Q-1: Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine 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) A quantity which is independent of path.

Reason:

Functions like pressure, volume and temperature depends on the state of the system only and not on the path.

Q-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

Reason:

For an adiabatic process heat transfer is zero, i.e. q = 0.

Q-3: The enthalpies of all elements in their standard states are:

(i) Unity   (ii) Zero

(iii) < 0   (iv) Different for every element

Ans:

(ii) Zero

Q-4: ΔU^0 of combustion of methane is $-$ X kJ mol^{-1}. The value of ΔH^0 is

(i) = $\Delta U^\ominus$

(ii) > $\Delta U^\ominus$

(iii) < $\Delta U^\ominus$

(iv) 0

Ans:

(iii) $< \Delta U^{\ominus}$

Reason:

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT \; ; \; \Delta U^{\ominus} = -Y \; kJmol^{-1},$$

$$\Delta H^{\ominus} = (-Y) + \Delta n_g RT \Rightarrow \Delta H^{\ominus} < \Delta U^{\ominus}$$

Q-5: The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, –890.3 kJ mol⁻¹ –393.5 kJ mol⁻¹, and –285.8 kJ mol⁻¹ respectively. Enthalpy of formation of CH₄ (g) will be

(i) -74.8 kJ mol⁻¹

(ii) -52.27 kJ mol⁻¹

(iii) +74.8 kJ mol⁻¹

(iv) +52.26 kJ mol⁻¹

Ans:

(i) $-74.8 kJ \; mol^{-1}$

1. $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

$$\Delta H = -890.3 kJmol^{-1}$$

2. $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$$\Delta H = -393.5 kJmol^{-1}$$

3. $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

$$\Delta H = -285.8 kJmol^{-1}$$

$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$
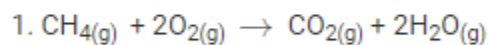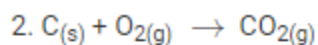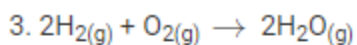
$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_f H_{H_2} - \Delta_f H_{CO_2}$

$= [-393.5 + 2(-285.8) - (-890.3)] \text{ kJ } mol^{-1}$

$= -74.8 \text{kJ } mol^{-1}$

Q-6: A reaction, A + B → 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:

(iv) possible at any temperature

ΔG should be −ve, for spontaneous reaction to occur

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

As per given in question,

ΔH is −ve (as heat is evolved)

ΔS is +ve

Therefore, ΔG is negative

So, the reaction will be possible at any temperature.

Q-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 for the process?

Ans:

As per Thermodynamics 1st law,

$\Delta U = q + W(i);$

ΔU internal energy = heat

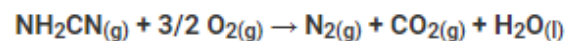W = work done

W = -594 J (work done by system)

q = +801 J (+ve as heat is absorbed)

Now,

$\Delta U = 801 + (-594)$

$\Delta U = 207$ J

Q-8: The reaction of cyanamide, NH₂CN₍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 enthalpy change for the reaction at 298 K.

$NH_2CN_{(g)} + 3/2\ O_{2(g)} \rightarrow N_{2(g)} + CO_{2(g)} + H_2O_{(l)}$

Ans:

ΔH is given by,

$\Delta H = \Delta U + \Delta n_g RT$ ....(1)

Δn_g = change in number of moles

ΔU = change in internal energy

Here,

$$\Delta n_g = \sum n_g(product) - \sum n_g(reactant)$$

= (2 − 1.5) moles

Δn_g = 0.5 moles

Here,

T = 298K

$\Delta U = -742.7\ kJmol^{-1}$

R = $8.314 \times 10^{-3} kJmol^{-1}K^{-1}$

Now, from (1)

$$\Delta H = (-742.7 kJmol^{-1}) + (0.5mol)(298K)(8.314 \times 10^{-3} kJmol^{-1}K^{-1})$$

= -742.7 + 1.2

$\Delta H = -741.5\ kJmol^{-1}$

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

Ans:

Expression of heat(q),

$$q = mCP\Delta T;\text{.....................}(a)$$

ΔT = Change in temperature

c = molar heat capacity

m = mass of substance

From (a)

$q = (\frac{60}{27}mol)(24 mol^{-1}K^{-1})(20K)$

q = 1066.67 J = 1.067 KJ

Q-10: Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0°C to ice at −10.0°C. $\Delta_{fus}H$ = 6.03 kJ mol⁻¹ at 0°C.

