THERMODYNAMICS

FACT/DEFINITION TYPE QUESTIONS

1. Thermodynamics is not concerned about____.
(a) energy changes involved in a chemical reaction.
(b) the extent to which a chemical reaction proceeds.
(c) the rate at which a reaction proceeds
(d) the feasibility of a chemical reaction.

2. Which of the following statements is not true regarding the laws of thermodynamics ?
(a) It deal with energy changes of macroscopic systems.
(b) It deal with energy changes of microscopic systems.
(c) It does not depends on the rate at which these energy transformations are carried out.
(d) It depends on initial and final states of a system undergoing the change.

3. A................... in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the..................
(a) surroundings, system (b) system, surroundings
(c) system, surroundings (d) system, boundary

4. The universe refers to
(a) only system
(b) only surroundings
(c) both system and surroundings
(d) None of these

5. Which of the following statements is correct?
(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

6. Which of the following is closed system ?
(a) Jet engine
(b) Tea placed in a steel kettle
(c) Pressure cooker
(d) Rocket engine during propulsion

7. An isolated system is that system in which
(a) There is no exchange of energy with the surroundings
(b) There is exchange of mass and energy with the surroundings
(c) There is no exchange of mass or energy with the surroundings
(d) There is exchange of mass with the surroundings

8. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. These are
(a) Pressure and volume
(b) Pressure, volume, temperature and amount
(c) Volume, temperature and amount
(d) Pressure and temperature

9. Which of the following are *not* state functions ?
(I) $q + w$ (II) q
(III) w (IV) $H - TS$
(a) (I) and (IV) (b) (II), (III) and (IV)
(c) (I), (II) and (III) (d) (II) and (III)

10. Among the following the state function(s) is (are)
(i) Internal energy
(ii) Irreversible expansion work
(iii) Reversible expansion work
(iv) Molar enthalpy
(a) (ii) and (iii) (b) (i), (ii) and (iii)
(c) (i) and (iv) (d) (i) only

11. Enthalpy change (ΔH) of a system depends upon its
(a) Initial state
(b) Final state
(c) Both on initial and final state
(d) None of these

12. .... is a quantity which represents the total energy of the system
(a) Internal energy (b) Chemical energy
(c) Electrical energy (d) Mechanical energy

13. Which of the following factors affect the internal energy of the system ?
(a) Heat passes into or out of the system.
(b) Work is done on or by the system.
(c) Matter enters or leaves the system.
(d) All of the above

14. The system that would not allow exchange of heat between the system and surroundings through its boundary is considered as

(a) isothermal (b) adiabatic
(c) isobaric (d) isochoric

15. The enthalpy change of a reaction does not depend on

(a) The state of reactants and products
(b) Nature of reactants and products
(c) Different intermediate reactions
(d) Initial and final enthalpy change of a reaction.

16. The q is ……………. when heat is transferred from the surroundings to the system and q is……………………….. When heat is transferred from system to the surroundings.

(a) positive , negative (b) negative , positive
(c) high, low (d) low, high

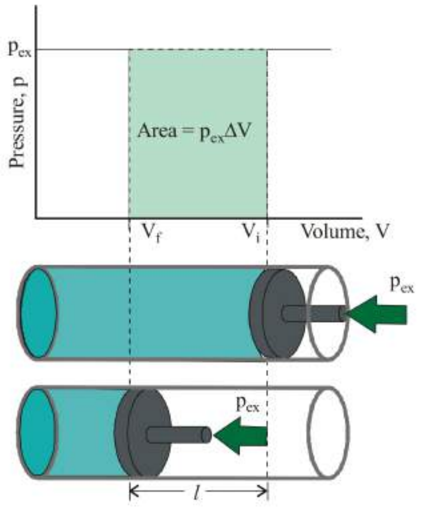
17. Adiabatic expansions of an ideal gas is accompanied by

(a) decrease in ΔE
(b) increase in temperature
(c) decrease in ΔS
(d) no change in any one of the above properties

18. Which of the following statements is incorrect?

(a) q is a path dependent function.
(b) H is a state function.
(c) Both H and q are state functions.
(d) Both (a) and (b)

19. Figure below is showing that one mole of an ideal gas is fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p is applied, piston is moved inward till the pressure inside becomes equal to p_{ex}.



What does the shaded area represents in the figure ?

(a) Work done (b) Pressure change
(c) Volume change (d) Temperature change

20. When 1 mol of a gas is heated at constant volume, temperature is raised from 298 to 308 K. If heat supplied to the gas is 500 J, then which statement is correct ?

(a) $q = w = 500\ J, \Delta U = 0$ (b) $q = \Delta U = 500\ J, w = 0$
(c) $q = -w = 500\ J, \Delta U = 0$ (d) $\Delta U = 0, q = w = -500\ J$

21. The work done during the expansion of a gas from a volume of 4 dm^3 to 6 dm^3 against a constant external pressure of 3 atm is (1 L atm = 101.32 J)

(a) -6 J (b) -608 J
(c) $+304$ J (d) -304 J

22. Which of the following statements/relationships is **not** correct in thermodynamic changes ?

(a) $\Delta U = 0$ (isothermal reversible expansion of a gas)
(b) $w = -nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(c) $w = nRT \ln \frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(d) For a system of constant volume heat involved directly changes to internal energy.

23. An ideal gas expands in volume from 1×10^{-3} to $1 \times 10^{-2}\ m^3$ at 300 K against a constant pressure of $1 \times 10^5\ Nm^{-2}$. The work done is

(a) 270 kJ (b) -900 kJ
(c) -900 J (d) 900 kJ

24. The difference between ΔH and ΔU is usually significant for systems consisting of

(a) only solids (b) only liquids
(c) both solids and liquids (d) only gases

25. If a reaction involves only solids and liquids which of the following is true ?

(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta E$
(c) $\Delta H > \Delta E$ (d) $\Delta H = \Delta E + RT\Delta n$

26. During isothermal expansion of an ideal gas, its

(a) internal energy increases
(b) enthalpy decreases
(c) enthalpy remains unaffected
(d) enthalpy reduces to zero.

27. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?

(a) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$
(b) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
(c) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
(d) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

28. For the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

Which one of the statement is correct at constant T and P ?

(a) $\Delta H = \Delta E$
(b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$
(d) ΔH is independent of physical state of the reactants

29. For a reaction in which all reactants and products are liquids, which one of the following equations is most applicable ?

(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta S$

(c) $\Delta H = \Delta E$ (d) $\Delta H = \Delta G$

30. The relationship between enthalpy change and internal energy change is

(a) $\Delta H = \Delta E + P\Delta V$ (b) $\Delta H = (\Delta E + V\Delta P)$

(c) $\Delta H = \Delta E - P\Delta V$ (d) $\Delta H = P\Delta V - \Delta E$

31. For the reaction

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O_{(l)}$$

at constant temperature, $\Delta H - \Delta E$ is

(a) $-RT$ (b) $+RT$

(c) $-3\,RT$ (d) $+3\,RT$

32. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?

(a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$

(c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

33. Among the following, the intensive properties are

(i) molar conductivity (ii) electromotive force

(iii) resistance (iv) heat capacity

(a) (ii) and (iii) (b) (i), (ii) and (iii)

(c) (i) and (iv) (d) (i) only

34. Which is an extensive property of the system ?

(a) Volume (b) Viscosity

(c) Temperature (d) Refractive index

35. Which of the following is an example of extensive property?

(a) Temperature (b) Density

(c) Mass (d) Pressure

36. Which of the following factors do not affect heat capacity?

(a) Size of system (b) Composition of system

(c) Nature of system (d) Temperature of the system

37. The heat required to raise the temperature of body by 1 C° is called

(a) specific heat (b) thermal capacity

(c) water equivalent (d) None of these.

38. Equal volumes of two monoatomic gases, A and B, at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be :

(a) 0.83 (b) 1.50

(c) 3.3 (d) 1.67

39. The molar heat capacity of water at constant pressure is 75 JK^{-1} mol^{-1}. When 1kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is

(a) 6.6 K (b) 1.2 K

(c) 2.4 K (d) 4.8 K

40. Calorie is equivalent to :

(a) 0.4184 Joule (b) 4.184 Joule

(c) 41.84 Joule (d) 418.4 Joule

41. Which of the following is not true regarding thermo-chemical equations?

(a) The coefficients in a balanced thermo-chemical equation refer to the number of moles of reactants and products involved in the reaction

(b) The coefficients in a balanced thermo-chemical equation refer to the number of molecules of reactants and products involved in the reaction

(c) The numerical value of $\Delta_r H$ refers to the number of moles of substances specified by an equation.

