CHEMICAL THERMODYNAMICS GPLUS EDUCATION
## VERY SHORT ANSWER TYPE QUESTIONS

1. Define thermodynamics.
2. What types of systems the following systems are ?
   (i) Hot tea placed in a cup
   (ii) Boiling water placed in a thermos flask
   (iii) Refrigerator
   (iv) An electric bulb
3. Sort out the intensive and extensive properties among the following :
   Temperature, mass, specific heat, density, enthalpy, entropy, concentration, free energy.
4. Which of the following are not state functions ?
   Temperature, entropy, heat, work, enthalpy, internal energy.
5. Which factor does remain constant in an isochoric process ?
6. What is the sign convention for heat ?
7. A system transfers 20 kJ of heat to the surroundings. Write the value of q for both the system and surroundings.
8. What is the sign convention for work ?
9. A gas expands by a volume ΔV against a constant pressure P. What is the work done by the system ?
10. Why is the internal energy of a system a state function ?
11. Write the mathematical statement of first law of thermodynamics.
12. What happens to the internal energy of a system if
    (i) work is done on the system;
    (ii) work is done by the system ?
13. For the reaction, $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, predict whether the work is done by the system or on the system.
14. Define internal energy of a system.
15. What is the value of ΔE when the work done by the system is equal to the heat absorbed by the system ?
16. Define enthalpy of a system.
17. Derive the relationship, $\Delta H = \Delta E + P\Delta V$.
18. What is the relationship between ΔH and ΔE for the process, $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$?
19. What do you understand by a spontaneous process ? Give two examples.
20. Which of the following processes are spontaneous and which are non-spontaneous ?
    (i) Flow of air from high pressure to low pressure.
    (ii) Formation of ice in a refrigerator.
    (iii) Spreading of a drop of ink in water kept in a beaker.
    (iv) Reverse osmosis.
    (v) Burning of coal in air.
    (vi) Dissolution of Cu in $ZnSO_4$ solution.
21. In which direction does a spontaneous process proceed ?
22. Although dissolution of ammonium chloride in water is endothermic, yet it dissolves, Why ?
23. Explain the term 'entropy'.
24. If a system absorbs q amount of heat at temperature T, what would be the change in the entropy of the system ?
25. Define the term absolute entropy.
26. Is the entropy of the universe constant ?

27. Amongst a gaseous substance and a liquid substance, which is expected to possess higher entropy and why ?
28. What is the entropy criterion for a process to be spontaneous ?
29. Which of the following are expected not to have zero entropy even at absolute zero ?
    NaCl, NO, CO_2, CO, ZnS
30. What is the sign of ΔS for a spontaneous reaction ?
31. How does the entropy change occur in the process of melting of a solid ?
32. Write the expression which gives the entropy of vaporisation of a liquid.
33. State the second law of thermodynamics.
34. What is Gibbs free energy and how is it defined mathematically ?
35. What is the enthalpy of formation of the most stable form of an element in its standard state ?
36. What does the term $T\Delta S_{total}$ total represent ?
37. What is the free energy criterion for a process to occur spontaneously ?
38. What is the status of the process for which $\Delta G = 0$?
39. An endothermic process involves an increase in the entropy of the system. Predict the condition under which the process would be feasible.
40. An exothermic reaction involves a decrease in the entropy of the system. Will the process be spontaneous ?
41. How is standard free energy change related to equilibrium constant ?
42. State the third law of thermodynamics.
43. What do you understand by the term thermochemistry ?
44. Can chemical energy be transferred into electrical energy ? If yes, give an example.
45. Why ΔH is negative for an exothermic reaction ?
46. Why is it necessary to mention the physical state of substances in a thermochemical equation ?
47. Define heat of reaction.
48. Is calorific value of a food or a fuel is equal to its heat of combustion ?
49. State whether each of the following processes is exothermic or endothermic :
    (i) $KCl(s) + aq \longrightarrow KCl(aq)$; $\Delta H = +18.6$ kJ
    (ii) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$;
    $\Delta H = -57.1$ kJ
    (iii) $H_2O(l) \longrightarrow H_2O(s)$; $\Delta H = -6.01$ kJ
    (iv) $H_2O(l) \longrightarrow H_2O(g)$; $\Delta H = +40.7$ kJ.
50. Name the heat that is involved in the conversion of one allotropic form into the other.
51. Can Hess's law be regarded as a particular form of law of conservation of energy ?
52. What would be the bond formation energy of C—H bond if its bond energy is $+416.18$ kJ mol^{-1} ?

