BHU M.Sc. CHEMISTRY ENTRANCE - 2014

Time : 2½ Hours   **Full Marks : 450**

Instructions:

(*i*)   Attempt as many questions as you can. Each question carries **3 marks**. **One mark** will be deducted for each incorrect answer. Zero mark will be awarded for each unattempted question.

(*ii*)   If more than one alternative answers seem to be approximate to the correct answer, choose the closest one.

1.   Oxine compound can better be estimated by
   (1) gravimetric method
   (2) conductometric method
   (3) potentiometric method
   (4) bromate- bromide reaction method

2.   The indicator Eriochrome black-T can only be used in the complexo-metric titrations of metal ion at pH
   (1) 7.0
   (2) 5.0
   (3) 10.0
   (4) 12.0

3.   The disodium salt of EDTA is always used metal analysis because
   (1) it severely imparts alkanity to the test solution
   (2) it moderately imparts acidity to the test solution
   (3) it severely imparts acidity to the test solution
   (4) it moderately imparts alkanity to the test solution

4.   The stability constant for the metal-EDTA complex should be
   (1) smaller than that for metal-Eriochrome-T complex
   (2) equal to the stability constant of metal-Eriochrome-T complex
   (3) greater than that for metal-Eriochrome-T complex
   (4) the half of the stability constant of metal-Eriochrome-T complex

5.   The quadrivalent cerium is used for the titration of reductants only in
   (1) Strong basic medium
   (2) Weak basic medium
   (3) Strong acidic medium
   (4) Weak acidic medium

6.   Which one is widely used as a primary standard in redox titrimetry?
   (1) Iodine
   (2) Arsenic (III) oxide
   (3) Sulfanilamide
   (4) 8-hydroxy quinoline

7.   In isotope dilution method for the determination of iron, W_0 g of iron as $^{59}FeCl_3$, that has a specific activity A_o, was mixed so that ^{59}Fe is equally distributed throughout the sample. A portion of the total iron is then isolated in a pure weighable form that has the specific activity A_1. If the original sample contained W_1 g of iron, then the fraction of initial activity found in this portion can be expressed as

   (1) $W_1 = W_0\left(\dfrac{A_0}{A_1}-1\right)$

   (2) $W_1 = W_0\left(1-\dfrac{A_0}{A_1}\right)$

   (3) $W_0 = W_1\left(\dfrac{A_0}{A_1}-1\right)$

   (4) $W_0 = W_1\left(1-\dfrac{A_0}{A_1}\right)$

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8. The equivalence point potential for the titration of Ce(IV) with standard Fe(II) is
   (1) 0.76 V
   (2) 1.06 V
   (3) 2.12 V
   (4) 1.44 V
   [given : E^0 Ce^{4+} / Ce^{3+} = 1.44V, E^0 Fe^{3+} / Fe^{2+} = 0.68]

9. The Mohr's salt is
   (1) $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$
   (2) $FeSO_4(NH_4)_2SO_4 \cdot 3H_2O$
   (3) $2FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$
   (4) $FeSO_4 \cdot 2(NH_4)_2SO_4 \cdot 6H_2O$

10. The bromate-bromide reaction is

    $$BrO_3^- + 5Br^- + 6H^+ \rightarrow 3Br_2 + 3H_2O$$

    The librated Br_2 is titrated with standard sodium thiosulfate solution. The one mol potassium bromate can thus be equated to
    (1) 1 mol $S_2O_3^{2-}$
    (2) 3 mol $S_2O_3^{2-}$
    (3) 6 mol $S_2O_3^{2-}$
    (4) 9 mol $S_2O_3^{2-}$

11. A 50.0 mL aliquot of 0.05m ammonia is titrated with 0.10 m acetic acid. What would be the nature of the solution at the equivalence point?
    (1) slightly acidic
    (2) slightly basic
    (3) turbid
    (4) neutral

12. The pH values of 10^{-9} M HCl, 1.0 M HCl, and 10^{-2} M NaOH could respectively be obtained as
    (1) 9.0, 1.0, 2.0
    (2) 6.9, 0.0, 12.0
    (3) 7.0, 0.1, 2.1
    (4) 9.1, 6.9, 12.1

13. The H^+ ion has abnormally high mobility in comparison to other monovalent ions since
    (1) H^+ ion is smallest in size
    (2) H^+ ion is largest in size
    (3) H^+ ion follows hopping mechanism in solution
    (4) H^+ ion concentration mechanism high

14. The methyl orange indicator in strong acid vs strong base
    (1) cannot be used
    (2) can be used
    (3) can be used with insignificant
    (4) can be used with large titration error

15. The conductometry titration curve given below
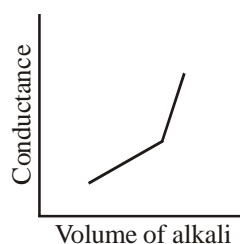
represents a titration involving
    (1) Strong acid VS strong base
    (2) Weak acid VS strong base
    (3) Strong acid VS weak base
    (4) Weak acid VS weak base

16. A common expression for the distribution coefficient (K) in ion-exchange resin is
    (1) K = amount of ion/mL of solution
    (2) K = amount of ion/1000mL of solution
    (3) $K \dfrac{\text{amount of ion/g of dry resin}}{\text{amount of ion/1000g of dry resin}}$
    (4) $K = \dfrac{\text{amount of ion/g of dry resin}}{\text{amount of ion/mLg of solution}}$

17. Which ones are strong cation and strong anion exchange resins?

(A) Sulfonated polystyrene

(B) Condensed acrylic acid

(C) Polystyrene with – $CH_2N\,Me_3Cl$

(D) Polystyrene with sec- amine

Answer Codes:

(1) A and C

(2) B and D

(3) A and D

(4) C and D

18. The height equivalent to a theoretical plate (HETP) can be expressed in terms of the column length (L), retention (t_R), and the peak-width (W) as

(1) $HETP = \dfrac{L}{16}\left(\dfrac{W}{\in t_R}\right)^2$

(2) $HETP = \dfrac{16}{L}\left(\dfrac{t_R}{W}\right)^2$

(3) $HETP = 16\left(\dfrac{L \times t_R}{W}\right)^2$

(4) $HETP = 16\left(\dfrac{t_R}{W}\right)^2$

19. The best procedure to improve resolution between two chromatographic peak is

(1) increasing column-length, decreasing band-width

(2) decreasing column-length, increasing band-width

(3) increasing column-length, increasing band-width

(4) decreasing column-length, decreasing band-width

20. The Van Deemter equation in terms of coefficient of multiple path effect (A), coefficient of longitudinal diffusion (B), coefficient of mass transfer (C), and linear velocity of mobile phase (u) can be represented as

(1) H = A + B/u + Cu

(2) H = B + A/u + Cu

(3) H = A + B/u + C/u

(4) H = A/u + B/u + Cu^2

21. The isocratic elution in chromatography can be defined as

(1) elution under conditions of constant temperature and pressure

(2) elution under conditions of variable temperature and pressure

(3) elution under conditions of constant mobile-phase composition

(4) elution under conditions of varying mobile-phase compositions

22. Which one could **not** be an ideal detector in gas chromatography?

(1) Photo-multiplier tube

(2) Flame-ionization detector

(3) Thermal-conductivity detector

(4) Electron-capture detector

23. In reversed-phase chromatography, which statement is **correct**?

(1) The least polar component is eluted first and increasing the polarity of the mobile-phase decreases the elution time

(2) The most polar component elutes first and increasing the mobile-phase polarity increases the elution time

(3) A non-polar component is eluted first without having any effect of the polarity of the mobile-phase

(4) There is no effect of polarity either of the component or the mobile-phase

24. For non-polar analytes having molecular mass greater than 10,000, one of the best HPLC technique would be

(1) ion-exchange chromatography

(2) liquid-liquid partition chromatography

(3) liquid-bonded phase partition chromatography

(4) gel permeation chromatography

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25. Two sets of the percentage iron in a sample resulted in the following data (true value = 36.32)

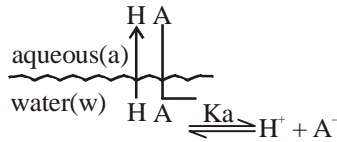$\overline{X} + S_x = 36.27 \pm 0.16$ $N_x = 5$

$\overline{Y} + S_y = 36.34 \pm 0.22$ $N_y = 8$

Which set of data is more accurate?

(1) X - set (2) Y - set (3) both sets (4) No - sets

26. If 'X' is an acid (HA), the pictorial representation of solvent extraction of 'X' can be depicted as

The relationship between distribution ratio (D) and distribution coefficient (K_D) can be obtained as

(1) $D = \dfrac{K_D}{1 + K_a / [H^+]_w}$

(2) $K_D = \dfrac{D}{1 + [H^+]_w / K_a}$

(3) $D = \dfrac{1 + K_a / [H^+]_w}{K_D}$

(4) $K_D = \dfrac{1 + K_a / [H^+]_w}{D}$

27. Employing Nernst's distribution law, V mL of solution containing W g of solute is repeatedly extracted with v mL of another solvent which is immiscible with first one. In n^{th} operation mass of solute (W_n) that remain extracted will be

(1) $W_n = W\left(\dfrac{K_D V}{K_D V + v}\right)^n$

(2) $W_n = W\left(\dfrac{K_D V + v}{K_D V}\right)^n$

(3) $W_n = W\left(\dfrac{K_D v}{K_D V + v}\right)^n$

(4) $W_n = W\left(\dfrac{K_D V + V}{K_D v + V}\right)^n$

28. A solution containing n independently absorbing species, the total absorbance is represented in terms of molar absorptivity ($\in$), analyte concentration (c) and path length (b) as

(1) $A = [\in_1 c_1 + \in_2 c_2 + ... \in_n c_n]b$

(2) $A = [\in_1 c_1^2 + \in_2 c_2^2 + ... \in_n c_n^2]b$

(3) $A = [\in_1 c_1^n + \in_2 c_2^n + ... \in_n c_n^n]b$

(4) $A = [\in_1 c_1 + \in_2 c_2 + ... \in_n c_n]b / n$

29. Beer's law governs the behaviour of

(1) dilute solutions (≤ 0.1 M) only

(2) concentrated solutions (≥ 0.1 M) only

(3) dilute solutions (≤ 0.01 M) only

(4) concentrated solutions (≥ 1.0 M) only

30. The units of absorbance (A) and molar absorptivity are, respectively

(1) no unit and $dm^3 \, mol^{-1} \, cm^{-1}$

(2) $dm^3 \, mol^{-1} \, cm^{-1}$ and no unit

(3) $mol.cm^{-1}$ and $dm^3 \, mol^{-1} \, cm^{-1}$

(4) both have no unit

31. The Beer's law is not obeyed if

(1) monochromatic light is not used

(2) monochromatic light is used

(3) polychromatic light is not used

(4) polychromatic light is used

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32. Iron (III) can quantitatively be extracted from hydrochloric acid medium into diethyl ether. The extracted species is
    (1) $Fe(III)[(C_2H_5)_2O]^-_2$
    (2) $FeCl_3 \cdot H_2O \cdot (C_2H_5)_2O$
    (3) $FeCl_4 : H^+[(C_2H_5)_2O]^-_2$
    (4) $(C_2H_5)_2O : H^+, FeCl_4[(C_2H_5)O]^-_2$

