CHAPTER - 6
THERMODYNAMICS

Question 6.1:

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.

Answer

A thermodynamic state function is a quantity whose value is independent of a path. Functions like p, V, T etc. depend only on the state of a system and not on the path. Hence, alternative (ii) is correct.

Question 6.2:

For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) $q = 0$

(iv) $w = 0$

Answer

A system is said to be under adiabatic conditions if there is no exchange of heat between the system and its surroundings. Hence, under adiabatic conditions, $q = 0$. Therefore, alternative (iii) is correct.

Question 6.3:

The enthalpies of all elements in their standard states are:

(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

Answer

The enthalpy of all elements in their standard state is zero. Therefore, alternative (ii) is correct.

Question 6.4:

$\Delta U^{\theta}$of combustion of methane is – X kJ mol^{-1}. The value of ΔH^{θ} is

(i) $= \Delta U^{\theta}$

(ii) $> \Delta U^{\theta}$

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

(iv) = 0

Answer

Since $\Delta H^{\theta} = \Delta U^{\theta} + \Delta n_g RT$ and $\Delta U^{\theta} = -X$ kJ mol^{-1},

$\Delta H^{\theta} = (-X) + \Delta n_g RT. \Rightarrow \Delta H^{\theta} < \Delta U^{\theta}$

Therefore, alternative (iii) is correct.

Question 6.5:

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

$CH_{4(g)}$ 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}.

Answer

According to the question,

(i) $CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(g)}$

$\Delta H = -890.3 \text{ kJ mol}^{-1}$

(ii) $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$

$\Delta H = -393.5 \text{ kJ mol}^{-1}$

(iii) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$

$\Delta H = -285.8 \text{ kJ mol}^{-1}$

Thus, the desired equation is the one that represents the formation of $CH_{4\,(g)}$ i.e.,

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$

$$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_c H_{H_2} - \Delta_c H_{CO_2}$$

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

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

∴ Enthalpy of formation of $CH_{4(g)}$ = −74.8 kJ mol^{-1} Hence, alternative (i) is correct.

Question 6.6:

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

Answer

For a reaction to be spontaneous, ΔG should be negative.

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

According to the question, for the given reaction,

ΔS = positive

ΔH = negative (since heat is evolved)

⇒ ΔG = negative

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

Question 6.7:

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?

Answer

According to the first law of thermodynamics,

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

Where,

ΔU = change in internal energy for a process q

= heat

W = work Given,

q = + 701 J (Since heat is absorbed)

W = –394 J (Since work is done by the system)

Substituting the values in expression (i), we get

ΔU = 701 J + (–394 J)

ΔU = 307 J

Hence, the change in internal energy for the given process is 307 J.

Question 6.8:

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 enthalpy change for the reaction at 298 K.

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

Answer

Enthalpy change for a reaction (ΔH) is given by the expression,

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

Where,

ΔU = change in internal energy

Δn_g = change in number of moles

For the given reaction,

$\Delta n_g = \Sigma n_g$ (products) – Σn_g (reactants)

= (2 – 2.5) moles

Δn_g = –0.5 moles

And,

ΔU = –742.7 kJ mol^{-1}

T = 298 K

R = 8.314 × 10^{-3} kJ mol^{-1} K^{-1}

Substituting the values in the expression of ΔH:

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

$= -742.7 - 1.2$

$\Delta H = -743.9 \text{ kJ mol}^{-1}$

Question 6.9:

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}.

Answer

From the expression of heat (q),

$q = m.\ c.\ \Delta T$ Where,

c = molar heat capacity m

= mass of substance

ΔT = change in temperature

Substituting the values in the expression of q:

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

$q = 1066.7$ J q

= 1.07 kJ

Question 6.10:

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.

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

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

Answer

Total enthalpy change involved in the transformation is the sum of the following changes:

(a) Energy change involved in the transformation of 1 mol of water at 10°C to 1 mol of water at 0°C.

(b) Energy change involved in the transformation of 1 mol of water at 0° to 1 mol of ice at 0°C.

(c) Energy change involved in the transformation of 1 mol of ice at 0°C to 1 mol of ice at −10°C.

$$\text{Total } \Delta H = C_p\left[H_2OCl\right]\Delta T + \Delta H_{\text{freezing}} + C_p\left[H_2O_{(s)}\right]\Delta T$$

= (75.3 J mol^{-1} K^{-1}) (0 − 10)K + (−6.03 × 10^3 J mol^{-1}) + (36.8 J mol^{-1} K^{-1}) (−10 − 0)K

= −753 J mol^{-1} − 6030 J mol^{-1} − 368 J mol^{-1}

= −7151 J mol^{-1}

= −7.151 kJ mol^{-1}

Hence, the enthalpy change involved in the transformation is −7.151 kJ mol^{-1}.