SHORT ANSWER TYPE QUESTIONS

1. Define thermodynamics. What is its importance and limitations ?
2. Define the following terms :
   (a) System   (b) State of a system   (c) State variables
3. Explain with examples the various types of systems.
4. What do you understand by intensive and extensive properties of a system ? Explain with examples.
5. Define the following processes :
   (a) Adiabatic process   (b) Cyclic process
   (c) Reversible process
6. Define heat and work and mention their sign conventions.
7. State and explain the first law of thermodynamics. Derive its mathematical form.
8. What are the limitations of first law of thermodynamics ?
9. Define internal energy and internal energy change.
10. What is the mathematical representation of the first law of thermodynamics ? Show that $\Delta E = q_v$.
11. Define enthalpy and enthalpy change. Show that $\Delta H = q_p$.
12. Define enthalpy. Show that the change in enthalpy at constant pressure for a reaction involving gases is given by the expression, $\Delta H = \Delta E + \Delta n_{(g)} \cdot RT$.
13. Establish a relationship between ΔH and ΔE. Under what conditions is $\Delta H = \Delta E$?
14. Predict whether the reaction,
    $H-H(g) + Cl-Cl(g) \longrightarrow 2H-Cl(g)$, will be exothermic or endothermic. Give reason for your answer.
15. What was the need of introducing the second law of thermodynamics ?
16. State a chemical reaction in which ΔH and ΔE are equal.
17. What is meant by the term 'Free energy' ? What was the necessity of introducing such a function ?
18. Define enthalpy. Show that change in enthalpy at constant pressure for a reaction involving gases is given by the expression, $\Delta H = \Delta E + \Delta nRT$.
19. What is the importance of free energy concept for a chemical reaction ?
20. Define the term 'entropy'. How does $T\Delta S$ determine the spontaneity of a process ?
21. State giving reason whether the following reaction would involve an increase, a decrease or no change in entropy.
    $$4Fe(s) + 3O_2(g) \longrightarrow 2Fe_2O_3(s)$$
22. Why is spontaneous process also called a natural process ?
23. What do you understand by spontaneity of a reaction and the driving force for a spontaneous process ?
24. Can ΔH be regarded as the sole criterion to explain the spontaneity of a process ? If no, explain why ?
25. With the help of at least two examples show that randomness increases in a spontaneous process.
26. What is entropy and in what units is it expressed ? Discuss the physical significance of entropy.
27. For the reaction $2H(g) \longrightarrow H_2(g)$, what are the signs of ΔH and ΔS and why ?

28. What happens to the entropy when a gas undergoes expansion ? Explain.
29. Comment on the statement : 'The entropy of the universe is tending towards a maximum.'
30. What is the entropy criterion for the spontaneity of a process ?
31. Show that the entropy changes in a reversible isothermal process is zero.
32. Show that the entropy change in an irreversible process is always positive.
33. Define 'entropy of fusion' and 'entropy of vaporisation' and write expressions to represent them.
34. State and explain the second law of thermodynamics.
35. Define Gibbs free energy and free energy change.
36. Derive the equation, $\Delta G = \Delta H - T\Delta S$.
37. Show that $\Delta G = -T\Delta S_{total}$.
38. What is the free energy criterion for the spontaneity of a process ?
39. For the process $A + B \longrightarrow C + D$, ΔG is positive. Comment on the spontaneity of the process.
40. What are spontaneous processes ? Mention the conditions for a reaction to be spontaneous at constant temperature and pressure.
41. What is entropy ? State the effect of increased temperature on the entropy of a substance.
42. State the thermodynamic conditions for spontaneous occurrence of a process.
43. ΔH and ΔS are positive for a chemical reaction. Under what conditions is the reaction expected to occur spontaneously?
44. What is meant by free energy of a substance ? How is it related to its enthalpy and entropy ?
45. Define and explain the term entropy of a system. Illustrate it using a spontaneous irreversible change.
46. Comment on the spontaneity of a process when
    (i) $\Delta H < 0$, $T\Delta S > 0$ (ii) $\Delta H > 0$, $T\Delta S < 0$
    (iii) $\Delta H > 0$, $T\Delta S > 0$ and $T\Delta S < \Delta H$ (iv) $\Delta H < 0$, $T\Delta S < 0$
    and $T\Delta S > \Delta H$.
47. Discuss the effect of temperature on the spontaneity of a process. Explain with a suitable example.
48. Define the term 'standard free energy change', ($\Delta G°$). How is it related to the equilibrium constant K ?
49. What do you understand by the standard free energy of formation of a substance ? How is it helpful in calculating $\Delta G°$ for a reaction ?
50. State the third law of thermodynamics.
51. Why is heat evolved or absorbed in a chemical reaction ?
52. What do you understand by exothermic and endothermic reactions ? How are they related to the change in enthalpy ?
53. What do you understand by standard enthalpy of a reaction and how is it represented ?
54. Define heat of formation. How is it useful in the calculation of the heat of a reaction ?
55. Calculate the calorific value of sugar if its heat of combustion is 5645 kJ mol^{-1}.
56. Why is heat of neutralisation for a strong acid and strong base constant ?

