Chapter – 6 (Thermodynamics)

Exercise Questions:

Question :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:

ii.) A quantity which is independent of path,

Reason:

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

Question :2 For the process to occur under adiabatic condition, the correct condition is:

- i.) $\Delta T = 0$
- ii.) $\Delta p = 0$
- iii.) $q = 0$
- iv.) $w = 0$

Answer:

iii.) $q = 0$

Reason:

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

Question :3 The enthalpies of all elements in their standard stars are:

    I.   **Unity**

    II.   **Zero**

    III.   **< 0**

Answer:

ii.) Zero.

Question:4 ΔU^- of combustion of methane is –X kJ mol^{-1}. The value of ΔH^- is

    i.) $= \Delta U^-$

    ii.) $> \Delta U^-$

    iii.) $< \Delta U^-$

    iv.) $= 0$

Answer:

iii.) $< \Delta U^-$

Reason:

$\Delta H^- = \Delta U^- + \Delta_{ng}RT$; $\Delta U^- = - y$ kJ mol^{-1}

$\Delta H^- = (-Y) + \Delta n_g RT = \Delta H^- < \Delta U^-$

Question :5 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, -890.3 kJ MIL) -1 -393.5 kJ Molly) -1, and -285.8 kJ mom) -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.   52.27 kJ mol)-1

Answer:

    i.)   -74.8 kJ mol^{-1}

           $CH4_{(g)} + 2O2_{(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$

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

    2.) $C(g) + O_2(g) \rightarrow CO_2(g)$

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

    3.) $2H_{2(g)} + O_2(g) \rightarrow 2H_2O(g)$

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

           $C_{(s)} + 2H_2(g) \rightarrow CH_4(g)$
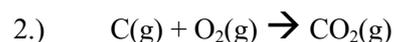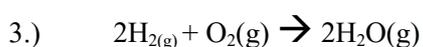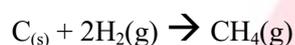
$\Delta_f H_{CH4} = \Delta_c H_c + 2\Delta_f H_{H2} - \Delta_f H_{CO2}$

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

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

Question :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**

Answer:

Possible at any temperature.

Δ G should be –ve, for spontaneous reaction to occur

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

As per given in equation,

Δ H is –ve

ΔS is positive

Therefore, ΔG is negative

So, the reaction will be possible at any temperature.

Question :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:
As per thermodynamics 1st law,

ΔU = 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,

ΔU = 801 + (-594)

ΔU = 207 J

Question :8 The reaction of cyanide, NH2CN (s), with dioxygen was carried out in a bomb calorimeter, ΔU was found to be -742.7 kJ mol)-1 at 298 K. Calculate enthalpy change for the reaction at 298 K.

NH2CN(g) + 3/2O2(g) → N2(g) + CO2(g) + H2O(l)

Answer:

ΔH = is given by,

ΔH = ΔU + Δn$_g$RT ......(1)

Δn$_g$ = change in number of moles

ΔU = change in internal energy

Here,

T = 298K

ΔU = -742.7 kJ mol^{-1}

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

Now, from (1)

ΔH = (-742.7 kJ mol^{-1}) + (0.5mol)(298K)(8.314 x 10^{-3}kJmol^{-1}K^{-1})

= -742.7 + 1.2

= -741.5 kJmol⁻¹

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

Answer:

Expression of heat,

$Q = mC_P\Delta T$ ………..(a)

ΔT = change in temperature

c = molar heat capacity

From (a)

q = (60 / 27 mol)(24mol⁻¹K⁻¹)(20K)

q = 1066.67 J = 1.067 KJ.

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

Cp (H2O(l)) = 75.3 J mol⁻¹ K⁻¹

Cp (H2O(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.