Question 6.11:

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.

Answer

Formation of CO_2 from carbon and dioxygen gas can be represented as:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta_f H = -393.5 \text{ kJ mol}^{-1}$$

(1 mole = 44 g)

Heat released on formation of 44 g CO_2 = −393.5 kJ mol^{-1}

∴ Heat released on formation of 35.2 g CO_2

$$= \frac{-393.5 \text{ kJ mol}^{-1}}{44 \text{ g}} \times 35.2 \text{ g}$$

= −314.8 kJ mol^{-1}

Question 6.12:

Enthalpies of formation of $CO_{(g)}$, $CO_{2(g)}$, $N_2O_{(g)}$ and $N_2O_{4(g)}$ are −110 kJ mol^{-1}, − 393 kJ mol^{-1}, 81 kJ mol^{-1} and 9.7 kJ mol^{-1} respectively. Find the value of $\Delta_r H$ for the reaction:

$$N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O_{(g)} + 3CO_{2(g)}$$

Answer

$\Delta_r H$ for a reaction is defined as the difference between $\Delta_f H$ value of products and $\Delta_f H$ value of reactants.

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

For the given reaction,

$N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O_{(g)} + 3CO_{2(g)}$

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

Substituting the values of $\Delta_f H$ for N_2O, CO_2, N_2O_4, and CO from the question, we get:

$$\Delta_r H = \left[\left\{81 \text{ kJ mol}^{-1} + 3(-393)\text{kJ mol}^{-1}\right\} - \left\{9.7\text{kJ mol}^{-1} + 3(-110)\text{kJ mol}^{-1}\right\}\right]$$

$$\Delta_r H = -777.7 \text{ kJ mol}^{-1}$$

Hence, the value of $\Delta_r H$ for the reaction is $-777.7 \text{ kJ mol}^{-1}$.

Question 6.13:

Given

$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$; $\Delta_r H^\theta = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of NH_3 gas?

Answer

Standard enthalpy of formation of a compound is the change in 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.

Re-writing the given equation for 1 mole of $NH_{3(g)}$,

$$\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \longrightarrow NH_{3(g)}$$

∴ Standard enthalpy of formation of $NH_{3(g)}$

= ½ $\Delta_r H^\theta$

= ½ (−92.4 kJ mol^{-1})

= −46.2 kJ mol^{-1}

Question 6.14:

Calculate the standard enthalpy of formation of $CH_3OH_{(l)}$ from the following data:

$CH_3OH_{(l)} + \frac{3}{2}O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$; $\Delta_r H^\theta = -726$ kJ mol^{-1}

$C_{(g)} + O_{2(g)} \longrightarrow CO_{2(g)}$; $\Delta_c H^\theta = -393$ kJ mol$_{-1}$

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$; $\Delta_f H^\theta = -286$ kJ mol^{-1}.

Answer

The reaction that takes place during the formation of $CH_3OH_{(l)}$ can be written as:

$C_{(s)} + 2H_2O_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CH_3OH_{(l)}$ (**1**)

The reaction (**1**) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) – equation (i)

$\Delta_f H^\theta [CH_3OH_{(l)}] = \Delta_c H^\theta + 2\Delta_f H^\theta [H_2O_{(l)}] - \Delta_r H^\theta$

$= (-393 \text{ kJ mol}^{-1}) + 2(-286 \text{ kJ mol}^{-1}) - (-726 \text{ kJ mol}^{-1})$

$= (-393 - 572 + 726) \text{ kJ mol}^{-1}$

$\therefore \Delta_f H^\theta [CH_3OH_{(l)}] = -239 \text{ kJ mol}^{-1}$

Question 6.15:

Calculate the enthalpy change for the process

$CCl_{4(g)} \rightarrow C_{(g)} + 4Cl_{(g)}$ and calculate bond enthalpy of C–Cl in $CCl_{4(g)}$.

$\Delta_{vap} H^\theta (CCl_4) = 30.5$ kJ mol^{-1}.