ESSAY (LONG ANSWER) TYPE *QUESTIONS*

1. What do you understand by the state of a system and the state functions ? Discuss the various types of processes that may occur in a system.
2. What is pressure-volume work ? Derive an expression for the pressure-volume work.
3. Derive an expression for the work done in the isothermal and reversible expansion of an ideal gas.
4. State and explain the first law of thermodynamics. Formulate the law in a mathematical form. What are its limitations ?
5. What is internal energy and internal energy change ? What is its significance ?
6. Define enthalpy and enthalpy change. Derive a relationship between ΔH and ΔE. Mention the conditions under which ΔH is equal to ΔE.
7. Define enthalpy of reaction and enthalpy of formation. How would you calculate the standard enthalpy of a reaction if standard enthalpies of formation of all substances involved are known?
8. Discuss the relationship between ΔE, ΔH, q_p and w for the dissociation of ammonia carried out under constant pressure.

$$2NH_3(g) \xrightarrow{\text{heat}} N_2(g) + 3H_2(g)$$
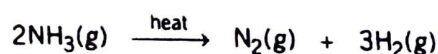
9. Show that the heat absorbed at constant volume is equal to the increase in the internal energy of the system, whereas that at constant pressure is equal to the increase in the enthalpy of the system.
10. What was the need of introducing the second law of thermodynamics ? State the law and explain it.
11. What do you understand by spontaneous and non-spontaneous processes ? What are the important features of a spontaneous process ?
12. What do you understand by the spontaneity of a process ? Discuss the spontaneity of a process in terms of entropy and free energy.
13. What is entropy and how is it related to the spontaneity of a process ?

14. Show that the entropy change is zero in a reversible process but it is positive in case of an irreversible process.
15. Define the following and write expressions for calculating each of them.
    (i) Entropy of fusion   (ii) Entropy of vaporisation
    (iii) Entropy of sublimation
16. How would you calculate the entropy change in a chemical reaction ? How is it helpful in discussing the spontaneity of the reaction ?
17. What is Gibbs free energy ? Derive the relation, $\Delta G = \Delta H - T\Delta S$. Discuss the free energy criterion for the spontaneity of a process.
18. For a system which is not isolated, show that $\Delta G = -T\Delta S_{total}$.
19. What is the status of a process when
    (i) $\Delta G < 0$ (ii) $\Delta G = 0$ (iii) $\Delta G > 0$?
    In which of the above cases, the process can be used for obtaining useful work ?
20. Discuss the effect of temperature on the spontaneity of a process when for the process
    (i) both ΔH and ΔS are negative,
    (ii) both ΔH and ΔS are positive.
21. State and explain the third law of thermodynamics. Suggest a molecular interpretation of the law.
22. What do you understand by enthalpy and change in enthalpy? Why does a chemical reaction involve a change in enthalpy ?
23. What are thermochemical equations and what is their significance in the study of chemical energetics ? State and explain the conventions used for writing a thermochemical equation.
24. What is heat of reaction and on what factors does it depend?
25. Write short notes on the following :
    (i) Heat of formation
    (ii) Heat of combustion
    (iii) Heat of solution
    (iv) Heat of transition.
26. Define heat of neutralisation. Why is its value constant for a strong acid and a strong base ? How is it helpful in determining the heat of dissociation of weak acids or weak bases ? Explain with examples.
27. State and explain Hess's law of constant heat summation. Illustrate it with examples. Discuss its important applications.

