I PUC – CHEMISTRY
CHAPTER - 06

Thermodynamics

One mark questions

1. Define System.
2. Define surroundings.
3. What is an open system? Give one example.
4. What is closed system? Give one example.
5. What is an isolated system? Give one example.
6. What is an extensive property? Give example.
7. What is an intensive property? Give example.
8. What is isothermal process?
9. What is an adiabatic process?
10. Write an expression for work done during an isothermal reversible expansion of an ideal gas.
11. State I law of Thermodynamics.
12. Write mathematical expression to represent I law.
13. Define Enthalpy.
14. Write mathematical statement of enthalpy.
15. What is an exothermic reaction?
16. Give one example for exothermic reaction.
17. What is an endothermic reaction?
18. Give one example for endothermic reaction.
19. Define heat of a reaction ($\Delta \overset{o}{H}$ r)
20. Define standard enthalpy of formation.
21. State Hess's law of constant heat summation.
22. What is spontaneous process?
23. Give one example for spontaneous reaction.
24. Define entropy.
25. Write the S.I.Unit of entropy.
26. State second law of thermodynamics.
27. Define free energy.
28. Write mathematical statement of free energy.
29. Define standard free energy change for a reaction.
30. Out of Diamond and graphite which one has zero value of standard free energy of formation.
31. What is the change in entropy when sugar is dissolved in water?
32. What happens to entropy when water freezes?
33. Give the mathematical form of Gibbs-Helmholtz equation.
34. What is the state of a chemical reaction when i) $\Delta G = 0$ ii) $\Delta G > 0$ iii) $\Delta G < 0$
35. Mention the sign of ΔH for the formation of explosives.
36. Write the thermochemical equation for combustion of Benzene(ℓ)
37. Write the mathematical statement of II law of thermodynamics.

38. How is change in enthalpy related to change in internal energy?
39. What is meant by free expansion?
40. State III Law of thermodynamics.
41. Define reversible process.
42. Define irreversible process.
43. Define internal energy.
44. Give an expression for the work done during an adiabatic process.
45. Define the term state function.
46. What is state of a system?
47. What is standard state of a system?
48. Define Enthalpy of combustion.
49. How is standard free energy change of a reaction is related to equilibrium constant?
50. What is the change in internal energy of a system if 10 joules of heat is supplied to it and 15 joules of work is done by it?
51. Give a chemical reaction for which $\Delta H = \Delta U$.
52. A closed thermos flask containing hot coffee represents what type of a system.
53. What is the relationship between ΔH and ΔU for the reaction.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

54. Choose the correct answer:
    a) 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
    b) 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
    c) The enthalpies of all elements in their standard states are
         i) unity   ii) zero   iii) < 0   iv) different for each element
    d) $\Delta U^{\ominus}$ of combustion of methane is $-X KJ\ mol^{-1}$. The value of $\Delta H^{\ominus}$ is
         i) $= \Delta U^{\ominus}$ ii) $> \Delta U^{\ominus}$ iii) $< \Delta U^{\ominus}$ iv) 0
    e) The enthalpy of combustion of methane, graphite and dihydrogen at 298K are $-890.3\ kJ\ mol^{-1}$, $- 393.5\ k\ J\ mol^{-1}$ and $- 285.8\ kJ\ mol^{-1}$ respectively. Enthalpy of formation of $CH4(g)$ will be
         i) $-74.8\ k\ J\ mol^{-1}$ ii) $-52.27\ k\ J\ mol^{-1}$
         iii) $+74.8\ k\ J\ mol^{-1}$ iv) $+ 52.26\ k\ J\ mol^{-1}$
    f) 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

Two Marks questions

1. In a process, 701J of heat is absorbed by a system and 394J of work is done by the system. What is the change in internal energy for the process?
2. For the reaction; $2Cl\ (g) \rightarrow Cl_2(g)$; what will be the signs of ΔH and ΔS?

