

Signature of Invigilator

ENTRANCE EXAMINATION, 2017

M.Sc. CHEMISTRY

[Field of Study Code : CHEM (227)]

Time Allowed : 3 hours

Maximum Marks: 100

INSTRUCTIONS FOR CANDIDATES

Candidates must read carefully the following instructions before attempting the Question Paper :

- (i) Write your Name and Registration Number in the space provided for the purpose on the top of this Question Paper and in the Answer Sheet.
- (ii) Please darken the appropriate circle of Question Paper Series Code on the Answer Sheet.
- (iii) All questions are compulsory. For each question one and only one of the five choices given is the correct answer.
- (iv) Answer all 25 questions in the Answer Sheet provided for the purpose by darkening the correct choice, i.e.,
 (a) or (b) or (c) or (d) or (e) with **BALLPOINT PEN** only against each question in the corresponding circle. Any overwriting or alteration will be treated as wrong answer.
- (v) Each correct answer carries 4 marks. There will be negative marking and 1 mark will be deducted for each wrong answer.
- (vi) Answer written by the candidates inside the Question Paper will not be evaluated.
- (vii) Calculators may be used.
- (viii) Please use the space provided for Rough Work.
- (ix) Return the Question Paper and Answer Sheet to the Invigilator at the end of the Entrance Examination. **DO NOT FOLD THE ANSWER SHEET.**

INSTRUCTIONS FOR MARKING ANSWERS

- 1. Use only Blue/Black Ballpoint Pen (Do not use pencil) to darken the appropriate Circle.
- 2. Please darken the whole Circle.
- 3. Darken <u>ONLY ONE CIRCLE</u> for each question as shown in the example below :

| Wrong | Wrong | Wrong | Wrong | Correct |
|---|----------------|------------------|-----------|--|
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- 4. Once marked, no change in the answer is allowed.
- 5. Please do not make any stray marks on the Answer Sheet.
- 6. Mark your answer only in the appropriate space against the number corresponding to the question.
- 7. Ensure that you have darkened the appropriate circle of Question Paper Series Code on the Answer Sheet.

/121-**B**

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| Fundamental Constants | Value | | |
|--|--|--|--|
| Speed of light (c) | $2.99792558 \times 10^8 \text{ ms}^{-1}$ | | |
| Elementary charge (e) | $1.602176 \times 10^{-19} \text{ C}$ | | |
| Boltzmann constant (k) | $1.38065 \times 10^{-23} \text{ JK}^{-1}$ | | |
| Gas constant ($R = N_A k$) | 8·31 JK ⁻¹ mol ⁻¹ or 1·9872036 cal K ⁻¹ mol ⁻¹ | | |
| Planck constant (h) | $6.62608 \times 10^{-34} \text{ Js}$ | | |
| Avogadro's constant (N _A) | $6.02214 \times 10^{23} \text{ mol}^{-1}$ | | |
| Electron mass (m _e) | $9.109390 \times 10^{-31} \text{ kg}$ | | |
| Proton mass (m _p) | $1.672623 \times 10^{-27} \text{ kg}$ | | |
| Neutron mass (m _n) | $1.674929 \times 10^{-27} \text{ kg}$ | | |
| Bohr radius ($a_0 = 4\pi\epsilon_0 \hbar^2 / m_e e^2$) | $5.3 \times 10^{-11} \text{ m}$ | | |
| Ionization energy of H atom | 13.6 eV | | |

- The number of skeletal electron pairs for the boranes [B₄H₄]²⁻, B₄H₈, B₄H₁₀ and B₅H₁₁ are
 - (a) 5, 6, 7 and 8, respectively
 - (b) 4, 5, 6 and 7, respectively
 - (c) 5, 7, 8 and 9, respectively
 - (d) 5, 4, 7 and 8, respectively
 - (e) 8, 6, 6, and 8, respectively
- 2. If in the reaction $A + 2B \rightarrow$ products, the rate law was found to be rate = $k[A][B]^2$, predict by what factor the rate of reaction will increase, when the concentration of A is doubled and the concentration of B is also doubled.
 - (a) 2
 - (b) 4
 - (c) 6
 - (d) 8
 - (e) 16
- 3. In case of water, with increase in pressure, chemical potential of solid
 - (a) increases
 - (b) decreases
 - (c) remains unchanged
 - (d) increases and then decreases
 - (e) None of the above
- 4. If a system loses 250 kJ of heat at the same time it is doing 500 kJ of work, what is the change in the internal energy of the system?
 - (a) +250 kJ
 - (b) -250 kJ
 - (c) +750 kJ
 - (d) +1500 kJ
 - (e) -750 kJ