OBJECTIVE (MULTIPLE CHOICE) TYPE *QUESTIONS*

Choose the correct option in the following questions :

1. Thermodynamics is concerned with
   (a) total energy of the system
   (b) energy changes in a system
   (c) rate of a chemical change
   (d) mass changes in nuclear reactions.   [M.P.P.E.T., 1993]
2. Thermodynamic equilibrium involves
   (a) chemical equilibrium
   (b) thermal equilibrium
   (c) mechanical equilibrium
   (d) all the three.   [C.E.T. Punjab, 1991]
3. During the isothermal expansion of an ideal gas, its
   (a) internal energy increases
   (b) enthalpy decreases
   (c) enthalpy remains unaffected
   (d) enthalpy reduces to zero.   [C.B.S.E. Med.,1991]

4. Evaporation of water is
   (a) a process in which heat is neither evolved nor absorbed
   (b) a process accompanied by chemical reaction
   (c) an exothermic change
   (d) an endothermic change.
5. Which of the following reactions is endothermic ?
   (a) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
   (b) $Fe(s) + S(s) \longrightarrow FeS(s)$
   (c) $NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l)$
   (d) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$.
6. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta H = ...$
   (a) $\Delta E - 2RT$ (b) $\Delta E + 2RT$
   (c) $\Delta E + RT$ (d) $\Delta E - RT$. [C.B.S.E. Med., 1991]

7. The difference between heats of reaction at constant pressure and constant volume for the reaction

$$2C_6H_6(l) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l)$$

at 25°C in kJ is

(a) + 7.43   (b) +3.72

(c) –7.43   (d) –3.72.   [I.I.T., 1991]

8. A spontaneous change is one in which the system suffers

(a) an increase in internal energy

(b) lowering in entropy

(c) lowering in free energy

(d) no energy change.

9. In which of the following changes does entropy decrease ?

(a) Crystallisation of sucrose from solution

(b) Dissolving sucrose in water

(c) Melting of ice

(d) Vaporisation of camphor.

10. For which reaction among the following, is ΔS maximum ?

(a) $Ca(s) + \dfrac{1}{2}O_2(g) \longrightarrow CaO(s)$

(b) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

(c) $C(s) + O_2(g) \longrightarrow CO_2(g)$

(d) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$.

11. The free energy change for a reversible reaction at equilibrium is

(a) zero   (b) small positive

(c) small negative   (d) large positive.

12. The spontaneous nature of a reaction is impossible if

(a) ΔH is +ve, ΔS is also +ve

(b) ΔH is –ve, ΔS is also –ve

(c) ΔH is –ve, ΔS is +ve

(d) ΔH is +ve, ΔS is –ve.

13. Which is an extensive property of the system ?

(a) Temperature   (b) Volume

(c) Refractive index   (d) Viscosity. [C.B.S.E. Med., 1993]

14. Which is not a state function of a thermodynamic system ?

(a) Internal energy (E) (b) Free energy (G)

(c) Enthalpy (H) (d) Work (W).

            [C.B.S.E. Med., 1993]

15. The entropy of the universe

(a) is increasing and tending towards a maximum value

(b) is decreasing and tending towards zero

(c) remains constant

(d) decreasing and increasing with a periodic rate.

            [M.P.P.M.T., 1993]

16. Decrease in free energy of a reacting system indicates

(a) an exothermic reaction

(b) an endothermic reaction

(c) a spontaneous reaction

(d) a slow reaction.   [M.P.P.M.T., 1993]

17. Gibbs free energy G, enthalpy H and entropy S are related as

(a) $G = H + TS$ (b) $G = H – TS$

(c) $G – TS = H$ (d) $S = H – G$.   [B.H.U., 1994]

18. A system is provided 50 J of heat and work done on the system is 10 J. The change in internal energy during the process is

(a) 40 J   (b) 60 J

(c) 80 J   (d) 50 J.

19. The entropy change for vaporisation of liquid water to steam at 100°C is ... $JK^{-1}mol^{-1}$. Given that heat of vaporisation is 40.8 kJ mol^{-1}.

(a) 109.38   (b) 100.38

(c) 110.38   (d) 120.38. [C.B.S.E Med., 1990]

20. The entropy change at a given temperature is expressed as

(a) $q = T\Delta S$ (b) $\Delta S = q/\Delta T$

(c) $\Delta S = q – T$ (d) $S = q/T$.

