l. Choose the correct answer. A thermodynamic state function is a quantity
   (i) used to determine the heat changes
   (ii) whose value is independent of path
   (iii) used to determine pressure–volume work
   (iv) whose value depends on temperature only.

Ans. (ii) whose value is independent of path

2. For the process to occur under adiabatic conditions, the correct condition is
   (i) $\Delta T = 0$ (ii) $\Delta p = 0$
   (iii) $q = 0$ (iv) $w = 0$.

Ans. (iii) $q = 0$

3. The enthalpies of all the elements in their standard states are:
   (i) unity   (ii) zero
   (iii) < 0 (iv) different for each element.

Ans. (ii) zero

4. $\Delta U°$ of combustion of methane is $-X$ kJ mol^{-1}. The value of $\Delta H°$ is
   (i) $= \Delta U°$ (ii) $> \Delta U°$
   (iii) $< \Delta U°$ (iv) $= 0$.

Ans. The balanced equation for combustion of methane will be

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
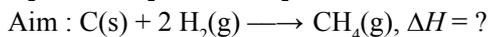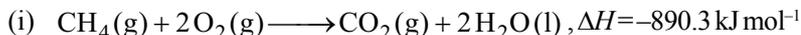Thus, $\Delta n_g = (n_p - n_r)_g = 1 - 3 = -2$
$\Delta H° = \Delta U° + \Delta n_g RT = -X - 2RT$ Thus, $\Delta H° < \Delta U°$.
Hence, (iii) is correct answer.

5. $\Delta H°$ of combustion of methane, graphite and dihydrogen at 298 K are —890·3 kJmol^{-1}, –393.5 kJmol^{-1} and –285.8 kJ mol^{-1}, respectively. Enthalpy of formation of CH_4 (g) will be
   (i) -74.8 kJmol^{-1} (ii) -52.27 kJ mol^{-1}
   (iii) $+74.8$ kJ mol^{-1} (iv) $+52.26$ kJ mol-1

Ans. Given
   (i) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$, $\Delta H = -890.3$ kJ mol^{-1}
   (ii) $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5$ kJ mol^{-1}
   (iii) $H_2(g) + ½ O_2(g) \longrightarrow H_2O(l)$, $\Delta H = -285.8$ kJ mol^{-1}
   Aim : $C(s) + 2 H_2(g) \longrightarrow CH_4(g)$, $\Delta H = ?$
   Equation (ii) + 2 Equation (iii) – Equation (i) gives the required equation with

$\Delta H = -393 \cdot 5 + 2 (-285 \cdot 8) - (-890.3)$ kJ mol^{-1} = -74.8 kJmol^{-1}.

Hence, (i) is correct answer.

6. A reaction, $A + B \rightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

   (i) possible at high temperature

  (ii) possible only at low temperature

 (iii) not possible at any temperature

  (iv) possible at any temperature.

Ans. Here, $\Delta H = $ –ve and $\Delta S = $ +ve. $\Delta G = \Delta H - T\Delta S$. For the reaction to be spontaneous, ΔG should be –ve which will be so at any temperature, i.e., option (iv) is correct.

7. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy of the process ?

Ans. $q = +701$ J, $w = -394$ J, $\Delta U = ?$

By first law of thermodynamics $\Delta U = q + w = +701$ J $+ (-394$ J$) = +307$ J, i.e., internal energy of the system increases by 307 J.

8. The reaction of cyanamide, $NH_2CN(s)$, with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be -742.7 kJ mol^{-1} at 298 K. Calculate the enthalpy change of the reaction at 298 K ?

NH_2CN (s) $+ 3/2$ O_2 (g) $\rightarrow N_2$ (g) $+ CO_2$ (g) $+ H_2O$ (l).

Ans. $\Delta n_g = (n_p - n_r)g = 2 - \dfrac{3}{2} = +1/2$ mol

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

$= -742.7$ kJ mol^{-1} $+ (+1/2$ mol $) (8.314 \times 10^{-3}$ kJ mol^{-1} K$^{-1}) (298$ K$)$

$= -742.7 + 1.2$ kJ mol^{-1} $= -741.5$ kJ mol^{-1}.

9. Calculate the number of kJ necessary to raise the temperature of 60.0 g of aluminium from 35 to 55°C. Molar heat capacity of aluminium is 24 J mol^{-1} K^{-1}.

Ans. $q = n \times C \times \Delta T = \left(\dfrac{60\,mol}{27} \right) (24\,\text{J mol}^{-1}\,\text{K}^{-1}) (55 - 35\text{K}) = 1066.7\text{J} = 1.07\text{kJ}.$

10. Calculate the enthalpy change on freezing 1.0 mol of water at 10.0°C to ice at –10°C,

$\Delta_{fus} H = 6.03$ KJ mol^{-1} at 0°C

C_p [H_2O (l)] $= 75.3$ J mol^{-1} K^{-1}

C_p [H_2O (s)] $= 36.8$ J mol^{-1} K^{-1}.