- 5. A dilute solution of NaCl is placed between two electrodes of 8 cm apart. If a potential difference of 5 volt is applied across the electrodes, then how far Na⁺ ions can travel in 1 hour within the solution? (Given : Ionic conductivity of Na⁺ at infinite dilution is $50.11 \ \Omega^{-1} \ cm^{2} \ mol^{-1} \ at \ 25 \ ^{\circ}C$ and 1 faraday = 96485.3 coulomb.)
 - (a) 11.270 cm
 - (b) 1.168 cm
 - (c) 0.019 cm
 - (d) 0.117 cm
 - (e) None of the above
- 6. If a measurement can provide the position of a (non-relativistic) proton with an accuracy of 2×10^{-11} m, then the uncertainty in the proton's position at 2s later is
 - (a) $\leq 1.00 \times 10^3$ m
 - (b) $\geq 3.16 \times 10^3$ m
 - (c) $\leq 9.92 \times 10^3$ m
 - (d) $\geq 6.31 \times 10^3$ m
 - (e) $\leq 7.25 \times 10^3$ m
- 7. An electron collision with hydrogen atom promotes the hydrogen atom to its 2nd excited state from its ground state. The energy inserted by the electron in this inelastic collision is
 - (a) 13.6 eV
 - (b) 10.2 eV
 - (c) 3.4 eV
 - (d) 5.1 eV
 - (e) None of the above

8. The eigenvalues of the linear matrix operator $A = \begin{pmatrix} 6 & 2 \\ -1 & 3 \end{pmatrix}$ are

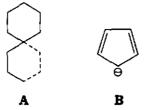
- (a) 6 and 3
- (b) -1 and 2
- (c) 1 and -2
- (d) 18 and -2
- (e) 4 and 5

- 9. The half-life of a first-order reaction having activation energy $39.3 \text{ kcal mol}^{-1}$ at 300 °C and largest frequency constant of 1.11×10^{11} Hz can be calculated as
 - (a) 0.9009 sec
 - (b) 9.009×10^{10} sec
 - (c) 6050 sec
 - (d) 60.50 sec
 - (e) None of the above
- Calculate the free energy differences between the carbonyl compound and its hydrate at 25 °C. [Note : at 25 °C, 2.3 RT = 1.364 kcal/mol.]

$$\begin{array}{c} H_{3}C \\ H_{3}C \end{array} \longrightarrow O \xleftarrow{H_{3}O^{+}} H_{3}C \\ H_{2}O \\ H_{3}C \end{array} \xrightarrow{H_{3}C} OH \\ H_{3}C \\ OH \\ k = 1.4 \times 10^{-3} \end{array}$$

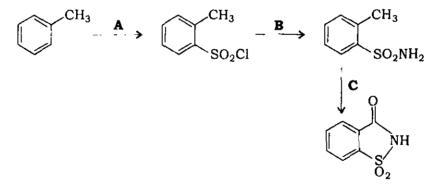
- (a) $\Delta G^{\circ} = +3.9 \text{ kcal/mol}$
- (b) $\Delta G^{\circ} = -3.9 \text{ kcal/mol}$
- (c) $\Delta G^{\circ} = +1.4 \text{ kcal/mol}$
- (d) $\Delta G^{\circ} = -1.4 \text{ kcal/mol}$
- (e) $\Delta G^{\circ} = -7 \cdot 8 \text{ kcal/mol}$

11. The point groups and the element/elements of symmetry in case of molecules A and B



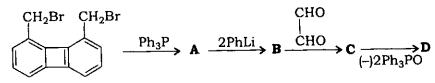
are

- (a) \mathbf{A} : D_{2d}; 3C₂, 2 σ_d and \mathbf{B} : D_{5h}; C₅, 5C₂, 5 σ_v , σ_h
- (b) \mathbf{A} : D_{2d}; 2C₂, 2 σ_d and \mathbf{B} : D_{5h}; C₃, 5C₂, σ_v , σ_d
- (c) \mathbf{A} : \mathbf{D}_{2h} ; $2\mathbf{C}_2$, $2\sigma_v$ and \mathbf{B} : \mathbf{D}_3 ; \mathbf{C}_3 , $5\mathbf{C}_2$, $5\sigma_v$, σ_h
- (d) $\mathbf{A} : \mathbf{D}_{2d}$; $3\mathbf{C}_2, \sigma_d$ and $\mathbf{B} : \mathbf{D}_{5h}$; $\mathbf{C}_5, 3\mathbf{C}_2, \sigma_h$
- (e) \mathbf{A} : \mathbf{D}_{2h} ; $3\mathbf{C}_2$, σ_d and \mathbf{B} : \mathbf{D}_3 ; \mathbf{C}_5 , $5\mathbf{C}_2$, σ_h
- 12. The stepwise synthesis to saccharin is given below. Predict the correct reactants **A**, **B** and **C**:

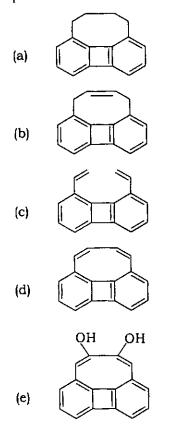


- (a) \mathbf{A} : SOCl₂; \mathbf{B} : NH₄OH; \mathbf{C} : Na₂CO₃
- (b) \mathbf{A} : SOCl₂; \mathbf{B} : NH₃; \mathbf{C} : Na₂CO₃
- (c) \mathbf{A} : CISO₃H; \mathbf{B} : NH₃; \mathbf{C} : KMnO₄
- (d) \mathbf{A} : SOCl₂; \mathbf{B} : NH₄OH; \mathbf{C} : KMnO₄
- (e) \mathbf{A} : CISO₃H; \mathbf{B} : NH₄OH; \mathbf{C} : KMnO₄

13. Predict the final product **D** of the following reaction :



[Note : There is a loss of two molecules in the final step]



14. From the stepwise reactions, predict the final products **D** and **E** of the following reaction :

$$H_{3C} \xrightarrow{H} \xrightarrow{CH_{3}I} \mathbf{A} \xrightarrow{OH^{-}} \mathbf{B} \xrightarrow{H_{2}O_{2}} \mathbf{C} \xrightarrow{Heat} \mathbf{D} + \mathbf{E}$$

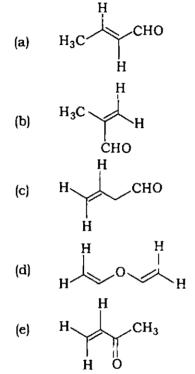
- (a) **D** : Ethylene; **E** : N,N-Dimethyl-hydroxylamine
- (b) **D** : Propylene; **E** : N,N-Dimethyl-hydroxylamine
- (c) **D** : Propyne; **E** : Dimethylamine
- (d) **D** : Propylene; **E** : Dimethylamine
- (e) **D** : Propyne; **E** : *N*,*N*-Dimethyl-hydroxylamine

/121-**B**

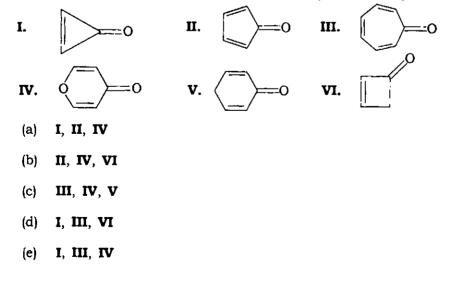
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- 15. A compound C_4H_6O has the following spectral data :
 - (a) Electronic absorption at $\lambda_{max} = 213 \text{ nm}$, $\varepsilon_{max} = 7100$ and $\lambda_{max} = 320 \text{ nm}$, $\varepsilon_{max} = 27$
 - (b) Infrared bands at 3000 cm⁻¹, 2900 cm⁻¹, 1675 cm⁻¹ and 1602 cm⁻¹
 - (c) NMR singlet at $\delta = 2 \cdot 1$ ppm (3H's), three multiplets each integrating for 1 H at $\delta = 5 \cdot 0 6 \cdot 0$ ppm

The structure of the compound is

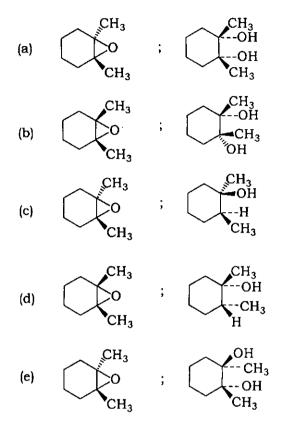


16. Protonation of a carbonyl group forms a cation with significant charge on the carbon atom. Which of the following carbonyl compounds form an aromatic cation on protonation? Select the correct answer using the codes given below :