21. For an adiabatic process, which of the following is correct ?

(a) $P\Delta V = 0$ (b) $q = + w$

(c) $\Delta E = q$ (d) $q = 0$.   [C.P.M.T., 1990]

22. The amount of heat measured for a reaction in a bomb calorimeter corresponds to

(a) ΔG (b) ΔH

(c) ΔE (d) $P\Delta V$.   [A.I.I.M.S., 1991]

23. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to a volume of 20 litres at 25°C is

(a) $2.303 \times 298 \times 0.082 \log_{10} 2$

(b) $298 \times 10^7 \times 8.31 \times 2.303 \log_{10} 2$

(c) $2.303 \times 289 \times 0.082 \log_{10} 0.5$

(d) $2.303 \times 298 \times 2 \log_{10} 2$.   [C.M.C. Vellore, 1991]

24. Which of the following values of heat of formation does indicate that the product is least stable ?

(a) – 94 kcal   (b) – 231.5 kcal

(c) +21.4 kcal   (d) +64.8 kcal. [M.P.P.M.T., 1997]

25. The heat of neutralisation is highest in

(a) $NaOH + CH_3COOH$ (b) $HCl + NaOH$

(c) $NH_4OH + HCl$ (d) $CH_3COOH + NH_4OH$.

            [M.P.P.M.T., 1991]

26. The heat of neutralisation of NaOH and HCl is 57.3 kJ mol^{-1} then the amount of heat liberated if 2 moles each of NaOH and HCl are reacted is

(a) 57.3 kJ mol^{-1} (b) 114.6 kJ mol^{-1}

(c) 28.65 kJ mol^{-1} (d) 215.2 kJ mol^{-1}.

            [C.P.M.T., 1990]

27. In a flask colourless N_2O_4 is in equilibrium with brown coloured NO_2. At equilibrium, when the flask is heated at 100°C the brown colour deepens and on cooling it becomes less coloured. The change in enthalpy, ΔH for this system is

(a) negative   (b) positive

(c) zero   (d) undefined.   [C.E.T., 1993]

28. The process of evaporation of a liquid is accompanied by

(a) increase in enthalpy

(b) decrease in entropy

(c) no change in free energy

(d) increase in entropy.   [N.C.E.R.T., 1983]

29. The enthalpies of combustion of carbon and carbon monoxide are –390 kJ and –278 kJ respectively. The enthalpy of formation of carbon monoxide is

(a) 668 kJ   (b) – 668 kJ

(c) 112 kJ   (d) – 112 kJ.   [B.H.U., 1994]

30. The standard enthalpy of formation of NH_3 is –46.0 kJ mol^{-1}. If the enthalpy of formation of H_2 from its atoms is –436 kJ mol^{-1} and that of N_2 is –712 kJ mol^{-1}, the average bond enthalpy of N—H bond in NH_3 is

(a) – 964 kJ mol^{-1} (b) + 352 kJ mol^{-1}

(c) + 1056 kJ mol^{-1} (d) – 1102 kJ mol^{-1}.

            [A.I.E.E.E., 2010]

31. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is
(a) 38.3 J mol^{-1} K^{-1} (b) 35.8 J mol^{-1} K^{-1}
(c) 32.3 J mol^{-1} K^{-1} (d) 42.3 J mol^{-1} K^{-1}.
[A.I.E.E.E., 2011]

32. In view of the signs of $\Delta_r G°$ for the following reactions
PbO_2 + Pb ⟶ 2PbO, $\Delta_r G° < 0$

SnO_2 + Sn ⟶ 2SnO, $\Delta_r G° > 0$

Which oxidation states are more characteristic for lead and tin?
(a) For lead + 4, for tin + 2 (b) For lead + 2, for tin + 2
(c) For lead + 4, for tin + 4 (d) For lead + 2, for tin + 4.
[A.I.E.E.E., 2011]

33. The value of enthalpy change (ΔH) for the reaction
$C_2H_5OH(l)$ + $3O_2(g)$ ⟶ $2CO_2(g)$ + $3H_2O(l)$

at 27°C is −1366.5 kJ mol^{-1}. The value of internal energy change for the above reaction at this temperature will be
(a) −1371.5 kJ (b) −1369.0 kJ
(c) −1364.0 kJ (d) −1361.5 kJ.
[A.I.E.E.E., 2011]

34. If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be
(a) 1.0 J mol^{-1} K^{-1} (b) 0.1 J mol^{-1} K^{-1}
(c) 100 J mol^{-1} K^{-1} (d) 10 J mol^{-1} K^{-1}.
[A.I.P.M.T., 2011]

35. Which of the following is correct option for free expansion of an ideal gas under adiabatic condition?
(a) $q \neq 0, \Delta T = 0, W = 0$
(b) $q = 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T < 0, W \neq 0$
(d) $q = 0, \Delta T \neq 0, W = 0$.
[A.I.P.M.T., 2011]

36. Enthalpy change for the reaction,
$4H(g)$ ⟶ $2H_2(g)$ is −869.6 kJ

The dissociation energy of H—H bond is
(a) −869.6 kJ (b) +434.8 kJ
(c) +217.4 kJ (d) −434.8 kJ. [A.I.P.M.T., 2011]