3. Define standard Enthalpy of vapourisation.
4. Write thermochemical equation for the vaporization of Ethanol.
5. Calculate the Enthalpy of vapourisation of Ethanol, given enthalpies of formation of liquid ethanol and gaseous Ethanol as -277.6kJ and -235.4kJ respectively.
6. Define standard enthalpy of fusion or molar enthalpy of fusion.
7. Define standard enthalpy of sublimation.
8. Define enthalpy of atomization ($\Delta aH^{\ominus}$)
9. Define bond dissociation enthalpy.
10. For a equilibrium reaction.

   A + 2B $\rightleftharpoons$ C ΔH = + 400kJ and ΔS is +200 J/K. Calculate the temperature above which the reaction becomes spontaneous
11. For $Cl_2 \rightarrow 2Cl$. Assign the signs for ΔH and ΔS
   (g)   (g)
12. Define enthalpy of a solution $\Delta_{sol}H^{\ominus}$
13. For the reaction

   $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$ Entropy change and enthalpy change at 298K are -549.4 J|K|mol and -1648 x 10^3 J | mol respectively. Calculate the free energy change for the reaction.
14. For an isolated system ΔU = 0; what will be ΔS.
15. Comment on the thermodynamic stability of NO(g) and NO_2(g) given

   ½ N_2(g) + ½ O_2(g) $\rightarrow$ NO(g) ; $\Delta_f H^{\ominus}$ = 90 kJ mol^{-1}

   NO(g) + ½ O_2(g) $\rightarrow$ NO_2(g) ; $\Delta_f H^{\ominus}$ = -74 kJ mol^{-1}
16. Given : N_2(g) + $3H_2$(g) $\rightarrow$ $2NH_3$(g) ; $\Delta_r H^{\ominus}$ = -92.4 kJ mol^{-1}

   What is the standard enthalpy of formation of NH_3 gas.
17. Explain the spontaineity of Exothermic reactions using Gibb's equation.
18. Explain the spontaineity of endothermic reactions using Gibb's equation.
19. Calculate the entropy change in surroundings when 1.0 mol of $H_2O(\ell)$ is formed under standard conditions. Given $\Delta H^{\ominus}$ = -286 kJ mol^{-1}
20. Under what conditions $\Delta H < \Delta U$. Give an example.
21. For an isolated system ΔU = 0; what will be ΔS?
22. For a reaction at 298 K 2A + B $\rightarrow$ 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?
23. Calculate the heat of formation of Carbon-monoxide from the following data.

   i)   C(s) + O_2(g) $\rightarrow$ CO_2(g) ; $\Delta_f H$ = -393.5 kJ

   ii) CO(g) + ½ O_2(g) $\rightarrow$ CO_2(g) ; $\Delta_f H$ = -282.8 kJ
24. Calculate the work done when a gas expands at a constant temperature from volume 2 x 10^{-3} m^3 to 4 x 10^{-3} m^3 against a constant pressure of 1.2 x 10^5 Nm^{-2}.
25. Define : specific heat capacity, Molar heat capacity.
26. Standard enthalpy of vapourisation of water at 373 K is 40.66 k J mol^{-1}. Calculate internal energy of vapourisation.

3 and 4 marks questions.

1. The reaction of cyanamide, $NH_2CN(s)$ with oxygen was affected in a bomb calorimeter and ΔU was found to be -742.7 kJ mol^{-1} of cyanamide at 298K. Calculate the enthalpy change for the reaction at 298 K.
   $$NH_2CN(s) + 3/2\ O_2\ (g) \rightarrow N_2(g) + CO_2(g) + H_2O(\ell)$$
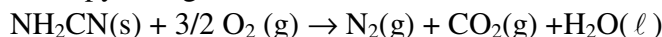
2. Calculate the number of kJ necessary to raise the temperature of 60 g of aluminium from 35° to 55° C. Molar heat capacity of Al is 24 J mol^{-1} K^{-1}.