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

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

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

Answer

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

(i) $CCl_{4(l)} \longrightarrow CCl_{4(g)}$ $\Delta_{vap}H^{\theta}$ = 30.5 kJ mol^{-1}

(ii) $C_{(s)} \longrightarrow C_{(g)}$ $\Delta_a H^{\theta}$ = 715.0 kJ mol^{-1}

(iii) $Cl_{2(g)} \longrightarrow 2Cl_{(g)}$ $\Delta_a H^{\theta}$ = 242 kJ mol^{-1}

(iv) $C_{(g)} + 4Cl_{(g)} \longrightarrow CCl_{4(g)}$ $\Delta_f H$ = –135.5 kJ mol^{-1}

Enthalpy change for the given process $CCl_{4(g)} \longrightarrow C_{(g)} + 4Cl_{(g)}$, can be calculated using the following algebraic calculations as:

Equation (ii) + 2 × Equation (iii) – Equation (i) – Equation (iv)

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

= (715.0 kJ mol^{-1}) + 2(242 kJ mol^{-1}) – (30.5 kJ mol^{-1}) – (–135.5 kJ mol^{-1})

$\therefore \Delta H$ = 1304 kJ mol^{-1}

Bond enthalpy of C–Cl bond in $CCl_{4\,(g)}$

$= \frac{1304}{4}$ kJ mol^{-1}

= 326 kJ mol^{-1}

Question 6.16:

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

Answer

ΔS will be positive i.e., greater than zero

Since $\Delta U = 0$, ΔS will be positive and the reaction will be spontaneous.

Question 6.17:

For the reaction at 298 K,

2A + B → C

ΔH = 400 kJ mol^{-1} and ΔS = 0.2 kJ K^{-1} mol^{-1}

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

Answer

From the expression,

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

Assuming the reaction at equilibrium, ΔT for the reaction would be:

$$T = (\Delta H - \Delta G)\frac{1}{\Delta S}$$

$$= \frac{\Delta H}{\Delta S} \qquad (\Delta G = 0 \text{ at equilibrium})$$

$$= \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}}$$

$T = 2000$ K

For the reaction to be spontaneous, ΔG must be negative. Hence, for the given reaction to be spontaneous, T should be greater than 2000 K.

Question 6.18:

For the reaction,

$2Cl_{(g)} \rightarrow Cl_{2(g)}$, what are the signs of ΔH and ΔS ?

Answer

ΔH and ΔS are negative

The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy is being released. Hence, ΔH is negative.

Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased, ΔS is negative for the given reaction.

Question 6.19:

For the reaction

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

$\Delta U^{\theta} = -10.5$ kJ and $\Delta S^{\theta} = -44.1$ JK^{-1}.

Calculate ΔG^{θ} for the reaction, and predict whether the reaction may occur spontaneously.

Answer

For the given reaction,

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

$\Delta n_g = 2 - (3)$

$= -1$ mole

Substituting the value of ΔU^θ in the expression of ΔH:

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

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

$= -10.5\ kJ - 2.48\ kJ$

$\Delta H^\theta = -12.98\ kJ$

Substituting the values of ΔH^θ and ΔS^θ in the expression of ΔG^θ:

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

$= -12.98\ kJ - (298\ K)\ (-44.1\ J\ K^{-1})$

$= -12.98\ kJ + 13.14\ kJ$

$\Delta G^\theta = +\ 0.16\ kJ$

Since ΔG^θ for the reaction is positive, the reaction will not occur spontaneously.

Question 6.20:

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

Answer

From the expression,

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

ΔG^θ for the reaction,

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

$= -5744.14\ Jmol^{-1}$

$= -5.744\ kJ\ mol^{-1}$

Question 6.21:

Comment on the thermodynamic stability of $NO_{(g)}$, given

$\frac{1}{2}N_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{(g)}$; $\Delta_r H^\theta$ = 90 kJ mol^{-1}

$NO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow NO_{2(g)}$: $\Delta_r H^\theta$= −74 kJ mol^{-1}

Answer

The positive value of $\Delta_r H$ indicates that heat is absorbed during the formation of $NO_{(g)}$. This means that $NO_{(g)}$ has higher energy than the reactants (N_2 and O_2). Hence, $NO_{(g)}$ is unstable.

The negative value of $\Delta_r H$ indicates that heat is evolved during the formation of $NO_{2(g)}$ from $NO_{(g)}$ and $O_{2(g)}$. The product, $NO_{2(g)}$ is stabilized with minimum energy.

Hence, unstable $NO_{(g)}$ changes to unstable $NO_{2(g)}$.

Question 6.22:

Calculate the entropy change in surroundings when 1.00 mol of $H_2O_{(l)}$ is formed under standard conditions. $\Delta_f H^\theta$ = −286 kJ mol^{-1}.

Answer

It is given that 286 kJ mol^{-1} of heat is evolved on the formation of 1 mol of $H_2O_{(l)}$. Thus, an equal amount of heat will be absorbed by the surroundings. q_{surr} = +286 kJ mol^{-1}

Entropy change (ΔS_{surr}) for the surroundings = $\frac{q_{surr}}{7}$

$= \frac{286 \text{ kJ mol}^{-1}}{298 \text{ k}}$

$\therefore \Delta S_{surr}$ = 959.73 J mol^{-1} K^{-1}