33. Marble wall may be affected with atmospheric sulfuric acid as
    (1) receptor
    (2) precipitator
    (3) sink
    (4) neutralizer

34. Which is called as 'killer' species in the environment?
    (1) NO
    (2) NO_2
    (3) CO
    (4) CO_2

35. The dissolved oxygen in water can be estimated by
    (1) the Volhard method
    (2) the Fajans method
    (3) the Mohr method
    (4) the Winkler's method

36. The altitude of troposphere is
    (1) 0-11 km
    (2) 11-50 km
    (3) 50-85 km
    (4) 85-500 km

37. Which one is **not** a primary air pollutant?
    (1) CO_2
    (2) CO
    (3) NO_2
    (4) SO_2

38. The domestic waste water involves the following sequence of treatments
    (1) Screening, Sedimentation, aerobic digestion, incineration
    (2) Sedimentation, aerobic digestion, screening, incineration
    (3) Aerobic digestion, screening, sedimentation, incineration
    (4) Incineration, aerobic digestion, screening, sedimentation

39. For which of the following ions is the colour in aqueous solution **not** caused by any *d-d* transition?
    (1) MnO_4^-
    (2) VO^{2+}
    (3) MnO_4^{2-}
    (4) Mn^{3+}

40. Which salt upon heating produces oxygen?
    (1) potassium oxide
    (2) potassium chlorate
    (3) potassium chloride
    (4) potassium carbonate

41. Which of the following isotopes is useful for archaeological dating purposes?
    (1) ^{11}C
    (2) ^{12}C
    (3) ^{13}C
    (4) ^{14}C

42. From each pair given below identify the ion which is larger is size
    $[Co^{2+}, Co^{3+}] [Fe^{2+}, Zn^{2+}] [Na^+, F^-] [O^{2-}, S^{2-}]$
    (1) $Co^{2+}, Zn^{2+}, F^-, S^{2-}$
    (2) $Co^{3+}, Fe^{2+}, Na^+, S^{2-}$
    (3) $Co^{2+}, Fe^{2+}, F^-, S^{2-}$
    (4) $Co^{3+}, Zn^{2+}, Na^+, O^{2-}$

43. Which one, among the given atoms, has the highest number of unpaired electrons in its ground state?
    (1) B
    (2) C
    (3) N
    (4) O

44. Which halide of silver is soluble in water?
    (1) AgF
    (2) AgCl
    (3) AgBr
    (4) AgI

45. How many moles of water will react with one mole of P_4O_{10}?
    (1) 1 mole
    (2) 2 moles
    (3) 4 moles
    (4) 6 moles

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46. A compound, A_2B_3 is prepared by reacting 1 mole of A with 2 moles of B_2. If 0.25 mole of A_2B_3 is obtained in the preparation, what is the percentage yield?

    (1) 25% (2) 50% (3) 75% (4) 100%

47. 10 ml of 0.10 N sodium hydroxide is added to 20 ml 0.10 N sulphuric acid and the resultant solution is titrated against 0.10 N sodium hydroxide. What will be the titre value at the end point?

    (1) 5 ml (2) 10 ml (3) 20 ml (4) 30 ml

48. An aqueous solution of a substance gives a white precipitate when a few drops of sodium hydroxide are added. The precipitate dissolves when excess of sodium hydroxide is added. The substance may be

    (1) aluminium sulphate
    (2) silver nitrate
    (3) cadmium chloride
    (4) mercuric chloride

49. Which reagent may be used to test for sulphate ions in solution?

    (1) hydrochloric acid
    (2) nitric acid
    (3) magnesium chloride
    (4) barium chloride

50. An element crystallizes in a FCC lattice. How many atoms are there per unit cell?

    (1) 1 (2) 2 (3) 3 (4) 4

51. What is the oxidation state of iron in $Na_2[Fe(CO)_4]$?

    (1) –2 (2) –1 (3) 0 (4) 2

52. What is the molality of a 0.001 M solution of $CaCl_2$ in water (M. W. of $CaCl_2$ = 111g)?

    (1) 1 m (2) 0.001 m (3) 0.111 m (4) 111 m

53. What is the charge (n) on the silicate ion $Si_2O_7^n$?

    (1) –2 (2) –4 (3) –6 (4) –7

54. Silver is extracted from the crude metal by leaching with a solution of NaCN in the presence of air. The role of NaCN is to

    (1) oxidize Ag to Ag^+
    (2) form the complex $[Ag(CN)_4]^{3-}$
    (3) form the complex $[Ag(CN)_4]^{2-}$
    (4) form the complex $[Ag(CN)_2]^-$

55. $CoCl_4^{2-}$ and $Co(H_2O)_6^{2+}$ have different colours. This is because

    (1) they have Co in different oxidation states
    (2) $CoCl_4^{2-}$ is tetrahedral while $Co(H_2O)_6^{2+}$ is octahedral
    (3) they have different number of unpaired electrons
    (4) $CoCl_4^{2-}$ is square planar while $Co(H_2O)_6^{2+}$ is octahedral

56. Dimethylglyoxime reagent is used to test for

    (1) Ca^{2+} (2) Ni^{2+} (3) Fe^{3+} (4) Al^{3+}

57. Which molecule has zero bond order?

    (1) H_2^+ (2) H_2 (3) HeH (4) He_2

58. What is the bond order in NO molecule?

    (1) 2.5 (2) 2 (3) 1.5 (4) 1

59. Which of the following is an example of a non-planar molecule (or ion)?

    (1) carbonate
    (2) perchlorate
    (3) xenon tetrafluoride
    (4) boron trifluoride

60. CuI_2 is unstable because, it readily decomposes to:

    (1) Cu and I^-
    (2) Cu and I_2
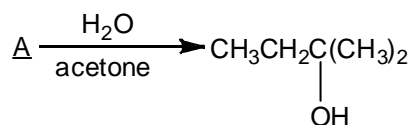   (3) CuI and I_2
    (4) CuI and I

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61. Which one among the chlorides, $ZnCl_2$, $HgCl_2$, $BaCl_2$, $AlCl_3$, is dissociated to the least extent in aqueous solutions?

