -1(20 - 10) = -10 \text{ dm}^3 \text{ atm}$$

$$= -1013 \text{ J} \qquad [\because \ 1 \text{ L atm} = 101.3 \text{ J}]$$

From the first law of thermodynamics,

$$\Delta E = q + W = 800 \text{ J} + (-1013 \text{ J}) = -213 \text{ J}$$

(b) $C\ (graphite) + 2H_2(g) \longrightarrow CH_4(g)$

$$\Delta H = -17900\ \text{cal}; \quad \Delta E = ?, \quad \Delta n_g = 1 - 2 = 1$$

$\because$ $$\Delta H = \Delta E + \Delta n_g RT$$

$\therefore$ $$\Delta H = \Delta E - 1 \times R \times T - 17900 = \Delta E - 1 \times 298 \times 2$$

$$-\Delta E = 17900 - 596$$

$\therefore$ $$-\Delta E = 17304\ \text{cal}$$

(c) $$\Delta G = \Delta H - T \cdot \Delta S$$

or $$T \cdot \Delta S = \Delta H - \Delta G$$

$\therefore$ $$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$= \frac{-10-(-16)}{300} = \frac{6}{300}\ \text{k cal K}^{-1}$$

$$= \frac{6 \times 1000}{300} = 20\ \text{cal K}^{-1}.$$

S30. (a) $N_2(g) + \frac{1}{2}O_2(g) \longrightarrow N_2O, \quad N \equiv N + \frac{1}{2}O = O \longrightarrow N = N = O$

(Hypothetical structure)

From the given BE values,

$$\Delta H_f^\circ(N_2O) = [(BE)_{N \equiv N} + \frac{1}{2}(BE)_{O=O}] - [(BE)_{N=N} + (BE)_{N=O}]$$

$$= \left(946 + \frac{498}{2}\right) - (418 + 607) = (1195) - (1025) = -170\ \text{kJ}$$

Resonance energy = Observed H_f° – Calculated H_f° = 82 – 170 = – 88 kJ mol^{-1}

(b) $C_2H_2(g) + H_2(g) \longrightarrow C_2H_4(g)$

$$\Delta n_g = 1 - 2 = -1, \quad \Delta H = -0.31\ \text{kJ mol}^{-1}$$

$$p = 1.5\ \text{atm}, \qquad \Delta V = -50\ \text{mL} = -0.050\ \text{L}$$

$\therefore$ $$p\Delta V = 1.5 \times (-0.050)\ \text{L atm}$$

$$= \frac{1.5 \times 0.050 \times 8.314 \times 10^{-3}}{0.0821}\ \text{kJ} = -0.0076\ \text{kJ}$$

$\therefore$ $$\Delta H = \Delta E + p\Delta V$$

$\Rightarrow$ $$-0.31 = \Delta E + (0.076)$$

$\Rightarrow$ $$\Delta E = -0.3024\ \text{kJ}$$

Note: To convert L atm into kJ, we have used value of R (gas constant)

$$R = 8.314 \times 10^{-3}\ \text{kJ mol}^{-1}\ \text{K}^{-1} = 0.0821\ \text{L atm mol}^{-1}\ \text{K}^{-1}.$$

S31. (a) $$\Delta S_{reaction} = \sum \Delta S^\circ_{products} - \sum \Delta S^\circ_{reactant} = S^\circ_{NO} - [S^\circ_{N_2} + S^\circ_{O_2}] = S^\circ_{NO} - S^\circ_{N_2} - S^\circ_{O_2}$$
$$= 2 \times 210.5 - 191.4 - 204.9 = 24.7\ JK^{-1}\ mol^{-1}$$

We know that, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G^\circ = 180.8 - (T \times 24.7 \times 10^{-3})\ kJ\ mol^{-1}$$

For spontaneity, $\Delta G^\circ < 0$ and this occurs when

$$T\Delta S^\circ > \Delta H^\circ$$

$$T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T > \frac{180.8 \times 10^3}{24.7} = 7320\ K$$

The reaction becomes spontaneous above the temperature of 7320 K.

(b) Adding reactions I and II

$$2Na + H_2O + \frac{1}{2}O_2 \longrightarrow 2NaOH, \quad \Delta H_1 = x - 56$$

Adding reactions III and IV

$$2Na + H_2O + \frac{1}{2}O_2 \longrightarrow 2NaOH, \quad \Delta H_2 = -156\ kcal$$

Both represent the same chemical change.

Hence, $\Delta H_1 = \Delta H_2$

$\therefore$ $x - 56 = -156$

$$x = -100\ kcal$$