Ans. Total ΔH = (1 mol water at 10°C ⟶1 mol of water at 0°C) + (1 mole of water at 0°C ⟶1 mol ice at 0°C) + (1 mole of ice at 0°C ⟶1 mol of ice at –10°C)

$$= C_p[H_2O.(l)] \times \Delta T + \frac{\Delta H_{freezing}}{T_f} + C_p[H_2O\ (s)] \times \Delta T$$

$$= (75.3\ JK^{-1}\ mol^{-1})\ (-10\ K) + (-6.03\ kJ\ mol^{-1}) + (36.8\ JK^{-1}\ mol^{-1})\ (-10\ K)$$

$$= -753\ J\ mol^{-1} - 6.03\ kJ\ mol^{-1} - 368\ J\ mol^{-1}$$

$$= 0.753kJ\ mol^{-1} - 6.03\ kJmol^{-1} - 0.368\ kJ\ mol^{-1} = -7.15\ kJmol^{-1}.$$

11. 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.

Ans. $C(s) + O_2(g) \longrightarrow CO_2(g)$, $\Delta H = -393.5\ kJ\ mol^{-1}$

For CO_2, 1 mol = 44 g

Heat released when 44 g CO_2 is formed = 393.5 kJ

∴ Heat released when 35.2 g CO_2 is formed

$$= \frac{393.5 \times 35.2\ kJ}{44} = 314.8\ kJ$$

12. Enthalpies of formation of CO (g), CO_2 (g), N_2O (g) and N_2O_4 (g) are –110, –393, 81 and 9.7kJ mol⁻¹, respectively. Find the value of $\Delta_r H$ for the reaction $N_2O_4(g) + 3CO(g) \longrightarrow N_2O(g) + 3\ CO_2(g)$

Ans. $\Delta_f H = \Sigma\Delta_f H$ (Products) $-\Sigma\ \Delta_f H$ (Reactants)

$$= (\Delta_f H\ (N_2O) + 3\ \Delta_f H\ (CO_2)] - [\Delta_f H\ (N_2O_4) + 3\ \Delta_f H\ (CO)]$$

$$= [81 + 3\ (-393)] - [9.7 + 3\ (-110)]\ kJ = -777.7\ kJ.$$

13. Given : $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta_r H° = -92.40\ kJ$. What is the standard enthalpy of formation of NH_3 gas?

Ans. Reaction for the enthalpy of formation of NH_3 (g) is $\frac{1}{2} N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$

$\Delta_f H° = -92.4 / 2 = -46.2\ kJ\ mol^{-1}.$

14. Calculate the standard enthalpy of formation of CH_3OH (l) from the following data :

(i) $CH_3OH\ (l) + 3/2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O\ (l)$; $\Delta_r H° = -726\ kJ\ mol^{-1}$

(ii) $C\ (s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta_c H° = -393\ kJ\ mol^{-1}$

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

Ans. Aim : $C(s) + 2H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow CH_3OH(l), \Delta_f H° = ?$
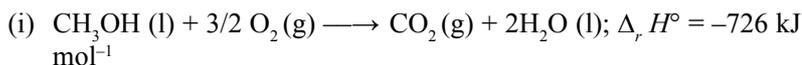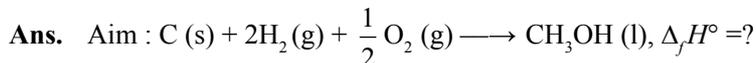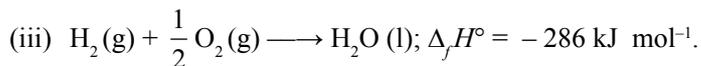
Equation (ii) + 2 × Eqn. (iii) – Eqn. (i) gives the required Equation. with
$\Delta H = -393 + 2(-286) - (-726) \text{ kJ mol}^{-1} = -239 \text{ kJ mol}^{-1}$.
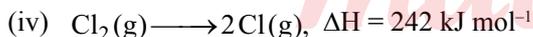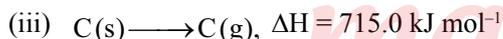
15. Calculate the enthalpy change for the process

$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$ and calculate bond enthalpy of C–Cl in $CCl_4(g)$
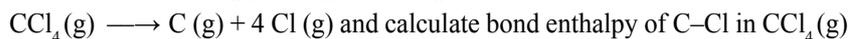
Given: $\Delta_{vap} H° (CCl_4) = 30.5 \text{ kJ mol}^{-1}$

$\Delta_f H° (CCl_4) = -135.5 \text{ kJ mol}^{-1}$

$\Delta_a H° (C) = 715.0 \text{ kJ mol}^{-1}$ where $\Delta_a H°$ is enthalpy of atomisation

$\Delta_a H° (Cl_2) = 242 \text{ kJ mol}^{-1}$.