    (1) $ZnCl_2$ (2) $HgCl_2$ (3) $CaCl_2$ (4) $AlCl_3$

62. Which one among the given ions, has the highest polarizing power?

    (1) Na^+ (2) Ca^{2+} (3) Mn^{3+} (4) Al^{3+}

63. Which compound can act as a Lewis acid as well as a Lewis base?

    (1) H_2O (2) $SnCl_2$ (3) NH_3 (4) BF_3

64. Perovskite is the mineral $CaTiO_3$. The perovskite crystal structure is adopted by several oxides as well as some fluorides. Which one, among the given formulae, most likely represents a known fluoride having the perovskite structure?

    (1) $CaTiF_3$ (2) $KMnF_3$ (3) $NaMnF_4$ (4) $CaFeF_3$

65. Upon heating to about 500ºC CsCl crystal changes its structure to rock salt structure. What happens to the coordination number of Cs?

    (1) changes from 6 to 12   (2) changes from 8 to 12

    (3) changes from 8 to 6   (4) does not change

66. The bond angles in ammonia molecule are ....

    (1) 90 degrees   (2) exactly tetrahedral

    (3) larger than tetrahedral   (4) less than tetrahedral

67. Which one of the following set contains one element each from *s*-block, *p*-block and *d*-block?

    (1) Na, K, Fe   (2) Rb, Ru, Sb

    (3) B, Cl, Sr   (4) Sc, Pt, Se

68. Which ligand can lead to linkage isomers?

    (1) azide   (2) cyanate   (3) oxalate   (4) nitrate

69. If you were to prepare $[Mn(en)_2(OH)_2]_2^{2+}$ ions (en = 1, 2-diaminoethane), how many isomers, including geometrical and optical, can you expect to get?

    (1) only one   (2) two

    (3) three   (4) four

70. Which of the following molecules / ions exhibit isomerism? (1) $Pt(NH_3)_2Cl_2$; (2) $Ni(NH_3)_2Cl_2$; (3) $Cu(H_2O)_3Cl_3$; (4) $[Cr(oxalate)_3]^{3-}$; (5) $[Fe(H_2O)_5Cl]^{2+}$

    (1) compounds (1), (3) and (5)   (2) compounds (1), (2) and (3)

    (3) compounds (2), (3) and (4)   (4) compounds (1), (3) and (4)

71. What is the change in oxidation state of cobalt in the following reaction?

    $[Co(NH_3)_4Cl_2]^+ + H_2O \rightarrow [Co(NH_3)_4(H_2O)Cl]^{2+} + Cl^-$

    (1) increases from +2 to +3   (2) decreases from +3 to +2

    (3) increases from +1 to +2   (4) does not change

72. Identify the acids in the following two reactions:

    $NOF + ClF_3 = NO + ClF_4^-$

    $XeO_3 + OH^- = HXeO_4^-$

    (1) ClF_3 and XeO_3 (2) ClF_3 and OH^-

    (3) NOF and OH^- (4) NOF and XeO_3

73. Which is the most common oxidation state observed for the lanthanide elements in their compounds?

    (1) –1   (2) +2   (3) +3   (4) +4

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74. The magnetic moment of $[Co(H_2O)]^{3+}$ is zero and that of $Mn(CN)_6]^{3-}$ is 2.9 B.M. From this it may be concluded that

    (1) both ions are high spin

    (2) both ions are low spin

    (3) $Co(H_2O)_6^{3+}$ is low spin, $Mn(CN)_6^{3-}$ is high spin

    (4) $Co(H_2O)_6^{3+}$ is diamagnetic, $Mn(CN)_6^{3-}$ is high spin

75. Which set contains two diamagnetic compounds?

    (1) $[K_2CoCl_4, Cu(SCN), Na_2PdCl_4]$

    (2) $[CuCl_2, CuI, Cr(NH_3)_4Cl_2]$

    (3) $[Na_2NiCl_4, GdCl_3, Ag_2S]$

    (4) $[NiO, Fe_3O_4, Ru(NH_3)Cl_3]$

76. Which one of the following reagents is a nucleophile?

    (1) BF_3
    (2) SO_3
    (3) $\overset{\bullet\bullet}{C}Cl_2$
    (4) NH_3

77. Which reactive intermediate is belived to be part of the reaction shown?

    $$RCH = CH_2 \xrightarrow{\text{HBr, ROOR}} RCH_2CH_2Br$$

    (1) Free radical
    (2) Carbocation
    (3) Bromonium ion
    (4) Oxacyclopropane

78. Rank the following alcohols in order of increasing acidity
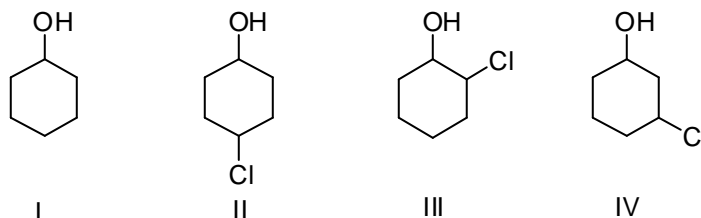
    Answer Codes:

    (1) I < II < III < IV

    (2) I < II < IV < III

    (3) I < III < IV < II

    (4) IV < I < III < II

79. The mechanism of chlorination of methane does **not** actually involve one of the following steps

    (1) $Cl_2 \xrightarrow{hv} 2Cl$

    (2) $Cl\bullet + CH_4 \rightarrow HCl + CH_3^\bullet$

    (3) $Cl\bullet + CH_4 \rightarrow CH_3Cl + H\bullet$

    (4) $CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$

80. In this transformation

    What is the best structure for A?