37. The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is
(a) 10.52 cal/(mol K) (b) 21.04 cal/(mol K)
(c) 5.260 cal/(mol K) (d) 0.526 cal/(mol K).
[A.I.P.M.T., 2012]

38. Standard enthalpy of vaporisation $\Delta_{vap} H$ for water at 100°C is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is
(Assume water vapour to behave like an ideal gas).
(a) + 37.56 (b) − 43.76
(c) + 43.76 (d) + 40.66. [A.I.P.M.T., 2012]

39. In which of the following reactions, standard reaction entropy changes ($\Delta S°$) is positive and standard Gibbs energy change ($\Delta G°$) decreases sharply with increasing temperature?
(a) C (graphite) + $\frac{1}{2} O_2(g)$ ⟶ CO(g)

(b) CO(g) + $\frac{1}{2} O_2(g)$ → $CO_2(g)$

(c) Mg(s) + $\frac{1}{2} O_2(g)$ → MgO(g)

(d) $\frac{1}{2}$ C (graphite) + $\frac{1}{2} O_2(g)$ → $\frac{1}{2} CO_2(g)$
[A.I.P.M.T., 20..]

40. A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The value of q and w for the process will be ($R = 8.314$ J/mol K, ln = 2.01)
(a) $q = + 208$ J, $W = −208$ J
(b) $q = −208$ J, $W = −208$ J
(c) $q = −208$ J, $W = +208$ J
(d) $q = + 208$ J, $W = + 208$ J. [J.E.E. Main, 2013]

41. For the complete combustion of ethanol
$C_2H_5OH(l)$ + $3O_2(g)$ ⟶ $2CO_2(g)$ + $3H_2O(l)$

the amount of heat produced as measured in bomb calorimeter is 1364.47 kJ mol^{-1} at 25°C.

Assuming ideality, the enthalpy of combustion, $\Delta_c H$ for the reaction will be [$R = 8.314$ Jk^{-1} mol^{-1}]
(a) −1366.95 kJ mol^{-1} (b) −1361.95 kJ mol^{-1}
(c) −1460.50 kJ mol^{-1} (d) −1350.50 kJ mol^{-1}.
[J.E.E. Main, 2014]

Answers

1. (b)	2. (d)	3. (c)	4. (d)	5. (a)	6. (a)	7. (c)	8. (c)	9. (a)	10. (b)
11. (a)	12. (d)	13. (b)	14. (d)	15. (a)	16. (c)	17. (b)	18. (b)	19. (a)	20. (a)
21. (d)	22. (c)	23. (b)	24. (d)	25. (b)	26. (b)	27. (b)	28. (d)	29. (d)	30. (b)
31. (a)	32. (d)	33. (c)	34. (c)	35. (b)	36. (b)	37. (c)	38. (a)	39. (a)	40. (a)
41. (a)									

'TRUE OR FALSE' TYPE QUESTIONS

State whether the following statements are True (T) or False (F) :

1. Chemical thermodynamics deals with the rates and mechanism of chemical reactions.
2. An animal is an open system.
3. Volume is an intensive property.
4. Heat (q) and work (w) are state functions.
5. For an isobaric process, $\Delta P = 0$.
6. According to the international convention, work done by the system is negative.
7. Work done in the isothermal reversible expansion of a gas is always greater than that done in isothermal irreversible expansion of the gas.
8. The total energy of the universe is increasing day by day.
9. $\Delta E = E_{initial\ state} - E_{final\ state}$.
10. ΔE is regarded as a measure of heat absorbed or evolved in a process occurring at constant volume and temperature.
11. A bomb calorimeter measures ΔG of a combustion process.
12. For the reaction,
$$Zn(s) + 2HCl(aq) \longrightarrow ZnCl(aq) + H_2(g), \quad \Delta H \text{ is}$$
equal to ΔE.

13. The decomposition of $CaCO_3$ (s) into CaO (s) and CO_2 (g) is not a spontaneous process because it takes place only when $CaCO_3$(s) is heated.
14. A spontaneous process always proceeds towards equilibrium.
15. The units of ΔS are $JK^{-1}\ mol^{-1}$.
16. The absolute entropy of a liquid is less than of the solid.
17. The entropy of the universe is constant.
18. A process is non-spontaneous when $\Delta S_{total} < 0$.
19. For an irreversible process, $\Delta S > 0$.
20. Heat can be converted completely into equivalent amount of work without producing changes elsewhere.
21. The change in Gibbs free energy (ΔG) for a change depends upon the path by which the change has been carried out.
22. A chemical process always proceeds in the direction in which the Gibbs free energy of the system decreases.
23. A process is feasible if ΔH is positive and ΔS is negative.
24. ΔG is a measure of the net work done by a system.
25. At absolute zero, the absolute entropy of a perfectly crystalline substance is zero.