$C_p[H_2O_{(l)}] = 75.3J\ mol^{-1}K^{-1}$

$C_p[H_2O_{(s)}] = 36.8J\ mol^{-1}K^{-1}$

Ans:

ΔH_{total} = sum of the changes given below:

(a) Energy change that occurs during transformation of 1 mole of water from $10°C\ to\ 0°C$.

(b) Energy change that occurs during transformation of 1 mole of water at $0°C$ to 1 mole of ice at $0°C$.

(c) Energy change that occurs during transformation of 1 mole of ice from $0°C\ to\ (-10)°C$.

$\Delta H_{total} = C_p[H_2OCl]\Delta T + \Delta H_{freezing}C_p[H_2O_s]\Delta T$

= (75.3 $Jmol^{-1}K^{-1}$)(0 − 10)K + (-6.03*1000 $Jmol^{-1}$ (-10-0)K

= -753 $Jmol^{-1}$ − 6030 $Jmol^{-1}$ − 368 $Jmol^{-1}$

= -7151 $Jmol^{-1}$

= -7.151 $kJmol^{-1}$

Thus, the required change in enthalpy for given transformation is -7.151 $kJmol^{-1}$.

Q-11 Enthalpy of combustion of carbon to CO₂ is –393.5 kJ mol⁻¹. Calculate the heat released upon formation of 35.2 g of CO₂ from carbon and dioxygen gas.

Ans:

Formation of carbon dioxide from di-oxygen and carbon gas is given as:

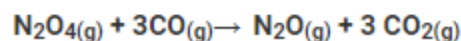$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$; $\Delta_f H$ = -393.5 $kJmol^{-1}$
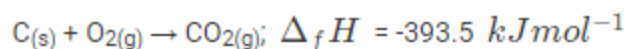
1 mole CO_2 = 44g

Heat released during formation of 44g CO_2 = -393.5 $kJmol^{-1}$

Therefore, heat released during formation of 35.2g of CO_2 can be calculated as

$= \dfrac{-393.5 kJmol^{-1}}{44g} \times 35.2g$

= -314.8 $kJmol^{-1}$

Q-12: Enthalpies of formation of CO (g), CO₂ (g), N₂O (g) and N₂O₄(g) are −110, − 393, 81 and 9.7 kJ mol⁻¹ respectively. Find the value of Δ,H for the reaction:
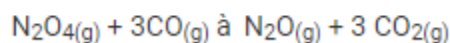
N₂O₄(g) + 3CO(g)→ N₂O(g) + 3 CO₂(g)

Ans:

" $\Delta_r H$ for any reaction is defined as the fifference between $\Delta_f H$ value of products and $\Delta_f H$ value of

reactants."

$\Delta_r H = \sum \Delta_f H(products) - \sum \Delta_f H(reactants)$

Now, for

N₂O₄(g) + 3CO(g) à N₂O(g) + 3 CO₂(g)

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

Now, substituting the given values in the above equation, we get:

$\Delta_r H$ = [{81 $kJmol^{-1}$ + 3(-393) $kJmol^{-1}$} – {9.7 $kJmol^{-1}$ + 3(-110) $kJmol^{-1}$}] $\Delta_r H$ = -777.7

$kJmol^{-1}$

Q-13: Given N$_2$ (g) + 3H$_2$ (g) → 2NH$_3$ (g) ; $\Delta_r H^0$= −92.4 kJ mol^{-1}
What is the standard enthalpy of formation of NH$_3$ gas?

Ans:

"Standard enthalpy of formation of a compound is the enthalpy that takes place during the formation of 1 mole of a substance in its standard form, from its constituent elements in their standard state."

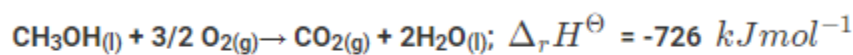Dividing the chemical equation given in the question by 2, we get

(0.5)N$_{2(g)}$ + (1.5)H$_{2(g)}$ → 2NH$_{3(g)}$
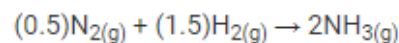
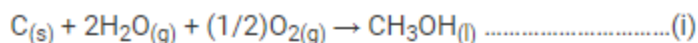Therefore, Standard Enthalpy for formation of ammonia gas

= (0.5) $\Delta_r H^\Theta$

= (0.5)(-92.4 $kJmol^{-1}$)

= -46.2 $kJmol^{-1}$

Q-14: Calculate the standard enthalpy of formation of CH$_3$OH$_{(l)}$ from the following data:

CH$_3$OH$_{(l)}$ + 3/2 O$_{2(g)}$→ CO$_{2(g)}$ + 2H$_2$O$_{(l)}$; $\Delta_r H^\Theta$ = -726 $kJmol^{-1}$

C$_{(g)}$ + O$_{2(g)}$→ CO$_{2(g)}$; $\Delta_c H\Theta$ = -393 $kJmol^{-1}$

H$_{2(g)}$ + 1/2 O$_{2(g)}$→ H$_2$O$_{(l)}$; $\Delta_f H^\Theta$ = -286 $kJmol^{-1}$

Ans:

$C_{(s)} + 2H_2O_{(g)} + (1/2)O_{2(g)} \rightarrow CH_3OH_{(l)}$ ....(i)

$CH_3OH_{(l)}$ can be obtained as follows,

$\Delta_f H_\Theta$ [$CH_3OH_{(l)}$] = $\Delta_c H_\Theta$

$2\Delta_f H_\Theta - \Delta_r H_\Theta$

= (-393 $kJmol^{-1}$) +2(-286 $kJmol^{-1}$) – (-726 $kJmol^{-1}$)

= (-393 – 572 + 726) $kJmol^{-1}$

= -239 $kJmol^{-1}$

Thus, $\Delta_f H_\Theta$ [$CH_3OH_{(l)}$] = -239 $kJmol^{-1}$

Q-15: Calculate the enthalpy change for the process

$CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ **and determine the value of bond enthalpy for C-Cl in** $CCl_{4(g)}$.

$\Delta_{vap} H^\Theta$ (CCl₄) = 30.5 $kJmol^{-1}$.

$\Delta_f H^\Theta$ (CCl₄) = -135.5 $kJmol^{-1}$.
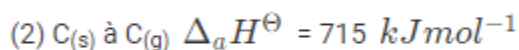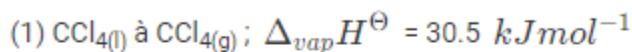
$\Delta_a H^\Theta$ (C) = 715 $kJmol^{-1}$,

$\Delta_a H^\Theta$ is a enthalpy of atomisation

$\Delta_a H^\Theta$ (Cl₂) = 242 $kJmol^{-1}$.

Ans:

" The chemical equations implying to the given values of enthalpies" are:

(1) $CCl_{4(l)}$ à $CCl_{4(g)}$; $\Delta_{vap}H^{\Theta}$ = 30.5 $kJmol^{-1}$

(2) $C_{(s)}$ à $C_{(g)}$ $\Delta_a H^{\Theta}$ = 715 $kJmol^{-1}$

(3) $Cl_{2(g)}$ à $2Cl_{(g)}$; $\Delta_a H^{\Theta}$ = 242 $kJmol^{-1}$

(4) $C_{(g)}$ + $4Cl_{(g)}$ à CCl4(g); $\Delta_f H^{\Theta}$ = -135.5 $kJmol^{-1}$ ΔH for the process $CCl_{4(g)}$ à $C_{(g)}$ + $4Cl_{(g)}$ can be measured as:

$$\Delta H = \ \Delta_a H^{\Theta}(C) + \ 2\Delta_a H^{\Theta}(Cl_2) - \Delta_{vap}H^{\Theta} - \Delta_f H$$

= (715 $kJmol^{-1}$) + 2($kJmol^{-1}$) – (30.5 $kJmol^{-1}$) – (-135.5 $kJmol^{-1}$)

Therefore, $H = \ 1304 kJmol^{-1}$

The value of bond enthalpy for C-Cl in CCl4(g)

= $\frac{1304}{4} kJmol^{-1}$

= 326 $kJmol^{-1}$

Q-16: For an isolated system, ΔU = 0, what will be ΔS?

Ans:

ΔU is positive ; ΔU > 0.

As, ΔU = 0 then ΔS will be +ve, as a result reaction will be spontaneous.

Q-17: For the reaction at 298K,

2A + B → C
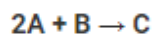
ΔH = 400 $kJmol^{-1}$

ΔH = 0.2 $kJmol^{-1}K^{-1}$

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

Ans:

Now,

$$\Delta G = \Delta H - T\Delta S$$
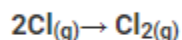
Let, the given reaction is at equilibrium, then ΔT will be:

T = $(\Delta H - \Delta G)\frac{1}{\Delta S}$ $\frac{\Delta H}{\Delta S}$; (ΔG = 0 at equilibrium)

= 400 $kJmol^{-1}$ /0.2 $kJmol^{-1}K^{-1}$

Therefore, T = 2000K

Thus, for the spontaneous, ΔG must be −ve and T > 2000K.