17.
$$(H_3 \xrightarrow{m-CPBA} A \xrightarrow{\text{LiAlH}_4} B$$

A and B respectively are



- 18. A metal crystallizes into face-centred cubic (f.c.c.) and body-centred cubic (b.c.c.) lattices whose unit cell lengths are 3.5 Å and 3.0 Å respectively. The ratio of densities of unit cell of f.c.c. and b.c.c. is
 - (a) 0·26
 - (b) 1·26
 - (c) 2·26
 - (d) 1.76
 - (e) 2·76

19. Predict the structure of the following metal-oxide compounds using crystal field model :

- (i) NiAl₂O₄
- (ii) Fe₃0₄
- (iii) ZnMn₂O₄
- (a) (i) Normal spinel
 - (ii) Inverse spinel
 - (iii) Inverse spinel
- (b) (i) Inverse spinel
 - (ii) Normal spinel
 - (iii) Inverse spinel
- (c) (i) Normal spinel
 - (ii) Inverse spinel
 - (iii) Normal spinel
- (d) (i) Inverse spinel
 - (ii) Inverse spinel
 - (iii) Normal spinel
- (e) (i) Normal spinel
 - (ii) Normal spinel
 - (iii) Inverse spinel

20. The correct order of addition of NH_3 , pyridine (py) and Br^+ to $[PtCl_4]^{2-}$ to obtain

Cl Pt Br

is

- (a) NH_3 , py and Br^-
- (b) Br^- , py and NH_3
- (c) py, Br⁻ and NH₃
- (d) NH_3 , Br^- and py
- (e) py, NH_3 and Br^-

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21. Predict the shape of the following molecular species and account the number of lone pair(s) present on the central atom :

| Column—I Molecular species | Column– II Shape and lone pair(s) |
|-------------------------------|--------------------------------------|
| P. ICl ₂ | I. V-shaped, one |
| Q. XeOF ₄ | II. Square planar, two |
| R. BrF ₄ | III. T-shaped, two |
| S. SO ₂ | IV. Pyramidal, one |
| | V. Linear, three |

VI. Square-based pyramidal, one

The correct combination is

| (a) | Р | Q | R | s |
|-----|-----|----|-----|---|
| | I | IV | III | V |
| (b) | P | Q | R | S |
| | V | VI | II | I |
| (c) | P | Q | R | S |
| | V | IV | II | I |
| (d) | P | Q | R | s |
| | I | II | IV | V |
| (e) | P | Q | R | s |
| | III | II | IV | v |

- 22. A drug contains radioactive ${}_{11}Na^{24}$ and its half life is 14.8 hours. It is injected into the body of an animal. How many hours will be required for the activity to come to one-tenth of its original intensity assuming that none is excreted from the body of the animal?
 - (a) 1.48
 - (b) 148
 - (c) 49·2
 - (d) 4·92
 - (e) 0·49

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23. All compounds in which one of the following options are diamagnetic?

(a) Cu(SCN), Ni(CO)₄ and
$$[PdCl_4]^{2-1}$$

- (b) Cu(SCN), $[NiCl_4]^2$ and $Ni(CO)_4$
- (c) $[CoF_6]^{3}$, $[Co(H_2O_6]^{2+}$ and $[CoCl_4]^{2-}$
- (d) Cu(SCN), $[NiCl_4]^2$, $Ni(CO)_4$ and $[PdCl_4]^{2-1}$
- (e) $[Ni(CN)_4]^{2-}$, $[NiCl_4]^{2-}$ and $Ni(CO)_4$
- 24. The metal ions associated with the metalloenzymes, carbonic anhydrase, sulphite oxidase, vitamin B_{12} coenzyme and haemocyanine are
 - (a) Co, Cu, Zn and Mo, respectively
 - (b) Zn, Co, Mo and Cu, respectively
 - (c) Zn, Mo, Co and Cu, respectively
 - (d) Co, Mo, Zn and Cu, respectively
 - (e) Mo, Zn, Cu and Co, respectively
- 25. 0.41 gm of iron containing mineral is dissolved in concentrated HCl acid and reduced to Fe(II) completely by SnCl₂ reagent. If the resulting solution is titrated with 0.112 (N) KMnO₄ solution, the titre value obtained is 5.1 mL. The percentage of iron in the given mineral is
 - (a) 7·5%
 - (b) 7·25%
 - (c) 7.00%
 - (d) 7·95%
 - (e) 7·75%

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