(d) Standard enthalpy change $\Delta_r H^{\ominus}$ will have units as kJ mol^{-1}.

42. The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

(a) is always negative

(b) is always positive

(c) may be positive or negative

(d) is never negative

43. If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O_{(l)}$ at 25°C and 1atm pressure are 52, – 394 and – 286 kJ/mol respectively, the change in ethalpy is equal to

(a) – 141.2 kJ/mol (b) – 1412 kJ/mol

(c) + 14.2 kJ/mol (d) + 1412 kJ/mol

44. The enthalpy change for a reaction does **not** depend upon

(a) use of different reactants for the same product

(b) the nature of intermediate reaction steps

(c) the differences in initial or final temperatures of involved substances

(d) the physical states of reactants and products

45. On the basis of thermochemical equations (i), (ii) and (iii), find out which of the algebric relationships given in options (a) to (d) is correct.

(i) $C\,(\text{graphite}) + O_2(g) \rightarrow CO_2(g);\ \Delta_r H = x\ \text{kJ mol}^{-1}$

(ii) $C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO\,(g);\ \Delta_r H = y\,\text{kJ mol}^{-1}$

(iii) $CO\,(g) + \frac{1}{2}O_2\,(g) \rightarrow CO_2\,(g);\ \Delta_r H = z\ \text{kJ mol}^{-1}$

(a) $z = x + y$ (b) $x = y - z$

(c) $x = y + z$ (d) $y = 2z - x$

46. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is – 90 kJ mol^{-1}, bond enthalpy of HCl is

(a) 380 kJ mol^{-1} (b) 425 kJ mol^{-1}

(c) 245 kJ mol^{-1} (d) 290 kJ mol^{-1}

47. Bond dissociation enthalpy of H_2, Cl_2 and HCl are 434 , 242 and 431 kJ mol^{-1} respectively. Enthalpy of formation of HCl is:

(a) 93 kJ mol^{-1} (b) – 245 kJmol^{-1}

(c) – 93 kJmol^{-1} (d) 245 kJmol^{-1}

48. From the following bond energies:

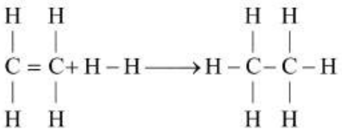
H – H bond energy: 431.37 kJ mol^{-1}

C = C bond energy: 606.10 kJ mol^{-1}

C – C bond energy: 336.49 kJ mol^{-1}

C – H bond energy: 410.50 kJ mol^{-1}

Enthalpy for the reaction,



$$\begin{array}{ccc} \mathrm{H}\quad\mathrm{H} & & \quad\mathrm{H}\quad\mathrm{H} \\ |\quad\;| & & \quad|\quad\;| \\ \mathrm{C=C+H-H} & \longrightarrow & \mathrm{H-C-C-H} \\ |\quad\;| & & \quad|\quad\;| \\ \mathrm{H}\quad\mathrm{H} & & \quad\mathrm{H}\quad\mathrm{H} \end{array}$$

will be:

(a) -243.6 kJ mol^{-1} (b) -120.0 kJ mol^{-1}

(c) 553.0 kJ mol^{-1} (d) 1523.6 kJ mol^{-1}

49. The following two reactions are known :

$Fe_2O_{3(s)} + 3CO_{(g)} \longrightarrow 2Fe_{(s)} + 3CO_{2(g)};\ \Delta H = -26.8$ kJ

$FeO_{(s)} + CO_{(g)} \longrightarrow Fe_{(s)} + CO_{2(g)};\ \Delta H = -16.5$ kJ

The value of ΔH for the following reaction

$Fe_2O_{3(s)} + CO_{(g)} \longrightarrow 2FeO_{(s)} + CO_{2(g)}$ is;

(a) +6.2 kJ (b) +10.3 kJ

(c) -43.3 kJ (d) -10.3 kJ

50. Consider the following processes :

	ΔH (kJ/mol)
$1/2\,A \to B$	+150
$3B \to 2C + D$	–125
$E + A \to 2D$	+350

For $B + D \to E + 2C$, ΔH will be :

(a) 525 kJ/mol (b) -175 kJ/mol

(c) -325 kJ/mol (d) 325 kJ/mol

51. The $\Delta_f H^\circ$ for $CO_2(g)$ $CO(g)$ and $H_2O(g)$ are –393.5, –110.5 and –241.8 kJ/mol respectively, the standard enthalpy change (in kJ) for the reaction

$CO_2(g) + H_2(g) \to CO(g) + H_2O(g)$ is :

(a) 524.1 (b) 41.2

(c) -262.5 (d) -41.2

52. If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1atm pressure are 52, – 394 and – 286 kJ/mol respectively, the change in enthalpy is equal to

(a) -141.2 kJ/mol (b) -1412 kJ/mol

(c) +14.2 kJ/mol (d) +1412 kJ/mol

53. Hess's law is used to calculate :

(a) enthalpy of reaction. (b) entropy of reaction

(c) work done in reaction (d) All of the above

54. Which thermochemical process is shown by the following figure ?

$$\begin{tikzcd} \boxed{X} \arrow[r, "\Delta_r H"] \arrow[d, "\Delta_r H_1"] & \boxed{Y} \\ \boxed{P} \arrow[r, "\Delta_r H_2"] & \boxed{Q} \arrow[u, "\Delta_r H_3"'] \end{tikzcd}$$

(a) Standard enthalpy of a reaction

(b) Born – Haber cycle of lattice enthalpy

(c) Hess's law of constant heat summation

(d) Standard enthalpy of a solution

55. The enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase is known as

(a) enthalpy of atomization.

(b) enthalpy of formation

(c) enthalpy of sublimation

(d) enthalpy of vaporization

56. Which of the following statements is true for the given reaction?

$$Na(s) \to Na(g);\ \Delta H^\ominus = 108.4 \text{ kJ mol}^{-1}$$

(a) The enthalpy of atomization is same as the enthalpy of vaporisation

(b) The enthalpy of atomization is same as the enthalpy of sublimation.

(c) The enthalpy of atomization is same as the bond enthalpy

(d) The enthalpy of atomization is same as the enthalpy of solution

57. The heat of combustion of a substance is :

(a) Always positive

(b) Always negative

(c) Numerically equal to the heat of formation

(d) Unpredictable

58. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \to 8CO_2(g) + 10H_2O(l)$ $\Delta_c H = -2658.0 \text{ kJ mol}^{-1}$

(b) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \to 4CO_2(g) + 5H_2O(g)$ $\Delta_c H = -1329.0 \text{ kJ mol}^{-1}$

(c) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \to 4CO_2(g) + 5H_2O(l)$ $\Delta_c H = -2658.0 \text{ kJ mol}^{-1}$

(d) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \to 4CO_2(g) + 5H_2O(l)$ $\Delta_c H = +2658.0 \text{ kJ mol}^{-1}$

59. Given that heat of neutralisation of strong acid and strong base is – 57.1 kJ. The heat produced when 0.25 mole of HCl is neutralised with 0.25 mole of NaOH in aqueous solution is :

(a) 14.275 kJ (b) 57.1 kJ

(c) 22.5 kJ (d) 28.6 kJ

60. For most of the ionic compounds, ΔH_{sol} is ....and the dissociation process is................

(a) positive ,exothermic (b) negative, exothermic

(c) positive, endothermic (d) negative,endothermic

61. Pick out the wrong statement

(a) The standard free energy of formation of all elements is zero

(b) A process accompanied by decrease in entropy is spontaneous under certain conditions

(c) The entropy of a perfectly crystalline substance at absolute zero is zero

(d) A process that leads to increase in free energy will be spontaneous

62. Identify the correct statement for change of Gibbs energy for a system (ΔG_{system}) at constant temperature and pressure

(a) If $\Delta G_{system} = 0$, the system has attained equilibrium

(b) If $\Delta G_{system} = 0$, the system is still moving in a particular direction

(c) If $\Delta G_{system} < 0$, the process is not spontaneous

(d) If $\Delta G_{system} > 0$, the process is not spontaneous

63. Identify the correct statement regarding a spontaneous process:

(a) Lowering of energy in the process is the only criterion for spontaneity.

(b) For a spontaneous process in an isolated system, the change in entropy is positive.

(c) Endothermic processes are never spontaneous.

(d) Exothermic processes are always spontaneous.

64. A chemical reaction will be spontaneous if it is accompanied by a decrease of

(a) entropy of the system.