Answers

1. F	2. T	3. F	4. F	5. T	6. T	7. T	8 F	9 F	10. T
11. F	12. F	13. F	14. T	15. T	16. F	17. F	18. T	19 T	20. F
21. F	22. T	23. F	24. T	25. T					

'FILL IN THE BLANKS' TYPE QUESTIONS

1. Chemical thermodynamics deals with the .... involved in chemical transformations.
2. The system which allows the exchange of ...... but not of ...... with the ...... is called a closed system.
3. A system is said to be in ...... equilibrium when the system and the surroundings are at the same temperature.
4. When the work is done by the system, w is taken as ......
5. The total ...... of the universe is constant but that of the universe is tending towards a maximum.
6. For a chemical process, $q_p = $ ...... but $q_v =$ ......
7. The sum of ...... energy and ...... energy of a system is called enthalpy of the system.
8. For the process occurring at constant ......, $\Delta H = \Delta E$.
9. A spontaneous process is also called a ...... process.
10. Dissolution of sugar in water is accompanied by ...... of entropy of the system.

11. A spontaneous process is an ...... process and occurs in ...... direction only.
12. The force responsible for the spontaneity of a reaction is called ......
13. For a spontaneous change, $\Delta S_{total} = $ ...... $+ \Delta S_{surroundings} > $ ......
14. If ΔS_{total} is positive the process is ..... and occurs in the ..... as mentioned. The reverse process is ....
15. Whenever a spontaneous process takes place, it is accompanied by an increase in the total ...... of the ......
16. When $\Delta G = 0$, the process is ......
17. When ΔH is negative and $T\Delta S$ is positive, the process is ...... at all ......
18. $\Delta G° = \Sigma \Delta G°_{f(...)} - \Sigma \Delta G°_{f(...)}$.
19. The greater the free energy change, the greater is the amount of ...... work that can be obtained from the process.
20. At absolute zero, the entropy of a ...... substance is ......

Answers

1. energy changes
2. energy, mass, surroundings
3. thermal
4. negative
5. energy, entropy
6. ΔH, ΔE
7. internal, pressure-volume
8. volume
9. natural
10. an increase
11. irreversible, one
12. driving force
13. ΔS_{system}, 0
14. spontaneous, direction, non-spontaneous
15. entropy, universe
16. at equilibrium
17. spontaneous, temperatures
18. products, reactants
19. useful
20. perfectly crystalline, zero.

NUMERICAL PROBLEMS

1. Calculate the free energy change when one mole of sodium chloride is dissolved in water at 298 K. (Given : Lattice energy of NaCl = $-$ 777.8 kJ mol^{-1}, Hydration energy of NaCl = $-$ 774.1 kJ mol^{-1} and ΔS at 298 K = 0.043 kJ mol^{-1}.
[Ans. $-$9.114 kJ]

2. Calculate the value of equilibrium constant, K for the following reaction at 400 K.
$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g);$$
$\Delta H° =$ 80.0 kJ mol^{-1}, $\Delta S° =$ 120 $JK^{-1} mol^{-1}$
at 400 K, $R =$ 8.31 J $K^{-1} mol^{-1}$. [Ans. 6.61 × 10^{-5}]

3. Calculate the standard free energy change for the following reaction at 27°C.
$$H_2(g) + I_2(g) \longrightarrow 2HI(g); \quad \Delta H° = +51.9 kJ$$
[Given :
$\Delta S°_{H_2} =$ 130.6 J $K^{-1} mol^{-1}$, $S°_{I_2} =$ 116.7 J $K^{-1} mol^{-1}$
and $S°_{HI} =$ 206.3 J $K^{-1} mol^{-1}$].
Predict whether the reaction is feasible at 27°C or not.
[Ans. +2310 J, not feasible at 27°C

4. (i) Using the data given below, calculate the value of equilibrium constant for the reaction
$$\underset{\text{acetylene}}{3HC\equiv CH(g)} \rightleftharpoons \underset{\text{benzene}}{C_6H_6(g)}$$
at 298 K, assuming ideal behaviour.
$\Delta_f G°$ HC $\equiv$ CH(g) = 2.09 x 10^5 J mol^{-1};
$\Delta_f G°$ $C_6H_6(g)$ = 1.24 × 10^5 J mol^{-1}
$R =$ 8.314 J $K^{-1} mol^{-1}$
(ii) Based on your calculated value, comment whether this process can be recommended as a practical method for making benzene. [Ans. (i) 1.43 × 10^{88}, (ii) Yes]