3. Calculate the enthalpy change on freezing of 1.0 mol of water at 10.0^oC to ice at -10.0^oC. $\Delta_{fus}H$ = 6.03 kJ mol^{-1} at 0^oC. Cp $[H_2O(\ell)]$ = 75.3 J mol^{-1} k^{-1}. $Cp[H_2O(s)]$ = 36.8 J mol^{-1} k^{-1}.

4. Enthalpy of combustion of carbon to carbon-di-oxide is -393.5 k J mol^{-1}. Calculate the heat released upon formation of 35.2g of CO_2 from carbon and oxygen gas.
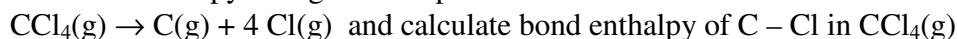
5. Calculate the enthalpy of the reaction
   $$N_2O_4\ (g) + 3CO(g) \rightarrow N_2O(g) + 3CO_2(g)$$
   Given that : $\Delta_f H\ CO(g)$ = -11- k J mol^{-1}
   $\Delta_f H\ CO2(g)$ = -393 k J mol^{-1}
   $\Delta_f HN_2O(g)$ = 81 k J mol^{-1}
   $\Delta_f H\ N_2O_4(g)$ = 9.7 k J mol^{-1}
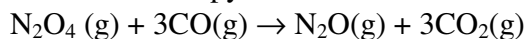
6. Calculate the standard enthalpy of formation of $CH_3OH(\ell)$ from the following data.
   i) $CH_3OH(\ell) + \dfrac{3}{2} O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$; $\Delta_f H^\Theta$ = -726 kJ mol^{-1} $\rightarrow$ (i)
   ii) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta_c H^\Theta$ = -393 kJ mol^{-1} $\rightarrow$ (ii)
   iii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$; $\Delta_f H^\Theta$ = -286 kJ mol^{-1} $\rightarrow$(iii)

7. Calculate the enthalpy change for the process
   $CCl_4(g) \rightarrow C(g) + 4\ Cl(g)$ and calculate bond enthalpy of C – Cl in $CCl_4(g)$
   Given : $\Delta_{vap}H^\Theta\ (CCl_4)$ = 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}

8. For a reaction ; $2A\ (g) + B(g) \rightarrow 2D(g)$
   ΔU_{298} = -10.5 kJ and ΔS^Θ = -44.1 J k^{-1}.
   Calculate ΔU_{298} for the reaction and predict whether the reaction is spontaneous or not.

9. The equilibrium constant for the reaction is 10. Calculate the value of ΔG^Θ ; given R = 8 J k^{-1} mol^{-1} ; T = 300 K

10. Explain the determination of ΔU using bomb caloriemeter.

11. Explain the determination of ΔH using caloriemeter.

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Thermodynamics

One mark Answers

1. It is the specific part of the universe in which energy changes are taking place.
2. Rest of the universe which surrounds the system.
3. A system is said to be open if both matter and energy can be exchanged with the surroundings. Example: Water kept in an open beaker.
4. A system is said to be closed if it exchanges only energy with the surroundings. Example. Water kept in a closed container.
5. A system is said to be isolated if it neither exchanges matter nor energy. Example: Coffee taken in a thermos flask.
6. Extensive properties of a system are the properties which depend upon the quantity of the matter present in the system. Example: Volume, internal energy, Enthalpy, heat capacity etc.
7. Intensive properties of a system are the properties which do not depend upon the quantity of the matter present in the system. Example: pressure, temperature, density, specific heat, surface tension etc.
8. A process is said to be isothermal if the temperature of the system remains constant. $(dT = 0)$
9. A process is said to be adiabatic if no heat exchange between the system and surroundings takes place. $(dq = 0)$
10. $W = -2.303 \ nRT \ \log \dfrac{P_1}{P_2}$

    $W = -2.303 \ nRT \ \log \dfrac{V_2}{V_1}$

11. Energy can neither be created nor destroyed, it can be transformed from one form to another.
12. $\Delta U = q + w,$ ΔU = change in internal energy
    q = heat supplied
    w = work done on the system
13. It is the sum of the internal energy and pressure volume energy.