(b) enthalpy of the system.

(c) internal energy of the system.

(d) free energy of the system.

65. In which of the following entropy decreases?

(a) Crystallization of sucrose solution

(b) Rusting of iron

(c) Melting of ice

(d) Vaporization of camphor

66. A spontaneous reaction is impossible if

(a) both ΔH and ΔS are negative

(b) both ΔH and ΔS are positive

(c) ΔH is negative and ΔS is positive

(d) ΔH is positive and ΔS is negative

67. For the gas phase reaction,

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

which of the following conditions are correct ?

(a) $\Delta H = 0$ and $\Delta S < 0$ (b) $\Delta H > 0$ and $\Delta S > 0$

(c) $\Delta H < 0$ and $\Delta S < 0$ (d) $\Delta H > 0$ and $\Delta S < 0$

68. The factor of ΔG values is important in metallurgy. The ΔG values for the following reactions at 800°C are given as :

$$S_2(s) + 2O_2(g) \longrightarrow 2SO_2(g)\ ;\ \Delta G = -544\ kJ$$

$$2Zn(s) + S_2(s) \longrightarrow 2ZnS(s)\ ;\ \Delta G = -293\ kJ$$

$$2Zn(s) + O_2(g) \longrightarrow 2ZnO(s)\ ;\ \Delta G = -480\ kJ$$

Then ΔG for the reaction :

$$2ZnS(s) + 3O_2(g) \longrightarrow 2ZnO(s) + 2SO_2(g)$$

will be :

(a) –357 kJ (b) –731 kJ

(c) –773 kJ (d) –229 kJ

69. Identify the correct statement regarding entropy.

(a) At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero.

(b) At absolute zero temperature, the entropy of a perfectly crystalline substance is positive.

(c) Absolute entropy of a substance cannot be determined.

(d) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero

70. Unit of entropy is

(a) $JK^{-1}\ mol^{-1}$ (b) $J\ mol^{-1}$

(c) $J^{-1}\ K^{-1}\ mol^{-1}$ (d) $JK\ mol^{-1}$

71. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

(a) $\Delta S_{system} + \Delta S_{surroundings} > 0$

(b) $\Delta S_{system} - \Delta S_{surroundings} > 0$

(c) $\Delta S_{system} > 0$ only

(d) $\Delta S_{surroundings} > 0$ only

72. In an exothermic reaction (reversible) which of the following has positive value?

(a) Enthalpy (b) Entropy

(c) Gibb's free energy (d) None of these

73. A reaction cannot take place spontaneously at any temperature when

(a) both ΔH and ΔS are positive

(b) both ΔH and ΔS are negative

(c) ΔH is negative and ΔS is positive

(d) ΔH is positive and ΔS is negative

74. A reaction is spontaneous at low temperature but non-spontaneous at high temperature. Which of the following is true for the reaction?

(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H < 0, \Delta S > 0$

(c) $\Delta H > 0, \Delta S = 0$ (d) $\Delta H < 0, \Delta S < 0$

75. At the sublimation temperature, for the process

$$CO_{2(s)} \rightleftharpoons CO_{2(g)}$$

(a) ΔH, ΔS and ΔG are all positive

(b) $\Delta H > 0, \Delta S > 0$ and $\Delta G < 0$

(c) $\Delta H < 0, \Delta S > 0$ and $\Delta G < 0$

(d) $\Delta H > 0, \Delta S > 0$ and $\Delta G = 0$

76. Choose the reaction with negative ΔS value.

(a) $2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$

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

(c) $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$

(d) $2KClO_{3(s)} \rightarrow 2KCl_{(s)} + 3O_{2(g)}$

77. A chemical reaction is spontaneous at 298 K but non-spontaneous at 350 K. Which one of the following is true for the reaction?

	ΔG	ΔH	ΔS
(a)	–	–	+
(b)	+	+	+
(c)	–	+	–
(d)	–	–	–

78. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

79. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction?

(a) Exothermic and increasing disorder

(b) Exothermic and decreasing disorder

(c) Endothermic and increasing disorder

(d) Endothermic and decreasing disorder

80. In which of the following reactions, standard entropy change ($\Delta S°$) is positive and standard Gibb's energy change ($\Delta G°$) decreases sharply with increasing temperature ?

(a) $\text{C graphite} + \frac{1}{2}O_2(g) \rightarrow CO(g)$

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

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

(d) $\frac{1}{2}\text{C graphite} + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$

81. Consider the following reaction occurring in an automobile

$$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$$

the sign of ΔH, ΔS and ΔG would be

(a) +, –, + (b) –, +, –

(c) –, +, + (d) +, +, –

82. A reaction occurs spontaneously if

(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are + ve

(b) $T\Delta S > \Delta H$ and ΔH is + ve and ΔS is – ve

(c) $T\Delta S > \Delta H$ and both ΔH and ΔS are + ve

(d) $T\Delta S = \Delta H$ and both ΔH and ΔS are + ve

83. 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)

STATEMENT TYPE QUESTIONS

84. Read the following statements carefully and choose the correct option

(i) The state of the system is specified by state functions or state variables.

(ii) Variables like P, V and T are called state variables or state functions

(iii) Their values depend only on the state of the system and not on how it is reached.

(a) (i) and (ii) are correct

(b) (ii) and (iii) are correct

(c) (i), (ii) and (iii) are correct

(d) Only (iii) is correct

85. Read the following statements carefully and choose the correct option

(i) Internal energy, U, of the system is a state function.

(ii) –w shows, that work is done on the system.

(iii) +w shows, that work is done by the system

(a) (i) and (ii) are correct (b) (ii) and (iii) are correct

(c) (i) and (iii) are correct (d) Only (i) is correct

86. Read the following statements carefully and choose the correct answer

(i) Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion.

(ii) Work is done during free expansion of an ideal gas whether the process is reversible or irreversible

(iii) No work is done during free expansion of an ideal gas whether the process is reversible or irreversible

(iv) No work is done during free expansion of an ideal gas when the process is reversible

(a) Only statement (iii) is correct

(b) Statements (i) and (iii) are correct

(c) Statements (ii) and (iv) are correct

(d) Statements (i) and (iv) are correct

87. Which of the following statement(s) is/are correct ?

(i) In case of expansion maximum amount of work can be obtained under isothermal conditions by reversibly carrying out the process rather than through irreversible route.

(ii) In case of compression, minimum amount of work can be done on system by carrying out the process irreversibly than reversibly.

(a) (i) and (ii) (b) Only (i)

(c) Only (ii) (d) Neither (i) nor (ii)

88. Read the following statements carefully and choose the correct option

(i) In case of diatomic molecules the enthalpy of atomization is also the bond dissociation enthalpy.

(ii) In case polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

(a) Both (i) and (ii) are correct

(b) (i) is correct but (ii) is incorrect

(c) (ii) is correct but (i) is incorrect

(d) Both (i) and (ii) are incorrect

89. Read the following statements regarding spontaneity of a process and mark the appropriate choice.

(i) When enthalpy factor is absent than randomness factor decides spontaneity of a process.

(ii) When randomness factor is absent then enthalpy factor decides spontaneity of a process.

(iii) When both the factors take place simultaneously, the magnitude of both the factors decide spontaneity of a process.

(a) Statements (i) and (ii) are correct and (iii) is incorrect.

(b) Statement (iii) is correct, (i) and (ii) are incorrect.

(c) Statements (i), (ii) and (iii) are correct.

(d) Statements (i), (ii) and (iii) are incorrect.

90. Which of the following statement is incorrect ?

(a) The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

(b) The standard state of a substance at a specified temperature is its pure form at 1 bar.