    (1) $BrCH_2CH_2CH(CH_3)_2$

    (2)

    (3)

    (4)

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81. When methyl bromide is hydrolyzed using hydroxide ions, methanol and bromide ions are produced. What will be the rate of reaction if the concentration of methyl bromide is tripled and that of hydroxide ions is doubled?

    (1) No change is reaction rate
    (2) Reaction rate is tripled
    (3) Reaction rate is doubled
    (4) Reaction rate is increased six-fold

82. The major product in the reaction given below is

$$CH_3CH_2-CH-CH_3 \xrightarrow[\Delta]{Ag_2O} (CH_3)_3N + ?$$

with $\overset{\oplus}{N}H(CH_3)I^{\ominus}$ group on the CH

    (1) *trans*-2-butene
    (2) *cis*-2-butene
    (3) 1-butene
    (4) 2-Iodobutane

83. The number of isomeric olefins that result from the treatment of 2-bromopentane with NaOEt is

    (1) one
    (2) two
    (3) three
    (4) four

84. Pyrrole is a much weaker base than pyrrolidine (azacyclopentane) for which of the following reasons

    (1) Pyrrole is aromatic
    (2) Pyrrole is a Lewis acid
    (3) The nitrogen in pyrrole is more electropositive than that in pyrrolidine
    (4) Pyrrolidine can give up the proton on the nitrogen atom more readily than can pyrrole

85. D-Glucose on treatment with excess of phenyl-hydrazine followed by hydrolysis of the product with aqueous HCl gives

    (1) D-Glucosazone
    (2) D-Glucosamine
    (3) D-Glutaric acid
    (4) D-Glucosone

86. Quinoline is obtained by heating a mixture of aniline, nitrobenzene, glycerol, conc. Sulphuric acid and ferrous sulphate. One of the steps in the reaction involves oxidation. What is the oxidizing agent here?

    (1) H_2SO_4
    (2) $C_6H_5NO_2$
    (3) $FeSO_4$
    (4) Glycerol

87. Epimers are a pair of diastereomeric aldoses that differ only in

    (1) configuration at C-1
    (2) configuration at C-2
    (3) configuration at C-3
    (4) None of the above

88. Bakelite is formed by the condensation of

    (1) Phenol and formaldehyde
    (2) Phenol and acetaldehyde
    (3) Urea and formaldehyde
    (4) Formaldehyde and acetaldehyde

89. Like other oxygen-containing compounds, *n*-butyl *tert*-butyl ether dissolves in cold conc. H_2SO_4. On standing, an acid-insoluble layer, made up of high-boiling hydrocarbon material slowly separates from the solution. What this material is likely to be?

    (1) $\sim(CH_2-CH_2)_n\sim$ with CH_2CH_3 substituent
    (2) $\sim(CH-CH)_n\sim$ with CH_3, CH_3 substituents
    (3) $\sim(CH_2-C)_n\sim$ with two CH_3 substituents
    (4) All of the above

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90. Which of the following proposed reactions would take place quickly under mild conditions?

    (1) $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + NaCl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + NaNH_2$

    (2) $Ph-\overset{O}{\overset{\|}{C}}-Cl + CH_3NH_2 \longrightarrow Ph_3-\overset{O}{\overset{\|}{C}}-NHCH_3 + HCl$

    (3) $(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-NH_2 + CH_3OH \longrightarrow (CH_3)_2CH-\overset{O}{\overset{\|}{C}}-OCH_3 + NH_3$

    (4) $CH_3CH_2-\overset{O}{\overset{\|}{C}}-Cl + CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow CH_3CH_2-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$
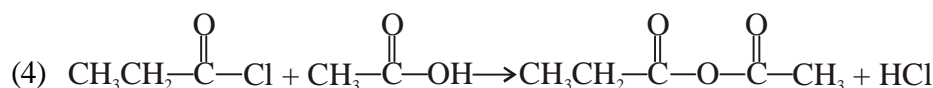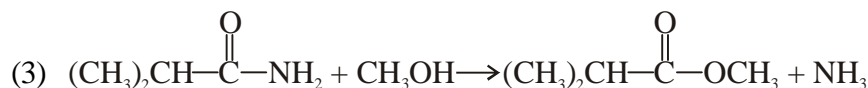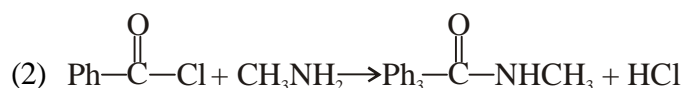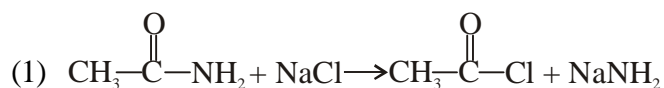
91. The reagent required to convert 3-hexyne into *trans*-3-hexene is

    (1) H_2/Pt
    (2) H_2, Pd/BaSO$_4$, quinoline
    (3) NaBH$_4$
    (4) Na, NH$_3$(liquid)