14. $H = U + PV$ H = Enthalpy
    U = Internal energy
    PV = pressure volume energy
15. A reaction in which heat energy is evolved is an exothermic reaction.
16. $C \ (s) + O_2 \ (g) \rightarrow CO_2 \ (g) ; \Delta H = -393.5 \ k \ J.$
17. A reaction in which heat energy is absorbed is an endothermic reaction.
18. $N_2(g) + O_2 \ (g) \rightarrow 2 \ NO \ (g)$
19. The change in heat that takes place in a chemical reaction represented by balanced chemical equation.
20. The change in enthalpy that takes place when one mole of compound is formed from its constituent elements, at standard conditions. [298 K, 101.3 k.Pa]

21. The heat change that takes place in a chemical reaction is independent of time taken and number of intermediate steps involved.
22. A process that can take place on its own with or without initiation is called spontaneous process.
23. $Zn + H_2SO_4 \rightarrow Zn\ SO_4 + H2 \uparrow$
24. Entropy is a measure of randomness or disorder of a system.
25. Joule / Kelvin / mole or $JK^{-1}\ mol^{-1}$
26. All spontaneous processes are thermodynamically irreversible
27. The amount of energy available for doing useful work under conditions of constant temperature and pressure.
28. $G = H - TS$.   G = free energy
                                   H = Enthalpy
                                   S = Entropy
                                   T = Temperature on Kelvin scale
29. The change in free energy that takes place when the reactants in their standard states are converted into product in their standard states at 298K and 101.3kPa.
30. Graphite.
31. Increases (or) positive
32. Decreases (or) negative
33. $\Delta G = \Delta H - T\Delta S$
34. i) Reaction attains equilibrium
       ii) Reaction is non spontaneous
      iii) Reaction is spontaneous
35. Positive
36. $C_6H_6\ (\ell)) + \frac{15}{2} O_2(g) \rightarrow 6\ CO_2(g) + 3\ H_2O(\ell)$ $\Delta H = - qkJ$
37. $\Delta S > 0$ or ΔS system $+ \Delta S$ surrounding > 0
38. $\Delta H = \Delta U + \Delta_{(g)}nRT$
39. Expansion of a gas in vacuum is called free expansion.
40. Entropy of perfectly crystalline solid at absolute zero is zero.
41. A process which can be reversed at any instant of time by increasing the opposing force by an infinitesimal amount.
42. A process which is carried out rapidly so that the system does not get a chance to attain equilibrium.
43. The energy possessed by the system due to its nature, chemical composition and thermodynamic state.
44. $W = n\ Cv(T_2 - T_1)$ for 'n' moles of a gas.
45. The variables like temperature, pressure, volume etc, which define the state of a system are called state functions.
46. Condition of the system expressed by giving definite values for its properties such as temperature, pressure, volume.
47. The state of a system at 298K and 101.3 k.Pa is known as standard state of a system.
48. The change in enthalpy that takes place when one mole of a substance is completely burnt in air or oxygen at a given temperature.
49. $\Delta G^o = - 2.303\ RT \log KP$
50. $\Delta U = q - w$

$$\Delta U = 10 - 15$$
$$\Delta U = -5 \text{ joules}$$
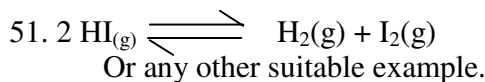
51. $2 HI_{(g)} \rightleftharpoons H_2(g) + I_2(g)$
    Or any other suitable example.
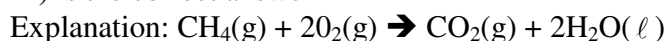52. Isolated system.
53. $\Delta H = \Delta U + RT$
54. a)   ii) is the correct answer
    b)   iii) is the correct answer
    c)   ii) is the correct answer
    d)   iii) is the correct answer
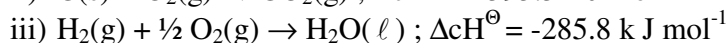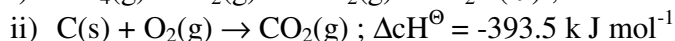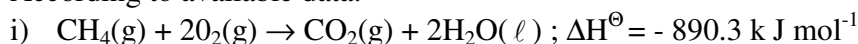   Explanation: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
$$\Delta^{ng} = 1 - 3 = -2$$
$$\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta^{ng}RT = \Delta U^{\ominus} - 2RT$$
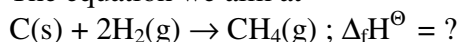$$\therefore \Delta H^{\ominus} < \Delta U^{\ominus}$$