(c) The standard state of solid iron at 298 K is pure iron at 1 bar

(d) Standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH e.g., $-\Delta H^{\ominus}$

MATCHING TYPE QUESTIONS

91. Match the columns

Column-I	**Column-II**
(A) C_m	(p) $C_v \Delta T$
(B) q	(q) C/n
(C) $\Delta \cup$	(r) $C_p \Delta T$
(D) ΔH	(s) $C \Delta T$

(a) A – (q), B – (s), C – (r), D – (p)

(b) A – (q), B – (s), C – (p), D – (r)

(c) A – (s), B – (q), C – (p), D – (r)

(d) A – (q), B – (p), C – (r), D – (s)

92. Match the columns

Column-I	**Column-II**
(A) Free expansion at $\Delta V = 0$	(p) $q = -w = nRT \ \ell n \dfrac{V_f}{V_i}$
(B) Isothermal irreversible change	(q) $\Delta U = w_{ad}$
(C) Isothermal reversible change	(r) $\Delta U = q_v$
(D) For adiabatic change	(s) $q = -w = P_{ex}(V_f - V_i)$

(a) A – (s), B – (p), C – (r), D – (q)

(b) A – (r), B – (q), C – (p), D – (s)

(c) A – (r), B – (s), C – (p), D – (q)

(d) A – (q), B – (r), C – (s), D – (p)

93. Match the columns

Column-I	**Column-II**
(A) $p_{ext} = 0$	(p) Free expansion of an ideal gas
(B) $q = p_{ext}(V_f - V_i)$	(q) Adiabatic change
(C) $q = 2.303\ nRT \log (V_f / V_i)$	(r) Isothermal reversible change
(D) $\Delta U = W_{ad}$	(s) Isothermal irreversible change

(a) A – (p), B – (s), C – (r), D – (q)

(b) A – (p), B – (q), C – (r), D – (s)

(c) A – (p), B – (r), C – (s), D – (q)

(d) A – (p), B – (r), C – (q), D – (s)

94. Match the columns

Column-I	**Column-II**
(A) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$	(p) $\Delta H = \Delta U - 2RT$
(B) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$	(q) $\Delta H = \Delta U + 3RT$
(C) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	(r) $\Delta H = \Delta U$
(D) $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	(s) $\Delta H = \Delta U + RT$

(a) A – (r), B – (p), C – (q), D – (s)

(b) A – (r), B – (s), C – (p), D – (q)

(c) A – (q), B – (p), C – (s), D – (r)

(d) A – (s), B – (q), C – (p), D – (r)

95. Match the columns

Column-I	**Column-II**
(A) $C_4H_{10} + \dfrac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O; \Delta H = -w$	(p) Enthalpy of atomisation
(B) $CH_4 \rightarrow C + 4H; \Delta H = x$	(q) Enthalpy of formation
(C) $H_2 + Br_2 \rightarrow 2HBr; \Delta H = y$	(r) Enthalpy of combustion
(D) $Na^-(s) \rightarrow Na(g); \Delta H = z$	(s) Enthalpy of sublimation

(a) A – (s), B – (p), C – (q), D – (r)

(b) A – (q), B – (r), C – (p), D – (s)

(c) A – (r), B – (p), C – (q), D – (s)

(d) A – (p), B – (q), C – (s), D – (r)

96. Match the columns

Column-I	**Column-II**
(A) Exothermic	(p) $\Delta H = 0, \Delta E = 0$
(B) Spontaneous	(q) $\Delta G = 0$
(C) Cyclic process	(r) ΔH is negative
(D) Equilibrium	(s) ΔG is negative

(a) A – (q), B – (r), C – (p), D – (s)

(b) A – (s), B – (p), C – (r), D – (q)

(c) A – (p), B – (q), C – (s), D – (r)

(d) A – (r), B – (s), C – (p), D – (q)

97. Match the columns

	Column-I		**Column-II**
(A)	$\Delta H = -ve\ ;\ \Delta S = -ve$ $\Delta G = -ve$	(p)	Reaction will be non-spontaneous at high temperature
(B)	$\Delta H = -ve\ ;\ \Delta S = -ve$ $\Delta G = +ve$	(q)	Reaction will be non-spontaneous at low temperature
(C)	$\Delta H = +ve\ ;\ \Delta S = +ve$ $\Delta G = +ve$	(r)	Reaction will be spontaneous at low temperature
(D)	$\Delta H = +ve\ ;\ \Delta S = +ve$ $\Delta G = -ve$	(s)	Reaction will be spontaneous at high temperature

(a) A – (q), B – (r), C – (p), D – (s)
(b) A – (r), B – (p), C – (q), D – (s)
(c) A – (r), B – (q), C – (s), D – (p)
(d) A – (q), B – (s), C – (p), D – (r)

ASSERTION-REASON TYPE QUESTIONS

Directions : Each of these questions contain two statements, Assertion and Reason. Each of these questions also has four alternative choices, only one of which is the correct answer. You have to select one of the codes (a), (b), (c) and (d) given below.

(a) Assertion is correct, reason is correct; reason is a correct explanation for assertion.
(b) Assertion is correct, reason is correct; reason is not a correct explanation for assertion
(c) Assertion is correct, reason is incorrect
(d) Assertion is incorrect, reason is correct.

98. **Assertion :** T, P and V are state variables or state functions.
Reason : Their values depend on the state of the system and how it is reached.

99. **Assertion :** At constant temperature and pressure whatever heat absorbed by the system is used in doing work.
Reason : Internal energy change is zero.

100. **Assertion :** For an isothermal reversible process Q = –W i.e. work done by the system equals the heat absorbed by the system.
Reason : Enthalpy change (ΔH) is zero for isothermal process.

101. **Assertion :** Absolute value of internal energy of a substance cannot be determined.
Reason : It is impossible to determine exact values of constitutent energies of the substances.

102. **Assertion :** A process is called adiabatic if the system does not exchange heat with the surroundings.
Reason : It does not involve increase or decrease in temperature of the system.

103. **Assertion :** There is exchange in internal energy in a cyclic process.
Reason : Cyclic proces is the one in which the sytem returns to its initial state after a number of reactions.

104. **Assertion :** Internal energy is an extensive property.
Reason : Internal energy depends upon the amount of the system.

105. **Assertion :** The mass and volume of a substance are the extensive properties and are proportional to each other.
Reason : The ratio of mass of a sample to its volume is an intensive property.

106. **Assertion :** First law of thermodynamics is applicable to an electric fan or a heater.
Reason : In an electric fan, the electrical energy is converted into mechanical work that moves the blades. In a heater, electrical energy is converted into heat energy.

107. **Assertion :** The value of enthalpy of neutralization of weak acid and strong base is numerically less than 57.1 kJ.
Reason : All the OH^- ions furnished by 1 g equivalent of strong base are not completely neutralized.

108. **Assertion :** When a solid melts, decrease in enthalpy is observed.
Reason : Melting of a solid is endothermic.

109. **Assertion :** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
Reason : Entropy of the system increases with increase in temperature.

110. **Assertion :** An exothermic process which is non-spontaneous at high temperature may become spontaneous at a low temperature.
Reason : There occurs a decrease in entropy factor as the temperature is decreased.

CRITICAL THINKING TYPE QUESTIONS

111. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
(a) $q = 0, \Delta T \neq 0, w = 0$
(b) $q \neq 0, \Delta T = 0, w = 0$
(c) $q = 0, \Delta T = 0, w = 0$
(d) $q = 0, \Delta T < 0, w \neq 0$

112. According to the first law of thermodynamics which of the following quantities represents change in a state function ?
(a) q_{rev}
(b) $q_{rev} - W_{rev}$
(c) q_{rev}/W_{rev}
(d) $q_{rev} + W_{rev}$

113. If ΔH is the change in enthalpy and ΔE, the change in internal energy accompanying a gaseous reaction, then
(a) ΔH is always greater than ΔE
(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
(c) ΔH is always less than ΔE
(d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants

114. For an isothermal reversible expansion process, the value of q can be calculated by the expression
(a) $q = 2.303nRT\log\dfrac{V_2}{V_1}$
(b) $q = -2.303nRT\log\dfrac{V_2}{V_1}$
(c) $q = -P_{exp}nRT\log\dfrac{V_1}{V_2}$
(d) None of these

115. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0ºC. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be:

(R = 8.314 J/mol K) (ln 7.5 = 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

116. According to the first law of thermodynamics, $\Delta U = q + W$. In special cases the statement can be expressed in different ways. Which of the following is not a correct expression ?

(a) At constant temperature $q = -W$

(b) When no work is done $\Delta U = q$

(c) In gaseous system $\Delta U = q + P\Delta V$

(d) When work is done by the system : $\Delta U = q + W$

117. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy ?

(a) > 40 kJ (b) < 40 kJ

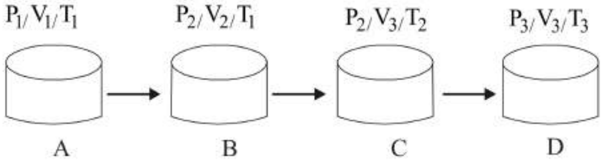
(c) Zero (d) 40 kJ

118. Under isothermal condition for one mole of ideal gas what is the ratio of work done under reversible to irreversible process, initially held at 20 atm undergoes expansion from 1L to 2L, at 298K, under external pressure of 10 atm?