92. Among the following statements about the nitration of aromatic compounds, the false one is:

    (1) Nitration is an electrophilic substitution
    (2) The rate of nitration of benzene is almost the same as that of hexadeuterobenzene
    (3) The nitration of benzene is very much faster than that of hexadeuterobenzene
    (4) The rate of nitration of toluene is greater than that of benzene

93. Which of the following has the most stable conjugate acid?

    (1) $(CH_3)_2NH$
    (2) $(CH_3)_3N$
    (3) $C_6H_5NH_2$
    (4) $C_6H_5NHCH_3$

94. The conversion of ethyl methyl ketoxime to N-methyl propanamide represents an example of the following reaction

    (1) Beckmann rearrangement
    (2) Hofmann rearrangement
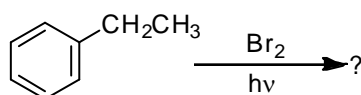   (3) Baeyer-Villiger oxidation
    (4) Wolff rearrangement

95. How many moles of periodic acid are needed for the complete cleavage of one mole of Glucose into formaldehyde and formic acid?

    (1) three
    (2) four
    (3) five
    (4) six

96. Which of the following compounds would not react with a dienophile in Diels-Alder reaction?
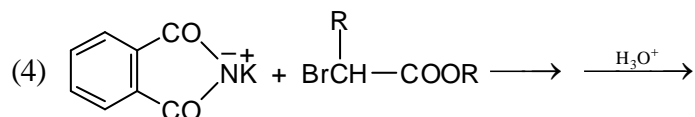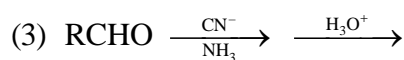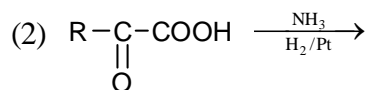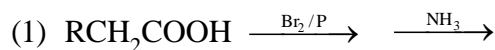
    (1) Anthracene
    (2) Phenanthrene
    (3)
    (4)

97. In the reaction

    The major product obtained is

    (1)
    (2)

    (3)
    (4)

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98.	Which of the following reaction sequence represents the Strecker synthesis of an α-aminoacid?

(1) $RCH_2COOH \xrightarrow{Br_2/P} \xrightarrow{NH_3}$

(2) $R-\underset{\underset{O}{\|}}{C}-COOH \xrightarrow[H_2/Pt]{NH_3}$

(3) $RCHO \xrightarrow[NH_3]{CN^-} \xrightarrow{H_3O^+}$

(4)

99.	In the reaction : Glucose $\xrightarrow[[O]]{HNO_3}$ Q, the product Q is

(1) Glucuronic acid	(2) Glucaric acid

(3) Gluconic acid	(4) Glyceric acid

100.	For electrophilic substitution in benzene derivatives, which one of the following types of substituents is unknown?
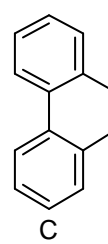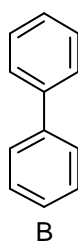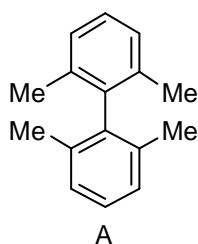
(1) Activating and *m*-directing	(2) Deactivating and *m*-directing

(3) Activating and *o*, *p*-directing	(4) Deactivating and *o*, *p*-directing

101.	Arrange the following compounds in decreasing order of reactivity towards electrophiles

A	B	C

Answer codes:

(1) A > B > C	(2) B > A > C

(3) B > C > A	(4) C > B > A

102.	Arrange the following compounds in order of decreasing ease of nucleophilic substitution reactions

(I) 4-Nitrochlorobenzene	(II) 2, 4-Dinitrochlorobenzene

(III) 2, 4, 6-Trinitrochlorobenzene	(IV) Benzyl chloride

Answer codes:

(1) IV > III > II > I	(2) I > II > III > IV

(3) III > II > I > IV	(4) III > IV > II > I

103.	Which of the following statements does **not** fit in the criteria of E2 reactions?

(1) follow second order kinetics	(2) are accompanied by rearrangement

(3) show a large deuterium isotope effect	(4) do not undergo hydrogen deuterium exchange

104.	Pyridine undergoes electrophilic substitution with fuming H_2SO_4 at elevated temperature to give
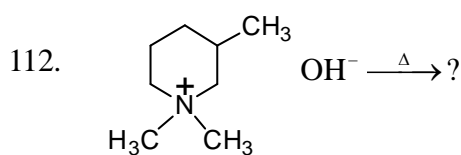
(1) Pyridine-2-sulphonic acid	(2) Pyridine-4-sulphonic acid
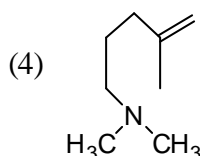
(3) Pyridine-3-sulphonic acid	(4) All of the above

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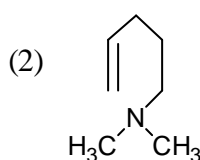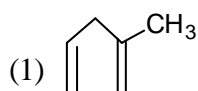
105. Which one of the following would clearly prove the configuration of *cis*-3-hexene from *trans*-3-hexene?
     (1) Boiling point
     (2) Rate of hydrogenation
     (3) Infrared spectrum
     (4) Dipole moment

106. The reagent used in N-terminal analysis of peptides by Sanger's method is
     (1) Phenyl isothiocyanate
     (2) Benzyl chloroformate
     (3) 2, 4-Dinitrofluorobenzene
     (4) Ninhydrin

107. Teflon is obtained by polymerization of the monomer
     (1) $CH_2 = CF_2$
     (2) $H_2C = C(CH_3)COOMe$
     (3) $CH_2 = CHF$
     (4) $CF_2 = CF_2$