Total ΔH = Cp [H2OCl] ΔT + ΔHfreezing + Cp [H2O(s)] ΔH

= (75.3 J mol⁻¹ K⁻¹) (0 - 10)K + (-6.03 × 10³ 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 :11 Enthaply of formation of CO2 is -393.5 kJ mol)-1. Calculate the heart released upon formation of 35.2 g of CO2 from carbon and dioxygen gas.

Answer:

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

$C(s) + O_{2(g)} \rightarrow CO_2(g)$: $\Delta_fH = -393.5$ kJ mol$_{-1}$
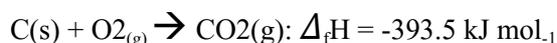
1 mole CO_2 = 44g

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

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

= -393.5kJ mol-1 x 35.2 g / 44g

= -314.8 kJ mol^{-1}

Question :12 Enthaplies of formation of CO(g), N2O(g), CO2(g) and N2O4(g) are -110, -393, 81 and 9.7 kJ mol^{-1} respectively. Find the value of H for the reaction : N2O4(g) + 3CO(g) -> N2O(g) + 3CO2(g)

Answer:

Δ_rH for any reaction is defined as the difference between Δ_fH value of product and Δ_fH value of reactants"

$\Delta_rH = \Sigma \Delta_fH$(products) - $\Sigma \Delta_fH$ (reactants)

Now, for

$N_2O_4(g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$

$\Delta_rH = [\Delta_fH+ (3 \Delta_fH(CO_2)) – (\Delta_fH(N_2O_4) + 3 \Delta_fH(CO))]$

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

$\Delta_rH = [\{81kJ/mol + 3(-393) kJ / mol\} – \{9.7 kJ / mol + 3(-110) kJ / mol\}]$

$\Delta_rH = -777.7$ kJ / mol.

Question :13 Given

N2(g) + 3H2(g) -> 2NH3(g); $\Delta_rH = -92.4$ kJ mol^{-1}

What is the standard enthalpy of formation of NH3 gas?

Answer:

" 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 constituents elements in their standard atste"

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

$(0.5)N_2(g) + (1.5)H_2(g) \rightarrow 2NH_3(g)$

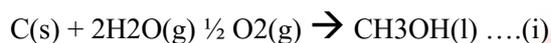Therefore, standard enthalpy for formation of ammonia gas

= 0.5 Δ_rH^-

= (0.5)(-92.4 kJ mol^{-1})

= -46.2 kJ / mol

Question :14 Calculate the standard enthaply of formation of CH3OH(l) from the following data:

CH3OH(l) + 3/2 O2(g) -> CO2(g) + 2H2O(l); H = -726kJ mol⁻¹; $\Delta_r H^-$ = -726 kJ mol⁻¹

C(graphite) + O2(g) -> CO2(g); $\Delta_c H^-$ = -393 kJ mol⁻¹

H2(g) + ½ O2(g) -> H2O(l); $\Delta_f H^-$ = -286 kJ mol⁻¹

Answer:

C(s) + 2H2O(g) ½ O2(g) → CH3OH(l) ….(i)
CH3OH(l) can be obtained as follows,

$\Delta_f H^-$[CH3OH(l)] = $\Delta_c H^-$

2 $\Delta_f H^-$ - $\Delta_r H^-$

= (-393 kJ / mol) + 2(-286 kJ / mol) – (-726 kJ / mol)

= (-393 – 572 + 726) kJ / mol

= -239 kJ / mol

Question :15 Calculate the enthalpy change for the process
CCl4(g) -> C(g) + 4Cl(g)

And calculate bond enthalpy of C-Cl in CCl4(g).