(a) 1.7 (b) 2.0

(c) 1.4 (d) 1.0

119. Processes A to B, B to C and C to D shown in the figure below respectively are ?



(a) Isothermal, isobaric and isochoric

(b) Isobaric, isothermal and isochoric

(c) Isothermal, isothermal and isobaric

(d) Isobaric, isobaric and isothermal

120. What is the internal energy (kJ) change occurs when 36g of $H_2O(l)$ converted to $H_2O(g)$? $\Delta H°$(vapourisation) = 40.79kJ/mol

(a) 75.38 (b) 80.98

(c) 70.98 (d) 45.89

121. Consider the reaction :

$$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g),$$

$\Delta_r H = -111$ kJ.

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be :

(given, ΔH of sublimation for N_2O_5 is -54 kJ mol^{-1})

(a) + 54 kJ (b) + 219 kJ

(c) – 219 J (d) – 165 kJ

122. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?

(a) $(T_f)_{rev} = (T_f)_{irrev}$

(b) $T_f = T_i$ for both reversible and irreversible processes

(c) $(T_f)_{irrev} > (T_f)_{rev}$

(d) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

123. Given

Reaction	**Energy Change (in kJ)**
$Li(s) \rightarrow Li(g)$	161
$Li(g) \rightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
$F(g) + e^- \rightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	– 1047
$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$	– 617

Based on data provided, the value of electron gain enthalpy of fluorine would be :

(a) – 300 kJ mol^{-1} (b) – 350 kJ mol^{-1}

(c) – 328 kJ mol^{-1} (d) – 228 kJ mol^{-1}

124. The standard enthalpy of formation $(\Delta_f H°_{298})$ for methane, CH_4 is – 74.9 kJ mol^{-1}. In order to calculate the average energy given out in the formation of a C – H bond from this it is necessary to know which one of the following?

(a) The dissociation energy of the hydrogen molecule, H_2.

(b) The first four ionisation energies of carbon.

(c) The dissociation energy of H_2 and enthalpy and sublimation of carbon (graphite).

(d) The first four ionisation energies of carbon and electron affinity of hydrogen.

125. For complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l),$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25ºC. Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be:

(R = 8.314 kJ mol^{-1})

(a) –1366.95 kJ mol^{-1} (b) –1361.95 kJ mol^{-1}

(c) –1460.95 kJ mol^{-1} (d) –1350.50 kJ mol^{-1}

126. Standard enthalpy of vapourisation $\Delta_{vap} H°$ 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 :

(a) +37.56 (b) – 43.76

(c) +43.76 (d) +40.66

(Assume water vapour to behave like an ideal gas).

127. Consider the following reactions:

(i) $H^+_{(aq)} + OH^-_{(aq)} = H_2O_{(l)}$, $\Delta H = -X_1$ kJ mol^{-1}

(ii) $H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O(l)$, $\Delta H = -X_2$ kJ mol^{-1}

(iii) $CO_{2(g)} + H_{2(g)} = CO_{(g)} + H_2O$, $\Delta H = -X_3$ kJ mol^{-1}

(iv) $C_2H_{2(g)} + \frac{5}{2}O_{2(g)} = 2CO_2(g) + H_2O(l)$' $\Delta H = +\ 4X_4$ kJ mol^{-1}

Enthalpy of formation of $H_2O_{(l)}$ is

(a) $+X_3$ kJ mol^{-1} (b) $-X_4$ kJ mol^{-1}
(c) $+X_1$ kJ mol^{-1} (d) $-X_2$ kJ mol^{-1}

128. Diborane is a potential rocket fuel which undergoes combustion according to the equation

$$B_2H_6(g) + 3O_2(s) \longrightarrow B_2O_3(s) + 3H_2O(g)$$

Calculate the enthalpy change for the combustion of diborane. Given

(i) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s);\ \Delta H = -1273$ kJ per mol

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H = -286$ kJ per mol

(iii) $H_2O(l) \longrightarrow H_2O(g);\ \Delta H = 44$ kJ per mol

(iv) $2B\,(s) + 3H_2\,(g) \longrightarrow B_2H_6\,(g);\ \Delta H = 36$ kJ per mol

(a) +2035 kJ per mol (b) –2035 kJ per mol
(c) +2167 kJ per mol (d) –2167 kJ per mol

129. How many molecules of ATP, undergo hydrolysis to raise the temperature of 180 kg of water which was originally at room temperature by 1°C ? C{P,m} water = 75.32J/mol/K, ΔH{P} for ATP hydrolysis= 7 kcal/mol

(a) 1.5×10^{25} (b) 2.00×10^{23}
(c) 3.4×10^{25} (d) 4.0×10^{24}

130. What is the amount of heat (in Joules) absorbed by 18 g of water initially at room temperature heated to 100°C ? If 10g of Cu is added to this water , than decrease in temperature (in Kelvin) of water was found to be? C (p,m) for water 75.32J/mol K ; C (p,m) for Cu = 24.47J/mol K.

(a) 5649, 369 (b) 5544, 324
(c) 5278, 342 (d) 3425, 425

131. The enthalpy changes for the following processes are listed below :

$Cl_2(g) \rightarrow 2Cl(g)$,	242.3 kJ mol^{-1}
$I_2(g) \rightarrow 2I(g)$,	151.0 kJ mol^{-1}
$ICl(g) \rightarrow I(g) + Cl(g)$,	211.3 kJ mol^{-1}
$I_2(s) \rightarrow I_2(g)$,	62.76 kJ mol^{-1}

Given that the standard states for iodine and chlorine are $I_2(s)$ and $Cl_2(g)$, the standard enthalpy of formation for $ICl(g)$ is :

(a) +16.8 kJ mol^{-1} (b) +244.8 kJ mol^{-1}
(c) –14.6 kJ mol^{-1} (d) –16.8 kJ mol^{-1}

132. What is the equilibrium constant if ATP hydrolysis by water produce standard free energy of –50 kJ/mole under normal body conditions ?

(a) 2.66×10^8 (b) 5.81×10^8
(c) 1.18×10^7 (d) 1.98×10^8

133. A reaction with $\Delta H = 0$, is found to be spontaneous. This is due to

(a) ΔS is negative (b) ΔS is positive
(c) TΔS is positive (d) Both (b) and (c)

134. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria

(a) $(dS)_{V,E} > 0,\ (dG)_{T,P} < 0$
(b) $(dS)_{V,E} = 0,\ (dG)_{T,P} = 0$
(c) $(dS)_{V,E} = 0,\ (dG)_{T,P} > 0$
(d) $(dS)_{V,E} < 0,\ (dG)_{T,P} < 0$

135. In conversion of lime-stone to lime,

$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ the values of ΔH° and ΔS° are + 179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

(a) 1118 K (b) 1008 K
(c) 1200 K (d) 845 K.

136. For vaporization of water at 1 atmospheric pressure, the values of ΔH and ΔS are 40.63 kJmol^{-1} and 108.8 JK^{-1} mol^{-1}, respectively. The temperature when Gibbs energy change (ΔG) for this transformation will be zero, is:

(a) 293.4 K (b) 273.4 K
(c) 393.4 K (d) 373.4 K.

HINTS AND SOLUTIONS

FACT/DEFINITION TYPE QUESTIONS

1. **(c)**

2. **(b)** The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.

3. **(b)**

4. **(c)** The universe = The system + The surroundings

5. **(c)**

6. **(c)** Closed system can exchange energy and not matter with surroundings. Pressure cooker provides closed system.

7. **(c)** Isolated system can not exchange mass or energy.

8. **(b)** We can describe the state of a gas by quoting its pressure (P), volume (V), temperature (T), amount (n) etc.

9. **(d)** We know that q (heat) and work (w) are not state functions but (q + w) is a state function. H – TS (i.e. G) is also a state functions. Thus II and III are not state functions so the correct answer is option (d).

10. **(c)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.

11. **(c)**

12. **(a)** Internal energy is a quantity which represents the total energy of the system. It may be chemical, electrical, and mechanical or any other type of energy you may think of, the sum of all these is the internal energy of the system.

13. **(d)** **14.** **(b)**

15. **(c)** In accordance with Hess's law.

16. **(a)**

17. **(a)** $\Delta E = \Delta Q - W$

For adiabatic expansion, $\Delta Q = 0$

$\Rightarrow \Delta E = -W$

The negative sign shows decrease in Internal energy, which is equal to the work done on the system by the surroundings.

18. **(d)** q is a path dependent function, H is a state function because it depends on U, p and V, all of which are state functions.