108. Which one of the following statements is **true** about the β D(t) glucopyranose conformer?
     (1) One OH group is axial but all remaining substituents are equatorial
     (2) The CH_2OH group is axial but all remaining substituents are equatorial
     (3) All groups are axial
     (4) All groups are equatorial

109. But-2-ene reacts with $CHCl_3$ in the presence of potassium *tert*-butoxide to give
     (1) 1, 1-dichloro-2, 3-dimethylcyclopropane
     (2) 2, 3-dichlorobutane
     (3) 2-Chlorobutane
     (4) 1-Chlorobutane

110. Consider the following statements about conformational isomers
     (I) They are interconverted by rotation about single bond
     (II) The energy barrier separating them is less than 15K cal/mole
     (III) They are best represented by means of Fisher projection formulae.
     Of these statements
     (1) I, II and III are correct
     (2) I and II are correct
     (3) II and III are correct
     (4) I and III are correct

111. Which one of the following on reaction with phthalic anhydride in the presence of conc. H_2SO_4 gives Fluorescein?
     (1) Catechol
     (2) Phenol
     (3) Resorcinol
     (4) Hydroquinone

112.

The major product in the above reaction will be

(1)

(2)

(3)

(4)

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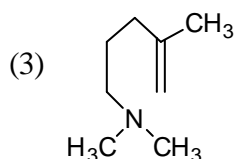
113. Disproportionation of benzaldehyde in the presence of concentrated aqueous alkali gives benzoate anion and benzyl alcohol. The reaction involves a
   (1) proton transfer from water
   (2) hydride transfer from water
   (3) proton transfer from aldehyde
   (4) hydride transfer from aldehyde

114. The probability of finding a molecule with a speed between C and (C+1) $m.s^{-1}$ at high values of C
   (1) falls off as C^{-1}
   (2) falls off as $-Log\ C$
   (3) falls off as $\exp(-C^2)$
   (4) rises as C^2

115. Liquid He boils at about $-269ºC$ and liquid H_2 boils at about $-253ºC$. The efficiency of a reversible engine operating between heat reservoirs at these temperatures
   (1) 20%
   (2) 80%
   (3) 10%
   (4) 90%

116. For Ne, HF, H_2O maximum entropy is prepossessed by
   (1) Ne
   (2) HF
   (3) H_2O
   (4) H_2O and Ne

117. The condition of equilibrium for a transformation at constant temperature is
   (1) $\Delta S = 0$
   (2) $\Delta A + W = 0$
   (3) $\Delta A = 0$
   (4) $\Delta G + W_{net} = 0$

118. The chemical potential of a component, μ_i in a given mixture is
   (1) $\left(\dfrac{\partial G}{\partial n_i}\right)_{T,V,n_j}$
   (2) $\left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_j}$
   (3) $\left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_i}$
   (4) $\left(\dfrac{\partial G}{n_i}\right)$

119. For an ideal solution, the osmotic pressure is proportional to
   (1) $-\ln x1$ (solvent mole fraction)
   (2) $\ln x_2$ (solute mole fraction)
   (3) x_2
   (4) c(solute concentration)

120. The Debye-Huckel limiting law relates
   (1) $\gamma_{\pm}$ with I
   (2) $\gamma_{\pm}$ with $\sqrt{I}$
   (3) $ln\ \gamma_{\pm}$ with I
   (4) $ln\ \gamma_{\pm}$ with $\sqrt{I}$

121. The potential of the $Ag^+|Ag$ electrode ($E° = 0.799V$) in a saturated solution of $AgI(K_{sp} = 10^{-16})$
   (1) 1.279 V
   (2) 0.319 V
   (3) –1.279 V
   (4) –0.319 V

122. The ratio of $\Delta G°$ to $\Delta H°$ for reactions in lead acid cell is 1.36.
   The extra 36% is the energy that
   (1) flows as $P\Delta V$ into the system
   (2) flows in as $T\Delta S°$ from the surrounding
   (3) flows as $T\Delta S°$ from the system
   (4) flows out as Q_{rev} into the surrounding

123. N_2 is adsorbed on iron at $-190ºC$, but not at room temperature. How ever at $\sim500ºC$, again it adsorbs. The observation on two adsorptions may be ascrubed to
   (1) absorption and adsorption
   (2) chemisorptions and physisorption
   (3) physisorption and chemisorption
   (4) both same types of adsorption

124. The energy of repulsion for molecules varies with distance as r^{-n}. The commonest value of n is
   (1) 12
   (2) 6
   (3) 2
   (4) 1

125. The coefficient of diffusion does not proportional to
   (1) mean free path
   (2) mean velocity
   (3) $(MW)^{-1}$
   (4) $(MW)^{-1/2}$

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126. The molar conductance of an 1 : 1 electrolyte at concentration below as 10^{-2} and lower
    (1) increases with concentration as C
    (2) decreases with concentration as C
    (3) remain constant
    (4) falls off as $\sqrt{C}$

127. Consider an electron in a box of the size of an atom, 10^{-10} m. By what factor its ground state energy would change, if the particle gets confined in a box of the size of a nucleus, 10^{-14} m?
    (1) 10^4
    (2) 10^{-4}
    (3) 10^8
    (4) 10^{-8}

128. The function $f(x) = 3x^2 - 1$ is an eigen function of the operation, $-(1-x^2)\left(\dfrac{d^2}{dx^2}\right) + 2x\left(\dfrac{d}{dx}\right)$.