    e) i) is the correct answer
       Explanation :
       According to available data:
       i) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$; $\Delta H^{\ominus} = -890.3$ k J mol^{-1}
       ii) $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta_cH^{\ominus} = -393.5$ k J mol^{-1}
       iii) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$; $\Delta_cH^{\ominus} = -285.8$ k J mol^{-1}
           The equation we aim at
           $C(s) + 2H_2(g) \rightarrow CH_4(g)$; $\Delta_fH^{\ominus} = ?$
           Equation (ii) + 2 × equation (iii) – equation (i) and the correct $\Delta_fH^{\ominus}$
           Value is
           $= (-393.5) + 2 × (-285.8) - (-890.3) = -74.8$ k J mol^{-1}
    f) (iv) is the correct answer.

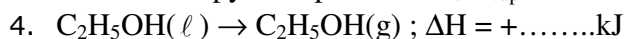## Two Marks Answers
1. Heat absorbed by the system, $q = 701J$
        Work done by the system, $w = -394J$
        Change in internal energy (ΔU) = q + w = 701 – 394
               = 307J
2. ΔH: negative (-ve) because energy is released in bond formation.
     ΔS : negative (-ve) because entropy decreases when atoms combine to form molecules.
3. Amount of heat required to vapourise one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its standard enthalpy of vapourisation or molar enthalpy of vapourisation, $\Delta_{vap}H^{\ominus}$
4. $C_2H_5OH(\ell) \rightarrow C_2H_5OH(g)$; $\Delta H = +........kJ$
5. $\Delta H_{vap} = H_p - H_R$
          = (-235.4 + 277.6)kJ
          = + 42.2kJ

6. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion.
   $\Delta_{fus} H^{\ominus}$

7. Standard enthalpy of sublimation, $\Delta_{sub}H^{\ominus}$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure.
   (1 bar)

8. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

9. It is the change in enthalpy when one mole of covalent bonds of the gaseous covalent compound is broken to form products in the gaseous phase.

10. $\Delta G = \Delta H - T \Delta S$
    At equilibrium $\Delta G = 0$, $\Delta H = T \Delta S$
    $$T = \frac{\Delta H}{\Delta S} = \frac{400 \times 10^3}{200}$$
    $$T = 2000 \text{ K}$$

11. $\Delta H = + ve$, $\Delta S = + ve$

12. It is the change in enthalpy when one mole of a substance is dissolved in a specified amount of a solvent.

13. $\Delta G = \Delta H - T\Delta S$
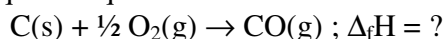 $$\Delta G = -1648 \times 10^3 - [(298)(-549.4)]$$
    $$= -1648000 + 163721.2$$
    $$= -1484278.8 \text{ J/mol} = -1484.27 \text{ kJ/mol}$$

14. Change in internal energy (ΔU) for an isolated system is zero because it does not exchange any energy with the surroundings. But entropy tends to increase in case of spontaneous reaction. Therefore, $\Delta S > 0$ or positive.

15. for NO(g) ; $\Delta_f H^{\ominus} = +ve$: unstable in nature
    For NO_2(g) ; $\Delta_f H^{\ominus} = -ve$: stable in nature.