19. **(a)** The shaded area shows work done on an ideal gas in a cylinder when it is compressed by a constant external pressure

20. **(b)** As volume is constant hence work done in this proces is zero hence heat supplied is equal to change in internal energy.

21. **(b)** $W = -\,p\Delta V$

$= -3(6-4) = -6$ litre atmosphere

$= -6 \times 101.32 = -608\,J$

22. **(c)** For isothermal reversible expansion.

$$w = -nRT \ln \frac{V_2}{V}$$

23. **(c)** $W = -P\Delta V = -10^5(1 \times 10^{-2} - 1 \times 10^{-3}) = -900J$

24. **(d)** The difference between ΔH and ΔU is not usually significant for systems consisting of only solids or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved.

25. **(b)** $\Delta H = \Delta E + P\Delta V$, for solid and liquid,

$\Delta V =$ or $\Delta H = \Delta E + \Delta n\,RT$, for solids and liquids $\Delta n = 0$.

26. **(c)** During isothermal expansion of an ideal gas,

$\Delta T = 0$. Now $H = E + PV$

$\because\ \Delta H = \Delta E + \Delta(PV)$

$\therefore\ \Delta H = \Delta E + \Delta(nRT)$;

Thus if $\Delta T = 0.$, $\Delta H = \Delta E$

i.e., remain unaffected

27. **(d)** We know that

$\Delta H = \Delta E + P\Delta V$

In the reactions, $H_2 + Br_2 \rightarrow 2HBr$ there is no change in volume or $\Delta V = 0$

So, $\Delta H = \Delta E$ for this reaction

28. **(b)** $\Delta n = -\frac{1}{2}; \Delta H = \Delta E - \frac{1}{2}RT; \Rightarrow \Delta E > \Delta H$

29. **(c)** As all reactant and product are liquid $\Delta n_{(g)} = 0$

$\Delta H = \Delta E - \Delta nRT$

$\Delta H = \Delta E \qquad (\because \Delta n = 0)$

30. **(a)** $\Delta H = \Delta E + P\Delta V$

31. **(c)** $\Delta H = \Delta E + \Delta nRT$

$\Delta n = 3 - (1 + 5)$

$= 3 - 6 = -3$

$\Delta H - \Delta E = (-3RT)$

32. **(b)** $\Delta H = \Delta U + \Delta nRT$ for $N_2 + 3H_2 \longrightarrow 2NH_3$

$\Delta n_g = 2 - 4 = -2$

$\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT \ \therefore \Delta U > \Delta H$

33. **(a)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.

34. **(a)** Volume depends upon mass. Hence it is extensive property.

35. **(c)** An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties

36. **(d)** The magnitude of the heat capacity depends on the size, composition and nature of the system.

37. **(b)** The heat required to raise the temperature of body by 1C° is called thermal capacity or heat capacity.

38. **(d)** $\frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$

39. **(c)** Given $C_p = 75\ JK^{-1}\ mol^{-1}$

$n = \frac{100}{18}$ mole, $Q = 1000\ J \quad \Delta T = ?$

$Q = nC_p\Delta T \Rightarrow \Delta T = \frac{1000 \times 18}{100 \times 75} = 2.4\ K$

40. **(b)** 1 calorie = 4.184 joule

41. **(b)** The coefficients in a balanced thermo-chemical equation refer to the number of moles (not to molecules) of reactants and products involved in the reaction.

42. **(c)**

43. **(b)** Enthalpy of formation of C_2H_4, CO_2 and H_2O are $52, -394$ and -286 kJ/ mol respectively. (Given)

The reaction is

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$

change in enthalpy,

$(\Delta H) = \Delta H_{products} - \Delta H_{reactants}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0)$

$= -1412$ kJ/ mol.

44. **(b)** **45.** **(c)**

46. **(b)** $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$\Delta H_{HCl} = \sum$ B.E. of reactant $- \sum$ B.E. of products

$-90 = \frac{1}{2} \times 430 + \frac{1}{2} + \frac{1}{2} \times 240 -$ B.E. of HCl

$\therefore$ B.E. of HCl $= 215 + 120 + 90$

$= 425\ kJ\ mol^{-1}$

47. **(c)** The reaction for formation of HCl can be written as

$H_2 + Cl_2 \rightarrow 2HCl$

$H-H + Cl-Cl \rightarrow 2\,(H-Cl)$

Substituting the given values, we get enthalpy of formation of

$2HCl = -(862 - 676) = -186$ kJ.

$\therefore$ Enthalpy of formation of

$HCl = \frac{-186}{2}$ kJ $= -93$ kJ.

48. **(b)** Enthalpy of reaction

$= B.E_{(Reactant)} - B.E_{(Product)}$

$= \left[B.E_{(C=C)} + 4\,B.E._{(C-H)} + B.E._{(H-H)}\right] - \left[B.E._{(C-C)} + 6\,B.E._{(C-H)}\right]$

$= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$

$= -120.0\ kJ\ mol^{-1}$

49. **(a)** $Fe_2O_{3(s)} + CO_{(g)} \longrightarrow 2FeO_{(s)} + CO_{2(g)}$

$\Delta H = -26.8 + 33.0 = +6.2$ kJ

50. **(b)** Given ΔH

$\frac{1}{2}A \longrightarrow B \qquad +150 \qquad ...(1)$

$3B \longrightarrow 2C + D \qquad -125 \qquad ...(2)$

$E + A \longrightarrow 2D \qquad +350 \qquad ...(3)$

To calculate ΔH operate

2 × eq. (1) + eq. (2) – eq. (3)

$\Delta H = 300 - 125 - 350 = -175$

51. **(b)** $\Delta H = \Sigma\left[\Delta H_f^\circ \text{ products}\right] - \Sigma\left[\Delta H_f^\circ \text{ reactants}\right]$

$\Delta H^\circ = [\Delta H_f^\circ(CO)(g) + \Delta H_f^\circ(H_2O)(g)] - [\Delta H_f^\circ(CO_2)(g) + \Delta H_f^\circ(H_2)(g)]$

$= [-110.5 + (-241.8)] - [-393.5 + 0] = 41.2$

52. **(b)** $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O.$

Change in enthalpy,

$\Delta H = \Delta H_{products} - \Delta H_{reactants}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0)$

$= -1412$ kJ/ mol.

53. **(a)** Hess's law is used for calculating enthalpy of reaction.

54. **(c)** $X \xrightarrow{\Delta H} Y$

$X \xrightarrow{\Delta H_1} P \xrightarrow{\Delta H_2} Q \xrightarrow{\Delta H_3} Y$

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

55. **(a)** **56.** **(b)**

57. **(b)** Heat of combustion of a substance is always negative as it is the amount of heat evolved (i.e. decrease in enthalpy) when one mole of the substance is completely burnt in air or oxygen.

58. **(c)**

59. **(a)** Conc. of HCl = 0.25 mole

Conc. of NaOH = 0.25 mole

Heat of neutralization of strong acid by strong base = – 57.1 kJ

$HCl + NaOH \longrightarrow NaCl + H_2O - 57.1kJ$

1 mole of HCl neutralise 1 mole of NaOH, heat evolved = 57.1 kJ

$\therefore$ 0.25 mole of HCl neutralise 0.25 mole of NaOH

$\therefore$ Heat evolved = 57.1 × 0.25 = 14.275 kJ

60. **(c)**

61. **(d)** A process is spontaneous only when there is decrease in the value of free energy, i.e., ΔG is –ve.

62. **(a)** If $\Delta G_{system} = 0$ the system has attained equilibrium is right choice.

In it alternative (d) is most confusing as when $\Delta G > 0$, the process may be spontaneous when it is coupled with a reaction which has $\Delta G < 0$ and total ΔG is negative, so right answer is (a).

63. **(b)** Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system the change in entropy is positive.

64. **(d)** ΔG is negative for a spontaneous process.

65. **(a)** Crystallization of sucrose solution. Entropy is a measure of randomness during the crystallisation of sucrose solution liquid state is changing into solid state hence entropy decreases.

66. **(d)** $\Delta G = \Delta H - T\Delta S$; ΔG is positive for a reaction to be non-spontaneous when ΔH is positive and ΔS is negative.

67. **(b)** For the reaction

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

The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, i.e, $\Delta H > 0$.