    The eigen value is
    (1) 2
    (2) 6
    (3) –6
    (4) –2

129. For a system described by $\hat{H}\psi_n = E_n\psi_n$, the value of the $\int_{-\infty}^{\infty} \psi_{10}^*\psi_{12} \, \infty T$ is
    (1) ∞
    (2) any finite number
    (3) 1
    (4) zero

130. A substance decomposes with a half life of 150000s when its initial concentration 0.01 mol. L^{-1} but with a half life of 29000s when the initial concentration is 0.05 mol. L^{-1}. The order of the reaction is
    (1) zero
    (2) 3/2
    (3) 2
    (4) 3

131. From the overpotential (η) vs log $|i|$ (current density), one can evaluate at high enough η for a given electrodic process
    (1) α
    (2) i_o only
    (3) α and i_o both
    (4) Z only

132. For the particle in a cubic box, the degree of degeneracy of the energy levels with the value of $\dfrac{8ma^2 E}{4^2}$ as 14 is
    (1) 2
    (2) 3
    (3) 6
    (4) 18

133. The IR absorption spectrum of HCl has its strongest band at 86.5 THz. The frequency of the strongest IR band of DCl will be
    (1) 86.5 THz
    (2) 62.0 THz
    (3) 43.3 THz
    (4) 121.1 THz

134. For which hydrogen atom state, ψ is zero at the nucleus ?
    (1) 2s
    (2) 2p
    (3) 3p
    (4) 3d

135. The third lowest microwave absorption frequency for $^{13}C\,^{16}O$ is 330567 MHz. The second lowest absorption frequency for $^{12}C\,^{16}O$ should be at
    (1) 220378 MHz
    (2) 230542 MHz
    (3) 345813 MHz
    (4) 205032 MHz

136. NMR experiment can not be done with
    (1) $^2H_1$
    (2) ^1n_o
    (3) $^3He_2$
    (4) $^4H_2$

137. The land distance in D_2 can be determined using
    (1) rovibronic spectroscopy
    (2) rovibrational spectroscopy
    (3) pure rotational spectroscopy
    (4) nmr spectroscopy

138. The Duhem-Margules equation for a liquid solution is applicable when
    (1) the solution is strictly ideal
    (2) the vapour is ideal only
    (3) the solution and the vapour are both ideal only
    (4) the solution and the vapour need not be ideal

139. Among the following electrolytes, which one at 5×10^{-3}M concentration would have the lowest activity coefficient?
    (1) NaBr
    (2) $CaCl_2$
    (3) KI
    (4) HCl

140. The ratio of translational partition function of D_2 to that of H_2 is
    (1) 2 : 1
    (2) 2.8 : 1
    (3) 1.4 : 1
    (4) 4 : 1

141. Which one among the following diatomic molecules has the highest characteristic rotational temperature?
    (1) H_2
    (2) HCl
    (3) HBr
    (4) HI

142. The equation, $d\mu_2 = -\dfrac{n_1}{n_2}d\mu_1$ is known as

    (1) Duhem-Margules equation   (2) Gibbs-Duhem equation

    (3) Gibbs equation   (4) Maxwell's equation

143. Which one is **not** the criterion for spontaneous change?

    (1) $dG_{P,T} < O$ (2) $dA_{v^2,T} < O$

    (3) $dS > O$ (4) $\sum dS > O$

144. The equation that correlates adsorption with variation of surface tension with concentration

    (1) Langmuir's adsorption isotherm   (2) Freundlich adsorption isotherm

    (3) Gibbs adsorption isotherm   (4) Hinshelwood adsorption isotherm

145. Which of the following is **not** the characteristic of an ideal solution?

    (1) $\overline{H}_i = \overline{H}_i^0$ (2) $\overline{V}_i = \overline{V}_i^0$

    (3) $\overline{G}_i = \overline{G}_i^0 + RT \ln N_i$ (4) $\overline{S}_i = \overline{S}_i^0 + R \ln N_i$

146. How many years would be required for the activity of Zn-65 (half life, 245 days) to reduce to 5% of its initial value?

    (1) 13.4 years   (2) 2.7 years

    (3) 3.6 years   (4) 2.9 years

147. If the activation energy for $H_2 + I_2 \rightarrow 2HI$ is 167 kJ and enthalpy of the reaction is –8 kJ, what is the activation energy for the decomposition of HI?

    (1) 159 kJ   (2) 175 kJ

    (3) 167 kJ   (4) 179 kJ

148. Consider the following mechanism for the thermal decomposition of acetaldehyde

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO \quad E_a = 320 \text{ kJ mol}^{-1}$$

$$CH_3CH_3CHO \xrightarrow{k_2} CH_4 + CH_2CHO \quad E_a = 40 \text{ kJ mol}^{-1}$$

$$CH_2CHO \xrightarrow{k_3} CO + CH_3 \quad E_a = 75 \text{ kJ mol}^{-1}$$

$$CH_3 + CH_3 \xrightarrow{k_4} C_2H_6 \quad E_a = 0$$

The overall rate constant for the formation of CH_4 is given by $k = k_2 \left(\dfrac{k_1}{k_2}\right)^{1/2}$

The overall activation energy

    (1) 435 kJ.mol^{-1} (2) 320 kJ.mol^{-1}

    (3) 0   (4) 200 kJ.mol^{-1}

149. In course of a chemical reaction, its free energy changes as

    (1) $dG = -SdT + Vdp$ (2) $dG = -SdT + Vdp + \sum_i \mu_i dn_i$

    (3) $dG = -SdT + Vdp + \sum_i n_i d\mu_i$ (4) $dG = -SdT - pdV + \sum_i {}^i\mu_i dn_i$

150. Langmuir adsorption isotherm does not apply when

    (1) adsorption is chemisorption

    (2) adsorption layer is monolayer

    (3) heat of adsorption is independent of surface coverage

    (4) heat of adsorption decreases with surface coverage

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