PART B — CHEMISTRY

31. In aqueous solution the ionization constants for carbonic acid are

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(1) The concentration of H^+ is double that of CO_3^{2-}.

(2) The concentration of CO_3^{2-} is 0.034 M.

(3) The concentration of CO_3^{2-} is greater than that of HCO_3^-.

(4) The concentrations of H^+ and HCO_3^- are approximately equal.

32. Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is

(1) 5.0×10^{-8} g

(2) 1.2×10^{-10} g

(3) 1.2×10^{-9} g

(4) 6.2×10^{-5} g

33. The correct sequence which shows decreasing order of the ionic radii of the elements is

(1) $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$

(2) $Al^{3+} > Mg^{2+} > Na^+ > F^- > O^{2-}$

(3) $Na^+ > Mg^{2+} > Al^{3+} > O^{2-} > F^-$

(4) $Na^+ > F^- > Mg^{2+} > O^{2-} > Al^{3+}$

34. In the chemical reactions,

$$\underset{\text{NH}_2}{\bigcirc} \xrightarrow[\text{HCl, 278 K}]{\text{NaNO}_2} A \xrightarrow{\text{HBF}_4} B$$
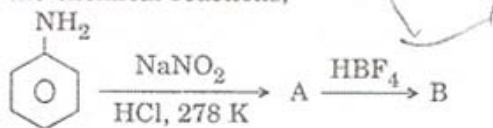
the compounds 'A' and 'B' respectively are

(1) nitrobenzene and chlorobenzene

(2) nitrobenzene and fluorobenzene

(3) phenol and benzene

(4) benzene diazonium chloride and fluorobenzene

35. If 10^{-4} dm^3 of water is introduced into a 1.0 dm^3 flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established ?

(Given : Vapour pressure of H_2O at 300 K is 3170 Pa; R = 8.314 J K^{-1} mol^{-1})

(1) 1.27×10^{-3} mol

(2) 5.56×10^{-3} mol

(3) 1.53×10^{-2} mol

(4) 4.46×10^{-2} mol

36. From amongst the following alcohols the one that would react fastest with conc. HCl and anhydrous $ZnCl_2$, is

(1) 1-Butanol

(2) 2-Butanol

(3) 2-Methylpropan-2-ol

(4) 2-Methylpropanol

37. If sodium sulphate is considered to be completely dissociated into cations and anions in aqueous solution, the change in freezing point of water (ΔT_f), when 0.01 mol of sodium sulphate is dissolved in 1 kg of water, is ($K_f = 1.86$ K kg mol^{-1})

(1) 0.0186 K

(2) 0.0372 K

(3) 0.0558 K

(4) 0.0744 K

38. Three reactions involving $H_2PO_4^-$ are given below :

(i) $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

(ii) $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

(iii) $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ?

(1) (i) only

(2) (ii) only

(3) (i) and (ii)

(4) (iii) only

39. The main product of the following reaction is

$$C_6H_5CH_2CH(OH)CH(CH_3)_2 \xrightarrow{\text{conc. } H_2SO_4} ?$$

(1)
$$\begin{array}{c} H_5C_6CH_2CH_2 \\ H_3C \end{array} C = CH_2$$

(2)
$$\begin{array}{c} H_5C_6 \\ H \end{array} C = C \begin{array}{c} H \\ CH(CH_3)_2 \end{array}$$

(3)
$$\begin{array}{c} C_6H_5CH_2 \\ H \end{array} C = C \begin{array}{c} CH_3 \\ CH_3 \end{array}$$

(4)
$$\begin{array}{c} C_6H_5 \\ H \end{array} C = C \begin{array}{c} CH(CH_3)_2 \\ H \end{array}$$

40. The energy required to break one mole of $Cl - Cl$ bonds in Cl_2 is 242 kJ mol^{-1}. The longest wavelength of light capable of breaking a single $Cl - Cl$ bond is ($c = 3 \times 10^8$ ms^{-1} and $N_A = 6.02 \times 10^{23}$ mol^{-1})

(1) 494 nm

(2) 594 nm

(3) 640 nm

(4) 700 nm

41. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralization. The percentage of nitrogen in the compound is

(1) 29.5

(2) 59.0

(3) 47.4

(4) 23.7

42. Ionisation energy of He^+ is 19.6×10^{-18} J $atom^{-1}$. The energy of the first stationary state (n = 1) of Li^{2+} is

(1) 8.82×10^{-17} J $atom^{-1}$

(2) 4.41×10^{-16} J $atom^{-1}$

(3) -4.41×10^{-17} J $atom^{-1}$

(4) -2.2×10^{-15} J $atom^{-1}$

SPACE FOR ROUGH WORK

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43. On mixing, heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components (heptane and octane) are 105 kPa and 45 kPa respectively. Vapour pressure of the solution obtained by mixing 25·0 g of heptane and 35 g of octane will be (molar mass of heptane = 100 g mol^{-1} and of octane = 114 g mol^{-1})