16. $\Delta_f H^{\ominus} NH_3$(g) = -(92.4) / 2 = -46.2 kJ mol^{-1}

17. Gibb's equation is $\Delta G = \Delta H - T \Delta S$ ➔ (1)
    For exothermic reaction ΔH is –ve
    i) If ΔS is +ve according to equation (1)
    ΔG is –ve, reaction is spontaneous at all temperature.
    ii) If ΔS is –ve, according to equation (1)
    ΔG is –ve at low temperature such that
    $T \Delta S < \Delta H$. Reaction is spontaneous.

18. Gibb's equation is $\Delta G = \Delta H - T \Delta S$ ➔ (1)
    For endothermic reaction, ΔH is +ve
    i) If ΔS is +ve according to equation (1)
    ΔG is –ve, at high temperature
    such that $T \Delta S > \Delta H$. Reaction is spontaneous
    ii) If ΔS is –ve, according to equation (1)
    ΔG is always +ve. Reaction is nonspontaneous at all temperature.

19. $q_{rev} = (-\Delta H^{\ominus}) = -286$ kJ $mol^{-1} = 286000$ J mol^{-1}

$$\Delta S_{(surroundings)} = \frac{q_{rev}}{T} = \frac{(286000 Jmol^{-1})}{298 K}$$
$$= 959 \text{ J k}^{-1} \text{ mol}^{-1}$$

20. $\Delta H < \Delta U$; if Δ^{ng} is negative

Example: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
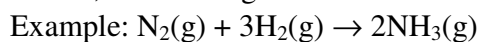
$\Delta^{ng} = 2 - 4 = -2$

21. Change in internal energy (ΔU) for an isolated system is zero because it does not exchange any energy with the surroundings. But entropy tends to increase in case of spontaneous reaction. Therefore, $\Delta S > 0$ or positive.

22. According to Gibbs – Helmholtz equation;

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

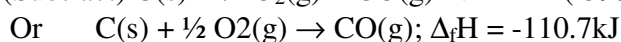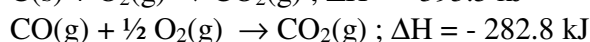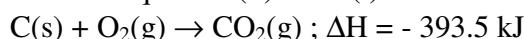For $\Delta G = O$; $\Delta H = T\Delta S$ or $T = \dfrac{\Delta H}{\Delta S}$

$$T = \frac{(400 kJmol^{-1})}{(0.2 kJk^{-1}mol^{-1})} = 2000 \text{ k}$$

Thus, reaction will be in a state of equilibrium at 2000K and will be spontaneous above this temperature.

23. Required equation

$C(s) + \frac{1}{2} O_2(g) \rightarrow CO(g)$; $\Delta_f H = ?$

Subtract equation (ii) from (i)

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

$CO(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g)$; $\Delta H = -282.8$ kJ

(Subtract) $C(s) + \frac{1}{2} O_2(g) - CO(g) \rightarrow \Delta H = (-393.5 + 282.8)$

Or $C(s) + \frac{1}{2} O2(g) \rightarrow CO(g)$; $\Delta_f H = -110.7$kJ

24. $W = -P\Delta V$

$P = 1.2 \times 10^5 \text{ Nm}^{-2}$

$\Delta V = V_2 - V_1 = (4 \times 10^{-3}) - (2 \times 10^{-3}) - 2 \times 10^{-3} \text{ m}^3$ $W = ?$

$= -1.2 \times 10^5 \text{ Nm}^{-2} \times 2 \times 10^{-3} \text{ m}^3$

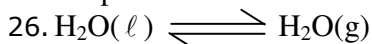$= -2.4 \times 10^2 \text{ Nm}$

$= -2.4 \times 10^2 \text{ J (since Nm = J)}$

Work done by the system $= -2.4 \times 10^2$ J

25. Specific heat capacity : It is defined as the quantity of heat required to raise the temperature of 1 gram of a substance by 1^oC or 1 K.