Ans. The given data imply as under :

(i) $CCl_4(l) \longrightarrow CCl_4(g)$, $\Delta H = 30.5 \text{ kJ mol}^{-1}$

(ii) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(l)$, $\Delta H = -135.5 \text{ kJ mol}^{-1}$

(iii) $C(s) \longrightarrow C(g)$, $\Delta H = 715.0 \text{ kJ mol}^{-1}$

(iv) $Cl_2(g) \longrightarrow 2Cl(g)$, $\Delta H = 242 \text{ kJ mol}^{-1}$

Aim: $CCl_4(g) \longrightarrow C(g) + 4Cl(g)$, $\Delta H = ?$

Equation (iii) + 2 × Eqn. (iv) – Eqn. (i) – Eqn. (ii) gives the required equation
with $\Delta H = 715.0 + 2(242) - 30.5 - (-135.5) \text{ kJmol}^{-1}$

$= 1304 \text{ kJ mol}^{-1}$

Bond enthalpy of C–Cl in CCl_4 (average value) $= \dfrac{1304}{4} = 326 \text{ kJ mol}^{-1}$.

16. For an isolated system, $\Delta U = 0$, what will be ΔS ?

Ans. Isolated system means no exchange of energy and mass. $\Delta U = 0$ means no involvement of energy. So, to make the process spontaneous ΔS has to become positive.

Consider the example of two gases contained separately in two bulbs connected by a stop-cock, and isolated from the surroundings as an example of an isolated system. On opening the stop-cock, the two gases mix up, i.e., the system becomes more disordered. This implies that $\Delta S > 0$.

17. For the reaction at 298 K, $2A + B \longrightarrow C$

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

At what temperature will the reaction become spontaneous considering ΔH

and ΔS to be constant over the temperature range?

Ans. Let us first calculate the temperature at which the reaction will be in equilibrium, i.e., $\Delta G = 0$.

Now, $\Delta G = \Delta H - T\Delta S \therefore 0 = \Delta H - T\Delta S$ or $T = \Delta H /\Delta S = 400$ kJ mol^{-1}/0.2kJ K^{-1} mol^{-1}= 2000 K.

For reaction to be spontaneous, i.e., for ΔG to be $-$ve, T should be greater than 2000 K.

18. For the reaction, 2 Cl (g) $\longrightarrow$ Cl$_2$ (g), what are the signs of ΔH and ΔS?

Ans. 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.

19. For the reaction, 2 A (g) + B (g) $\longrightarrow$ 2D (g),

$\Delta U^\circ = -10.5$kJ and $\Delta S^\circ = -44.10$ JK^{-1} Calculate ΔG° for the reaction and predict whether the reaction may occur spontaneously.

Ans. For the given reaction, $\Delta n_g = 2 - (3) = -1$

$\therefore \quad \Delta H^\circ = \Delta U^\circ + \Delta n_g RT = -10.5\ kJ + (-1)\ (8.314 \times 10^{-3}\ kJ) \times (298)$

$= -10.5 - 2.48 = -12.98\ kJ$

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

$= -12{\cdot}98$kJ $-298\ (-44{\cdot}1 \times 10^{-3}\ kJ)$

$= -12.98$kJ $+ 13.14$kJ $= 0.16$ kJ

As ΔG° comes out to be $+$ve, the reaction will not occur spontaneously.

20. The equilibrium constant for a reaction is 10. What will be the value of ΔG°? $R = 8.314$ JK^{-1} mol^{-1}, $T = 300$ K.

Ans. $\Delta G^\circ = -2.303\ RT \log K = -2.303 \times 8.314$ JK^{-1} mol$^{-1} \times 300$K $\times \log 10 = -5744.1$ J.

21. Comment on the thermodynamic stability of NO (g), given

1/2 N$_2$ (g) + 1/2 O$_2$(g) $\longrightarrow$ NO(g); Δ_r H$^\circ$ = 90 kJ mol^{-1}

NO(g) + 1/2 O$_2$(g) $\longrightarrow$ NO$_2$(g); Δ_r H$^\circ$ = -74 kJ mol^{-1}
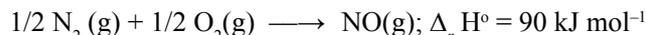
Ans. As energy is absorbed in the first reaction, NO (g) is unstable. As energy is released in the second reaction, NO$_2$ (g) is stable. Thus, unstable NO (g) changes into the stable NO$_2$ (g).

22. Calculate the entropy change in the surroundings when 1·00 mol of H$_2$O (l) is formed under standard conditions: $\Delta_f H^\circ = -286$ kJ mol^{-1}.

Ans. H$_2$ (g) + ½O$_2$ (g) $\longrightarrow$ H$_2$O (l) Δ_fH^0 = -286 kJ mol^{-1}

This means that when 1 mol of H$_2$O (l), is formed, 286 kJ of heat is released. This heat is absorbed by the surroundings, i.e., q_{surr} =1 + 286 kJmol^{-1}.

$\Delta S = q_{surr} / T = \dfrac{286\ \text{kJ mol}^{-1}}{298\ \text{K}} = 0.9597$ kJ K^{-1} mol^{-1} = 959.7 JK^{-1} mol^{-1}.