(1) 144·5 kPa

(2) 72·0 kPa

(3) 36·1 kPa

(4) 96·2 kPa

44. Which one of the following has an optical isomer ?

(1) [Zn(en)$_2$]$^{2+}$

(2) [Zn(en)(NH$_3$)$_2$]$^{2+}$

(3) [Co(en)$_3$]$^{3+}$

(4) [Co(H$_2$O)$_4$(en)]$^{3+}$

(en = ethylenediamine)

45. Consider the following bromides :

Me⌣⌣⌣Br   Me (B)   Me (C)
   (A)
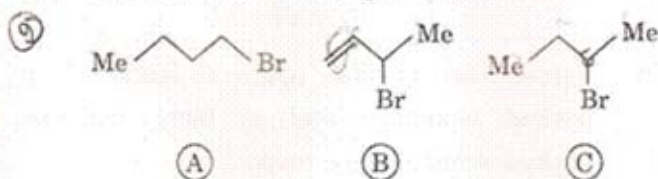
The correct order of S$_N$1 reactivity is

(1) A > B > C

(2) B > C > A

(3) B > A > C

(4) C > B > A

46. One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is

(1) ethene

(2) propene

(3) 1-butene

(4) 2-butene

47. Consider the reaction :

$$Cl_2 (aq) + H_2S (aq) \rightarrow S (s) + 2 H^+ (aq) + 2 Cl^- (aq)$$
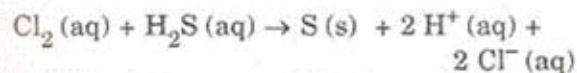
The rate equation for this reaction is
$$rate = k [Cl_2] [H_2S]$$

Which of these mechanisms is/are consistent with this rate equation ?

A. $Cl_2 + H_2S \rightarrow H^+ + Cl^- + Cl^+ + HS^-$ (slow)
   $Cl^+ + HS^- \rightarrow H^+ + Cl^- + S$ (fast)

B. $H_2S \Leftrightarrow H^+ + HS^-$ (fast equilibrium)
   $Cl_2 + HS^- \rightarrow 2 Cl^- + H^+ + S$ (slow)

(1) A only

(2) B only

(3) Both A and B

(4) Neither A nor B

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48. The Gibbs energy for the decomposition of Al_2O_3 at 500 °C is as follows :

$$\frac{2}{3} Al_2O_3 \rightarrow \frac{4}{3} Al + O_2, \Delta_r G = +966 \text{ kJ mol}^{-1}$$
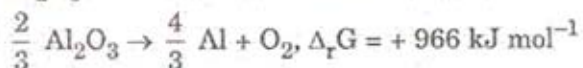
The potential difference needed for electrolytic reduction of Al_2O_3 at 500 °C is at least

(1) 5·0 V

(2) 4·5 V

(3) 3·0 V

(4) 2·5 V

49. The correct order of increasing basicity of the given conjugate bases ($R = CH_3$) is

(1) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$

(2) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$

(3) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$

(4) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

50. The edge length of a face centered cubic cell of an ionic substance is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is

(1) 144 pm

(2) 288 pm

(3) 398 pm

(4) 618 pm

51. Out of the following, the alkene that exhibits optical isomerism is

(1) 2-methyl-2-pentene

(2) 3-methyl-2-pentene

(3) 4-methyl-1-pentene

(4) 3-methyl-1-pentene

52. 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

(1) $T = T_e$

(2) $T_e > T$

(3) $T > T_e$

(4) T_e is 5 times T

53. Percentages of free space in cubic close packed structure and in body centered packed structure are respectively

(1) 48% and 26%

(2) 30% and 26%

(3) 26% and 32%

(4) 32% and 48%

54. The polymer containing strong intermolecular forces e.g. hydrogen bonding, is

   (1) natural rubber

   (2) teflon

   (3) nylon 6,6

   (4) polystyrene

55. At 25 °C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ?

   (1) 8

   (2) 9

   (3) 10

   (4) 11

56. The correct order of $E^{\circ}_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is

   (1) Cr > Mn > Fe > Co

   (2) Mn > Cr > Fe > Co

   (3) Cr > Fe > Mn > Co

   (4) Fe > Mn > Cr > Co

57. Biuret test is *not* given by

   (1) proteins

   (2) carbohydrates

   (3) polypeptides

   (4) urea

58. The time for half life period of a certain reaction A $\longrightarrow$ Products is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1}, how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction ?

   (1) 1 h

   (2) 4 h

   (3) 0.5 h

   (4) 0.25 h

59. A solution containing 2.675 g of $CoCl_3 . 6 NH_3$ (molar mass = 267.5 g mol^{-1}) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 4.78 g of AgCl (molar mass = 143.5 g mol^{-1}). The formula of the complex is (At. mass of Ag = 108 u)

   (1) $[CoCl(NH_3)_5] Cl_2$

   (2) $[Co(NH_3)_6] Cl_3$

   (3) $[CoCl_2(NH_3)_4] Cl$

   (4) $[CoCl_3(NH_3)_3]$

60. 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

   (1) -1102 kJ mol^{-1}

   (2) -964 kJ mol^{-1}

   (3) $+352$ kJ mol^{-1}

   (4) $+1056$ kJ mol^{-1}

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