Further

$\Delta n = (1 + 1) - 1 = +1$

Hence more number of molecules are present in products which shows more randomness i.e. $\Delta S > 0$ (ΔS is positive)

68. **(b)** For the reaction

$2ZnS \rightarrow 2Zn + S_2$; $\Delta G_1{}^{o} = 293$ kJ ....(1)

$2Zn + O_2 \rightarrow 2ZnO$; $\Delta G_2{}^{o} = -480$ kJ ....(2)

$S_2 + 2O_2 \rightarrow 2SO_2$; $\Delta G_3{}^{o} = -544$ kJ ....(3)

ΔG^{o} for the reaction

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

can be obtained by adding eqn. (1), (2) and (3)

$\Rightarrow \Delta G^{o} = 293 - 480 - 544 = -731$ kJ

69. **(a)** Third law of Thermodynamics.

70. **(a)** $\Delta S = \dfrac{q}{T}$

$q \longrightarrow$ required heat per mole

$T \longrightarrow$ constant absolute temperature

Unit of entropy is JK^{-1} mol^{-1}

71. **(a)** For a spontaneous process, ΔS_{total} is always positive.

72. **(d)** For an exothermic reaction all three enthalpy, entropy and Gibb's free energy change have negative values.

73. **(d)** Gibb's-Helmholtz equation is

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

For a reaction to be non-spontaneous at all temperatures, ΔH should be +ve and ΔS should be –ve $\therefore \Delta G = +ve - T \times (-ve)$; the value of ΔG is always positive for such a reaction and hence it will be non-spontaneous at all temperatures.

74. **(d)** We know that $\Delta G = \Delta H - T\Delta S$

When $\Delta H < 0$ and $\Delta S < 0$ then ΔG will be negative at low temperatures (positive at high temperature) and the reaction will be spontaneous.

75. **(d)** Since the process is at equilibrium $\Delta G = 0$ for $\Delta G = 0$, they should be $\Delta H > 0$, $\Delta S > 0$.

76. **(c)** ΔS has negative value if number of gaseous moles decreases during a reaction, $\Delta n_g = -ve$

For the reaction

$2SO_2 + O_2 \rightarrow 2SO_3$

$\Delta n_g = 2 - 3 = -1$

77. **(d)** $\Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous,

$\Delta H = -ve$, $\Delta S = +ve$

at all temperatures.

but at high temperature, $\Delta G = \underbrace{\Delta H}_{-ve} - \underbrace{T\Delta S}_{+ve}$

Thus the second term will have high positive value and reaction will be non-spontaneous.

78. **(b)** At equilibrium $\Delta G = 0$

Hence, $\Delta G = \Delta H - T_e\Delta S = 0$

$\therefore \Delta H = T_e\Delta S$ or $T_e = \dfrac{\Delta H}{\Delta S}$

For a spontaneous reaction

ΔG must be negative which is possible only if

$\Delta H - T\Delta S < 0$

$\therefore \Delta H < T\Delta S$ or $T > \dfrac{\Delta H}{\Delta S}$; $T_e < T$

79. **(a)** Measure of disorder of a system is nothing but Entropy. For a spontaneous reaction, $\Delta G < 0$. As per Gibbs Helmholtz equation,

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

Thus ΔG is –ve only

When $\Delta H = -ve$ (exothermic)

and $\Delta S = +ve$ (increasing disorder)

80. **(a)** Since, in the first reaction gaseous products are forming from solid carbon hence entropy will increase i.e. $\Delta S = +ve$.

$$C\,(gr.) + \frac{1}{2}\,O_2(g) \rightarrow CO(g);\ \Delta S^{o} = +ve$$

Since, $\Delta G^{o} = \Delta H^{o} - T\Delta S$ hence the value of ΔG decrease on increasing temperature.

81. **(b)** This is combustion reaction, which is always exothermic hence

$\Delta H = -ve$

As the no. of gaseous molecules are increasing hence entropy increases

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

For a spontaneous reaction

$\Delta G = -ve$

Which is possible in this case as $\Delta H = -ve$ and $\Delta S = +ve$.

82. **(c)** For a spontaneous reaction $\Delta G(-ve)$, which is possible if $\Delta S = +ve$, $\Delta H = +ve$
and $T\Delta S > \Delta H$ [As $\Delta G = \Delta H - T\Delta S$]

83. **(c)** $\Delta S = \frac{\Delta H}{T} = \frac{1.435 \times 10^3}{273}$

$= 5.260\ \text{cal} / (\text{mol K})$

STATEMENT TYPE QUESTIONS

84. **(c)** Variables like P, V and T which describes the state of system are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

85. **(d)** The positive sign expresses when work is done on the system. Similarly, negative sign expresses when work is done by the system

86. **(b)** **87.** **(a)** **88.** **(a)**

89. **(c)** All the statements regarding spontaneity of a reaction are correct.

90. **(c)** The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar. Standard state of solid ion at 500 K is pure iron at 1 bar. The standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH e.g., $-\Delta H^{\ominus}$.

MATCHING TYPE QUESTIONS

91. **(b)** **92.** **(c)**

93. **(a)** A – (p), B – (s), C – (r), D – (q)

Expansion of a gas in vacuum ($p_{ext} = 0$) is called free expansion.

For isothermal irreversible change

$q = -W = p_{ext}(V_f - V_i)$

for isothermal reversible change

$q = -W = nRT \ln (V_f/V_i)$

$= 2.303\ nRT \log V_f/V_i$

For adiabatic change, $q = 0$, $\Delta U = W_{ad}$

94. **(b)** (A) $\Delta n_g = 2 - 2 = 0$ hence $\Delta H = \Delta U$

(B) $\Delta n_g = 2 - 1 = 1$ hence $\Delta H = \Delta U + RT$

(C) $\Delta n_g = 2 - 4 = -2$ hence $\Delta H = \Delta U - 2RT$

(D) $\Delta n_g = 5 - 2 = 3$ hence $\Delta H = \Delta U + 3RT$

95. **(c)** **96.** **(d)** **97.** **(b)**

ASSERTION-REASON TYPE QUESTIONS

98. **(c)** Values of state functions depend only on the state of the system and not on how it is reached.

99. **(a)** $Q = -W$ if $\Delta E = 0$

100. **(b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).

$\therefore$ According to first law of thermodynamics

$\because Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)

If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.

101. **(a)** It is fact that absolute values of internal energy of substances cannot be determined. It is also true that it is not possible to determine exact values of constitutent energies of a substance.

102. **(c)** It may involve increase or decrease in temperature of the system. Systems in which such processes occur, are thermally insulated from the surroundings.

103. **(a)** As internal energy is a state function so its value depends on intial and final states of the system. In case of cyclic system initial and final states are same. So $\Delta E = 0$, and similarly $\Delta H = 0$.

104. **(a)** The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties eg, internal energy.

105. **(b)** The mass and volume depend upon the quantity of matter so these are extensive properties while ratio of mass to its volume does not depend upon the quantity of matter so this ratio is an extensive property.

106. **(a)** In case of electric fan electrical energy is converted into mechanical energy and in case of heater, electrical energy is converted into heat energy. Therefore, these follow the first law of thermodynamics.

107. **(c)** The value of enthalpy of neutralisation of weak acid by strong base is less than 57.1 kJ. This is due to the reason that the part of energy liberated during combination of H^+ and OH^+ ions is utilised in the ionisation of weak acid.

108. **(d)** When a solid melts, increase in enthalpy is observed.

109. **(b)** The factor $T\Delta S$ increases with increase in temperature.

110. **(b)** Both assertion and reason are true but reason is not the correct explanation of assertion.

For a process to be spontaneous ΔG must be negative.

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

Exothermic process (ΔH is negative) is non-spontaneous if ΔS is negative and temperature is high because in such condition $T\Delta S > \Delta H$. ($\Delta G = \Delta H - T\Delta S = +$ tive). When temperature is decreased, $T\Delta S < \Delta H$ ($\Delta G = \Delta H - T\Delta S = -$tive) and so the reaction becomes spontaneous.

CRITICAL THINKING TYPE QUESTIONS

111. (c) Justification : free expansion $w = 0$
adiabatic process $q = 0$
$\Delta U = q + w = 0$, this means that internal energy remains constant. Therefore,
$\Delta T = 0$.

112. (d) Mathematical expression of first law of thermodynamics
$\Delta E = q + w$, ΔE is a state function.

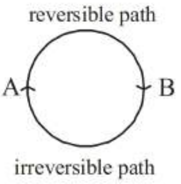
113. (d) As $\Delta H = \Delta E + \Delta n_g RT$
if $n_p < n_r$; $\Delta n_g = n_p - n_r = -$ ve.
Hence $\Delta H < \Delta E$.