Q-18: For the reaction

$2Cl_{(g)} \rightarrow Cl_{2(g)}$

**What are the signs of ΔS and ΔH ?**

Ans:

ΔS and ΔH are having negative sign.

The reaction given in the question represents the formation of Cl molecule from Cl atoms. As the formation of bond takes place in the given reaction. So, energy is released. So, ΔH is negative.

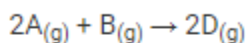Also, 2 moles of Chlorine atoms are having more randomness than 1 mole of chlorine molecule. So, the spontaneity is decreased. Thus, ΔS is negative.

Q-19: For the reaction

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$
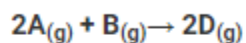
$\Delta U^{\ominus}$ = -10.5 kJ and $\Delta S^{\ominus}$ = -44.1 JK^{-1}

Calculate $\Delta G^{\ominus}$ for the reaction, and predict whether the reaction may occur spontaneously.

Ans:

$2A_{(g)} + B_{(g)} \rightarrow 2D_{(g)}$

Δn_g = 2 – 3

= -1 mole

Putting value of $\Delta U^{\ominus}$ in expression of ΔH :

$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta n_g RT$$

= (-10.5KJ) – (-1)($8.314 \times 10^{-3} kJK^{-1}mol^{-1}$)(298K)

= -10.5kJ -2.48kJ

$\Delta H^{\ominus}$ = -12.98kJ

Putting value of $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ in expression of $\Delta G^{\ominus}$:

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

= -12.98kJ –(298K)(-44.1 JK^{-1})

= -12.98kJ +13.14kJ

$\Delta G^{\ominus}$ = 0.16kJ

As, $\Delta G^{\ominus}$ is positive, the reaction won't occur spontaneously.

Q-20: The equilibrium constant for a reaction is 10. What will be the value of ΔG_0? R = 8.314 JK^{-1} mol^{-1}, T = 300 K.

Ans:

Now,

$$\Delta G^{\ominus} = -2.303 RT \log eq$$

= (2.303)(8.314 × $kJK^{-1}mol^{-1}$)(300K) $\log 10$

= -5744.14 $Jmol^{-1}$

= -5.744 $kJmol^{-1}$

Q-21: Comment on the thermodynamic stability of NO(g), given,

(1/2)N$_{2(g)}$ + (1/2)O$_{2(g)}$ → NO$_{(g)}$; $\Delta_r H^{\ominus} = 90 kJmol^{-1}$

NO$_{(g)}$ + (1/2)O$_{2(g)}$ → NO$_{2(g)}$; $\Delta_r H^{\ominus} = -74 kJmol^{-1}$
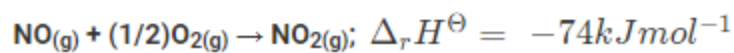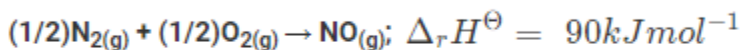
Ans:

The +ve value of $\Delta_r H$ represents that during $NO_{(g)}$ formation from O_2 and N_2, heat is absorbed. The obtained

product, $NO_{(g)}$ is having more energy than reactants. Thus, $NO_{(g)}$ is unstable.

The -ve value of $\Delta_r H$ represents that during $NO_{2(g)}$ formation from $O_{2(g)}$ and $NO_{(g)}$, heat is evolved. The

obtained product, $NO_{2(g)}$ gets stabilized with minimum energy.

Thus, unstable $NO_{(g)}$ converts into stable $NO_{2(g)}$.

Q-22: Calculate the entropy change in surroundings when 1.00 mol of $H_2O(l)$ is formed under standard conditions. $\Delta_f H^0$= −286 kJ mol⁻¹.

Ans:

$\Delta_r H^{\Theta} = -286 kJmol^{-1}$ is given so that amount of heat is evolved during the formation of 1 mole of

$H_2O_{(l)}$.

Thus, the same heat will be absorbed by surrounding Q_{surr} = +286 $kJmol^{-1}$.

Now, ΔS_{surr} = $Q_{surr}/7$

$= \dfrac{286kJmol^{-1}}{298K}$

Therefore, $\Delta S_{surr} = 959.73 Jmol^{-1}K^{-1}$