5. A gas expands from 3 dm^3 to 5 dm^3 against a constant pressure of 3 atm. The work done during expansion is used to heat 10 moles of water of temperature 290 K. Calculate the final temperature of water. (sp. heat of water = 4.184 J $g^{-1} K^{-1}$).
[Ans. 290.81 K]

6. The enthalpy change involved in the oxidation of glucose is $-$2880 kJ mol^{-1}. Twenty five per cent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometre, what is the maximum distance that a person will be able to walk eating 120 g of glucose ?
[Ans. 4.8 km]

7. 10 g of argon is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Calculate q, w, ΔE and ΔH for the process. $R =$ 2.0 cal $K^{-1} mol^{-1}$, log 2 = 0.30, At. wt. of argon = 40.
[Ans. 103.99 cal, + 103.99 cal, 0, 103.99 cal]

8. Using the data (all values are in kcal/mole at 25°C) given below, calculate the bond energy of C—C and C—H bonds.
$\Delta_C H°$ (ethane) = $-$ 372.0
$\Delta_C H°$(propane) = $-$ 530.0
$\Delta H°$ for C(graphite) $\longrightarrow$ $C_{(gas)}$ = 172.0
Bond energy of H—H = 104.0
$\Delta_f H°$ of $H_2O(l)$ = $-$ 68.0
$\Delta_f H°$ of $CO_2(g)$ = $-$ 94.0

[Ans. C—C B.E. = 82.0 kcal, H—H B.E. =99.0 kcal]

9. An athlete is given 100 g of glucose ($C_6H_{12}O_6$) of energy equivalent to 1560 kJ. He utilises 50% of this gained energy in the event. In order to avoid the storage of energy in the body, calculate the weight of water he would need to perspire. The enthalpy of evaporation of water is 44 kJ $mole^{-1}$
[Ans. 319.09 g]

10. When 2 moles of $C_2H_6(g)$ are completely burnt, 3129 kJ of heat is liberated. Calculate the heat of formation of $C_2H_6(g)$. $\Lambda_f H$ for CO_2 (g) and H_2O (l) are $-$395 and $-$ 286 kJ per mole respectively. [Ans. $-$83.5 kJ]

11. The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are $-$76.2, $-$394.8 and $-$241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning $1m^3$ of methane measured under normal conditions.
[Ans. 35794.8 kJ]

12. The heat of combustion of acetylene is 312 kcal. If the heat of formation of CO_2 is 94·38 k cal and that of water is 68·38 k cal, calculate C $\equiv$ C bond energy assuming that the bond energy of C —H is 93·6 k cal. Heat of atomisation of carbon and hydrogen are 150 and 51·5 k cal respectively.
[Ans. 160.94 k cal mol^{-1}]

13. If a man submits to a diet of 9500 kJ per day and expends energy in all forms to a total of 12000 kJ per day, what is the change in internal energy per day ? If the energy lost was stored as sucrose (1632 kJ per 100 g), how many days should it take to lose 1 kg ? (Ignore water loss for this problem.) [Ans. 6.528 days]

14. $$C(s) + O_2(g) \longrightarrow CO_2(g) + 394 kJ$$
$$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO + 111 kJ$$
(i) In an oven using coal (assume the coal is 80% C in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% of carbon is converted to CO. Find out the heat generated when 10 kg of coal is burnt in this fashion.
(ii) Calculate the heat generated if a more efficient oven is used so that only CO_2 is formed.
(iii) Calculate the percentage loss in heating value for the inefficient oven.
[Ans. (i) 1.87 × 10^5 kJ (ii) 2.63 × 10^5 kJ (iii) 28.9]

15. Gobar gas obtained by bacterial fermentation of animal refuse contains mainly methane. The heat of combustion of methane to CO_2 and water (gas) is given by
$$CH_4(g) + 2O_2(g) \longrightarrow$$
$$CO_2(g) + 2H_2O(g) + 809 kJ.$$
How much gobar gas would have to be produced per day for a small village community of 100 families, if we assume that each family has to be supplied 20,000 kJ of energy per day to meet all its needs and that the methane content in gobar gas is 80% by weight ? [Ans. 49.444 kg]