114. (a) $q = -W = 2.303 nRT \log \frac{V_2}{V_1}$

115. (a) Process is isothermal reversible expansion, hence $\Delta U = 0$, therefore $q = -W$.
Since $q = +208$ J, $W = -208$ J

116. (d) When work is done by the system, $\Delta U = q - W$

117. (c) For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.



118. (a) $-W_{\text{irreversible}} = P_{ext}(V_2 - V_1)$
$= 10 \text{ atm } (2L - 1L)$
$= 10 \text{ atm} - L$

$$-W_{\text{reversible}} = \int_{V_1}^{V_2} P_{ex} dv$$

$$= 2.303 \, nRT \log \frac{V_2}{V_1}$$

$$= 1 \times 2.303 \times 0.0821 \text{ atm–L/K/mol} \times \log \frac{2}{1}$$

$$= 16.96 \text{ atm–L}$$

$$\frac{W_{\text{reversible}}}{W_{\text{irreversible}}} = \frac{16.96}{10.00} = 1.69 \approx 1.7$$

119. (a)

120. (a) $H_2O(l) \rightarrow H_2O(g)$
$\Delta H_{vap} = 40.79$ kJ/mol
$\Delta H = \Delta U + \Delta n_g RT$
$\Rightarrow 40.79 \text{ kJ/mol} = \Delta U + (1)(8.314 \text{ JK}^{-1} \text{ mol}^{-1})(373 \text{ K})$

$$\Rightarrow \Delta U^o = \left(40.79 \text{ kJ/mol} - \frac{8.314 \times 373}{1000} \text{kJ/mol}\right)$$

$$= (40.79 - 3.10) \text{ kJ/mol}$$

$$= 37.69 \frac{\text{kJ}}{\text{mol}}$$

Internal energy change for 36 g of water

$$= 37.69 \frac{\text{kJ}}{\text{mol}} \times \frac{36\text{g}}{18\text{g/mol}}$$

$\Delta U = 75.98$ kJ

121. (d)

$$\begin{tikzcd} 4NO_2(g) + O_2(g) \arrow[r] \arrow[dr, "\Delta H'"'] & 2N_2O_5(g), \Delta_r H = -111 \text{ kJ} \arrow[d, "-54 \text{ kJ}"] \\ & 2N_2O_5(s) \end{tikzcd}$$

$-111 - 54 = \Delta H'$
$\Delta H' = -165$ kJ

122. (c) In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So

$$T_f(\text{rev.}) < T_f(\text{irr.})$$

123. (c) Applying Hess's Law

$$\Delta_f H^\circ = \Delta_{sub} H + \frac{1}{2} \Delta_{diss} H + \text{I.E.} + \text{E.A} + \Delta_{lattice} H$$

$-617 = 161 + 520 + 77 + \text{E.A.} + (-1047)$
$\text{E.A.} = -617 + 289 = -328 \text{ kJ mol}^{-1}$
$\therefore$ electron affinity of fluorine
$= -328 \text{ kJ mol}^{-1}$

124. (a) To calculate average enthalpy of C – H bond in methane following informations are needed

(i) dissociation energy of H_2 i.e.

$$\frac{1}{2} H_2(g) \longrightarrow H(g); \Delta H = x(\text{suppose} \quad)$$

(ii) Sublimation energy of C(*graphite*) to C(*g*)

$$C(graphite) \longrightarrow C(g); \Delta H = y\,(\text{Suppose})$$

Given

$$C(graphite) + 2H_2(g) \longrightarrow CH_4(g); \Delta H = 75 \text{ kJ mol}^{-1}$$

125. (a) $C_2H_5OH(\ell) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(\ell)$
Bomb calorimeter gives ΔU of the reaction
Given, $\Delta U = -1364.47 \text{ kJ mol}^{-1}$
$\Delta n_g = -1$

$$\Delta H = \Delta U + \Delta n_g RT = -1364.47 - \frac{1 \times 8.314 \times 298}{1000}$$

$$= -1366.93 \text{ kJ mol}^{-1}$$

126. (a) $H_2O(\ell) \rightleftharpoons H_2O(g) + Q$
$\Delta E = 37558$ J/mol
$\Delta E = 37.56 \text{ kJ mol}^{-1}$

127. (d) This reaction shows the formation of H_2O, and the X_2 represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent atoms.

128. (b) For the equation

$$B_2H_6(g)+3O_2(g)\longrightarrow B_2O_3(g)+3H_2O(g)$$

Eqs. (i) + 3 (ii) + 3 (iii) – (iv)

$$\Delta H = -1273+3(-286)+3(44)-36$$
$$= -1273-858+132-36$$
$$= -2035 \text{ kJ/mol}$$

129. (a) $q_p = \Delta H = C_p dT$

$$\Rightarrow q_p = 75.32\frac{J}{K\,mol}\times(299-298)K$$

$$\Rightarrow q_p = 75.32\frac{J}{K\,mol}$$

For 180 kg of water, no. of moles of water

$$= \frac{180\times10^3 g}{18 g/mol} = 10^4 g \text{ moles}$$

$$q_p = 75.32\frac{J}{mol}\times10^4 \text{ moles}$$

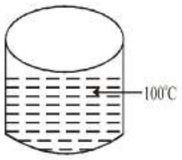
$$= 753.2\times10^3 J = 753.2 \text{ kJ}$$

ΔH for ATP = 7 kcal / mol
= 7 × 4.184 kJ/mol
= 29.2 kJ/mol

6.022×10^{23} molecules of ATP produce = 29.2 kJ
29.2 kJ produced from 6.022×10^{23} molecules

753.2 kJ produced from $6.022\times10^{23}\times\frac{75.8}{29.2}$
$= 1.5\times10^{25}$ molecules

130. (a) 18gm of water at 100°C
10gm of Cu at 25°C is added.



$$q_p = C_{p,m}dT$$

$$= 75.32\times\frac{J}{K\,mol}\times\frac{18g}{18g/mol}(373-298\ K)$$

$$= 75.32\frac{J}{K}\times75 K$$

$$= 5.649\times10^3 J$$

If now 10g of copper is added $C_{p,m} = 24.47$ J/ mol K
Amount of heat gained by Cu

$$= 24.47\frac{J}{K\,mol}\times\frac{10g}{63g/mol}(373-298)K$$

$= 291.3$ J
Heat lost by water = 291.30 J

$$-291.30 J = 75.32\frac{J}{K}\times(T_2-373K\quad)$$

$$\Rightarrow -3.947 K = T_2 - 373 K$$
$$\Rightarrow T_2 = 369.05 K$$

131. (a) $I_2(s)+Cl_2(g)\longrightarrow 2ICl(g)$

$\Delta_r H = [\Delta H(I_2(s)\rightarrow I_2(g)) + \Delta H_{I-I} + \Delta H_{Cl-Cl}] - [\Delta H_{I-Cl}]$
$= 151.0+242.3+62.76-2\times211.3 = 33.46$

$$\Delta_f H^\circ(ICl) = \frac{33.46}{2} = 16.73 \text{ kJ/mol}$$

132. (a) $\Delta G = -RT\ln K_{eq}$: Normal body temperature = 37°C

$$\Rightarrow -50\frac{kJ}{mol} = 8.314\frac{J}{K\,mol}\times310\ \ln K_{eq}$$

$$\Rightarrow 19.39 = \ln K_{eq}$$

$$\Rightarrow K_{eq} = 2.6\times10^8$$

133. (b) $\Delta G = \Delta H - T\Delta S$
$\Delta G = -T\Delta S$ (when $\Delta H = 0$ and $\Delta S = +ve$)
$\Delta G = -ve$

134. (a) For spontaneous reaction, $dS > 0$ and dG should be negative i.e. < 0.

135. (a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
For a spontaneous reaction $\Delta G^\circ < 0$

$$\text{or } \Delta H^\circ - T\Delta S^\circ < 0 \Rightarrow T > \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$\Rightarrow T > \frac{179.3\times10^3}{160.2} > 1117.9K \approx 1118K$$

136. (d) $H_2O_{(\ell)} \xrightleftharpoons{1atm} H_2O_{(g)}$

$\Delta H = 40630 \text{ J mol}^{-1}$
$\Delta S = 108.8 \text{ JK}^{-1}\text{ mol}^{-1}$
$\Delta G = \Delta H - T\Delta S$ When $\Delta G = 0$,
$\Delta H - T\Delta S = 0$

$$T = \frac{\Delta H}{\Delta S} = \frac{40630 \text{ J mol}^{-1}}{108.8 \text{ J mol}^{-1}} = 373.4 \text{ K.}$$