$\Delta_{vao} H^-$(CCl4) = 30.5 kj mol⁻¹

$\Delta_f H^-$(CCl4) = -135.5 kJ mol⁻¹

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

$\Delta_a H^-$(CCl2) = 242 kJ mol⁻¹

Answer:

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

(i) CCl4(l) → CCL4(g) $\Delta vapH^0$ = 30.5 kJ mol⁻¹

(ii) C(s) → C(g) ΔaH^0 = 715.0 kJ mol⁻¹

(iii) Cl2(g) → 2Cl(g) ΔaH^0 = 242 kJ mol⁻¹

(iv) C(g) + 4Cl(g) → CCl4(g) ΔfH = -135.5 kJ mol⁻¹

Enthalpy change for the given process C(g) + 4Cl(g) → CCl4(g) can be calculated using the following algebraic calculations as:

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

$\Delta H = \Delta aH^0$(C) + 2ΔaH^0 (Cl2) - $\Delta vapH^0$ - ΔfH

= (715.0 kJ mol-1) + 2(242 kJ mol-1) - (30.5 kJ mol-1) - (-135.5 kJ mol-1)

∴ΔH = 1304 kJ mol⁻¹

Bond enthalpy of C-Cl bond in CCl4(g) = 326 kJ mol^{-1}

Question :16 For an isolated system, ΔU = 0 , what will be S?

Answer:

ΔU is positive; ΔU > 0

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

Question :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:

Now,

ΔG $_=$ ΔH - TΔS

Let, the given reaction is at equilibrium, then ΔT will be:

T = (ΔH - ΔG)1/ΔS $\Delta H / \Delta S$; (ΔG = 0 at equllibrium0

= 400 kJ / mol / 0.2 kJ mol^{-1}K^{-1}

Therefore, T = 2000K

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

Question :18 For the reaction,

2Cl(g) -> Cl2(g), what are the signs of ΔH and ΔS?

Answer:

Δ S and ΔH are having –ve signs.

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.
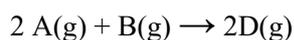
Question :19 For the reaction

2A(g) + B(g) -> 2D(g)

$\Delta U^- = -10.5$ kJ and $\Delta S^- = -44.1 JK-1$

Calculate ΔG^- for the reaction, and predict whether the reaction may occur spontaneously.

Answer:

For the given reaction,

2 A(g) + B(g) $\longrightarrow$ 2D(g)

$\Delta ng = 2 - (3) = -1$ mole

Substituting the value of ΔU^0, in the expression of ΔH:

$\Delta H^o = \Delta U^o + \Delta ngRT$

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

$= -10.5 \text{ kJ} - 2.48 \text{ kJ}$

$\Delta H^o = -12.98$ kJ

Substituting the values of ΔH^o and ΔS^o, in the expression of ΔH:

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

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

$= -12.98 \text{ kJ} + 13.14 \text{ kJ}$

$\Delta G^o = + 0.16$ kJ

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

Question :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.

Answer:

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

$= (2.303)(8.314 \times \text{kJ} / \text{k} / \text{mol0}(300K) \text{ log 10}$

$= -5744.14 \text{ J mol}^{-1}$

$= -5.744 \text{ kJ} / \text{mol}.$

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

½ N2(g) + ½ O2(g) -> NO(g) ; $\Delta H^- = 90$ kJ mol^{-1}

NO(g) + ½ O2(g) -> NO2(g) ; $\Delta H^- = -74$ kJ mol^{-1}

Answer:

The +ve of $\Delta_r H$ represents that during NO(g) formation from O2 and N2, heat is absorbed. The obtained product, NO(g) is having more energy than reactants. Thus, NO(g) is unstable.

The –ve value Δ_rH 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 $NO_2(g)$.

Question :22 Calculate the entropy change in surrounding when 1.00 mol of H2O(l) is formed under standard conditions. $\Delta_fH^- = -286$ kJ mol^{-1}.

Answer:

Δ_rH^- = -286 kJ / mol is given so that amount of heat is evolved during the formation of 1 mole of H2O(l).

Thus, the same heat will be absorbed by surrounding Q_{surr} = +286 kJ / mol

Now, $\Delta S_{surr} = Q_{surr}/7$

$= \dfrac{286 \text{ kJ / mol}}{298 \text{ K}}$

Therefore, ΔS_{surr} = 959.73 J/ mol K.