Molar heat capacity: It is defined as the quantity of heat required to raise the temperature of 1 mol of a substance by one degree celsius or one Kelvin.

26. $H_2O(\ell) \rightleftharpoons H_2O(g)$

$\Delta n = \eta_{gp} - \eta_{gR}$

$= 1 - 0$

$= 1$

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

$\Delta U = \Delta H - \Delta\eta_g RT$

$= 40.66 - (1) \times 8.314 \times 10^{-3} \times 373$

$= 40.66 - 3.1011$

$= 37.5589 \text{ k J mol}^{-1}$

3 and 4 marks Answers

1. $\Delta U - 742.7$ kJ mol^{-1} ; $\Delta^{ng} = 2 - 3/2 = +\dfrac{1}{2}$ mol

   R= 8.314 x 10^{-3} kJ k^{-1} mol^{-1} ; T = 298 K

   According to the relation, $\Delta H = \Delta U + \Delta^{ng} RT$

   ΔH = (-742.7 kJ) + (½ mol) x (8.314 x 10^{-3} kJ k^{-1} mol^{-1}) x 298K

   = - 742.7 kJ + 1.239 kJ = -741.5 kJ

2. No. of moles of Al(m) = $\dfrac{60\,g}{(27\,gmol^{-1})}$ = 2.22 mol

   Molar heat capacity (c) = 24 J mol^{-1} k^{-1}

   Rise in temperature (ΔT) = 55 – 35 = 20°C = 20 K

   Heat evolved (q) = c $\times$ m $\times$ T

   = (24 J mol^{-1} k^{-1}) $\times$ (2.22 mol) $\times$20 K

   = 1065.6 J = 1.067 kJ

3. Ans: The change may be represented as

   H_2O (ℓ) (10°C) $\xrightarrow{\Delta H}$ H_2O (s) (-10°C)

   $\downarrow \Delta H_1$ $\qquad\qquad\qquad\qquad$ $\uparrow\Delta H_3$

   H_2O(ℓ) (0°C) $\xrightarrow{\Delta H_2}$ H_2O (s) (0°C)
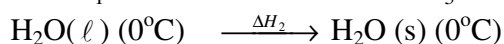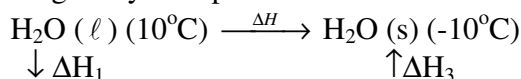
   According to Hess's law;

   $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

   ΔH_1 = 75.3 J mol^{-1} k^{-1} (10K) = 753 J mol^{-1}

   ΔH_2 (solidification) = - 6.03 k J mol^{-1} = -6030 J mol^{-1}

   (sign changed)

   ΔH_3 = 36.8 J mol^{-1} k^{-1} (-10K) – 36.8 J mol^{-1}

   ΔH = (753 – 6030 – 368) J mol^{-1} = -5645 J mol^{-1}

   = -5.645 k J mol^{-1}

4. Ans: The combustion equation is

   C(s) + O_2 (g) $\rightarrow$ CO_2 (g) ; ΔcH = -393.5 k J mol^{-1}

   (44g)
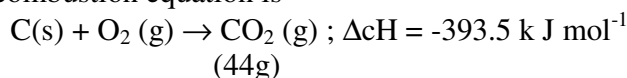
   Heat released in the formation of 44 g of

   CO2 = 393.5 k J

   Heat released in the formation of 35.2 g of

   CO_2 = $\dfrac{(393.5 kJ) \times (35.2 g)}{(44 g)}$ = 314.8 kJ
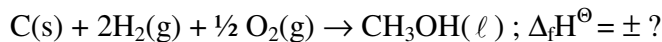
5. Enthalpy of reaction (ΔrH)

   = [81 + 3(-393)] – [9.7 + 3(-110)]

   = (81 – 1179) – (9.7 – 330)

   = - 778 k J mol^{-1}

6. The equation we aim at;

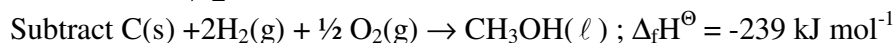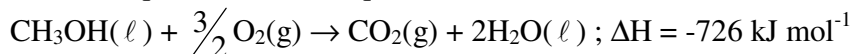$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(\ell)$; $\Delta_fH^{\ominus} = \pm$?

Multiply equation (iii) by 2 and add to equation (ii)
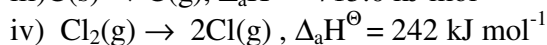
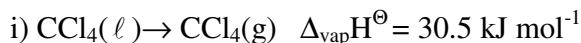$C(s) + 2H_2(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$
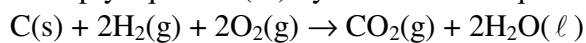
$\Delta H = -(393 + 522) = -965$ kJ mol^{-1}

Subtract equation (i) from equation (iv)

$CH_3OH(\ell) + \frac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$; $\Delta H = -726$ kJ mol^{-1}

Subtract $C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(\ell)$; $\Delta_fH^{\ominus} = -239$ kJ mol^{-1}

7. The available data is

    i) $CCl_4(\ell) \rightarrow CCl_4(g)$ $\Delta_{vap}H^{\ominus} = 30.5$ kJ mol^{-1}

    ii) $C(s) + 2Cl_2(g) \rightarrow CCl_4(\ell)$, $\Delta_fH^{\ominus} = -135.5$ kJ mol^{-1}

    iii) $C(s) \rightarrow C(g)$, $\Delta_aH^{\ominus} = 715.0$ kJ mol^{-1}

    iv) $Cl_2(g) \rightarrow 2Cl(g)$, $\Delta_aH^{\ominus} = 242$ kJ mol^{-1}
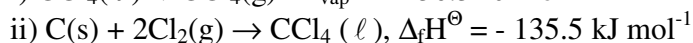
    The equation we aim at is

        $CCl_4(g) \rightarrow C(g) + 4Cl(g)$; $\Delta H = $?
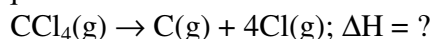
Equation (iii) + 2 x equation (iv) – equation (i) – equation (ii) gives the required equation with

$\Delta H = 715.0 + 2(242) - 30.5 - (-135.5)$ kJ mol^{-1}

    = 1304 kJ mol^{-1}

Bond enthalpy of C-Cl in CCl$_4$ (average value)

    $= \dfrac{1304}{4} = 326$ kJ mol^{-1}

8. $\Delta H^{\ominus} = \Delta U^{\ominus} + \Delta^{ng}RT$

    $\Delta U^{\ominus} = -10.5$ kJ ; $\Delta^{ng} = 2 - 3 = -1$ mol

    $R = 8.314 \times 10^{-3}$ kJ mol^{-1} ; $T = 298$ K

    $\therefore \Delta H^{\ominus} = (-10.5$ kJ$) + [(-1$mol$) \times 8.314 \times 10^{-3}$ kJ k^{-1}mol$^{-1} \times (298$K$)]$

        $= -10.5$ kJ $- 2.478$ kJ $= -12.978$ kJ

  According to Gibb's Hemholtz equation

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

    $\Delta G^{\ominus} = (-12.978$ kJ$) - (298$K$) \times (-0.0441$ kJ k$^{-1})$

      $= -12.978 + 13.142$

      $= -12.978 + 13.142$

      $= 0.164$ kJ

Since $\Delta G^{\ominus}$ is positive, the reaction is non spontaneous in nature.

9. $\Delta G^{\ominus} = -RT \ln K = -2.303\ RT \log K$

    $R = 8.0$ J k^{-1} mol^{-1} ; $T = 300$ K ; k = 10

    $\Delta G^{\ominus} = -2.303 \times (8$ J k^{-1} mol$^{-1}) \times (300$K$) \times \log 10$

        $= -5527$ J mol$^{-1} = -5.527$ kJ mol^{-1} .

10. Refer page 163 and 164 of the prescribed text book

11. Refer page 164 of the prescribed text book

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