

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
$\mathbf{O} \odot \mathbf{O} \odot \mathbf{d} \mathbf{O}$	<b>\$</b> 6000	<b>Ø</b> @ @ @ @	@ D © O ©	@ (D (C)

- 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.

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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 <sup>-1</sup> mol <sup>-1</sup> or 1·9872036 cal K <sup>-1</sup> mol <sup>-1</sup>		
Planck constant (h)	$6.62608 \times 10^{-34} \text{ Js}$		
Avogadro's constant (N <sub>A</sub> )	$6.02214 \times 10^{23} \text{ mol}^{-1}$		
Electron mass (m <sub>e</sub> )	$9.109390 \times 10^{-31} \text{ kg}$		
Proton mass (m <sub>p</sub> )	$1.672623 \times 10^{-27} \text{ kg}$		
Neutron mass (m <sub>n</sub> )	$1.674929 \times 10^{-27} \text{ kg}$		
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 [B<sub>4</sub>H<sub>4</sub>]<sup>2-</sup>, B<sub>4</sub>H<sub>8</sub>, B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>11</sub> 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<sup>+</sup> ions can travel in 1 hour within the solution? (Given : Ionic conductivity of Na<sup>+</sup> 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  $2 \times 10^{-11}$  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

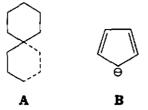
- (a) 6 and 3
- (b) -1 and 2
- (c) 1 and -2
- (d) 18 and -2
- (e) 4 and 5

- 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  $1.11 \times 10^{11}$  Hz can be calculated as
  - (a) 0.9009 sec
  - (b)  $9.009 \times 10^{10}$  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.]

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

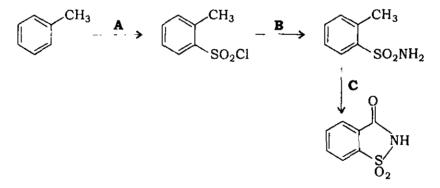
- (a)  $\Delta G^{\circ} = +3.9 \text{ kcal/mol}$
- (b)  $\Delta G^{\circ} = -3.9 \text{ kcal/mol}$
- (c)  $\Delta G^{\circ} = +1.4 \text{ kcal/mol}$
- (d)  $\Delta G^{\circ} = -1.4 \text{ kcal/mol}$
- (e)  $\Delta G^{\circ} = -7 \cdot 8 \text{ kcal/mol}$

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



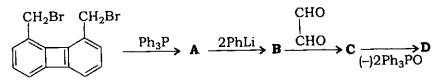
are

- (a)  $\mathbf{A}$ : D<sub>2d</sub>; 3C<sub>2</sub>, 2 $\sigma_d$  and  $\mathbf{B}$ : D<sub>5h</sub>; C<sub>5</sub>, 5C<sub>2</sub>, 5 $\sigma_v$ ,  $\sigma_h$
- (b)  $\mathbf{A}$ : D<sub>2d</sub>; 2C<sub>2</sub>, 2 $\sigma_d$  and  $\mathbf{B}$ : D<sub>5h</sub>; C<sub>3</sub>, 5C<sub>2</sub>,  $\sigma_v$ ,  $\sigma_d$
- (c)  $\mathbf{A}$  :  $\mathbf{D}_{2h}$ ;  $2\mathbf{C}_2$ ,  $2\sigma_v$  and  $\mathbf{B}$  :  $\mathbf{D}_3$ ;  $\mathbf{C}_3$ ,  $5\mathbf{C}_2$ ,  $5\sigma_v$ ,  $\sigma_h$
- (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)  $\mathbf{A}$  :  $\mathbf{D}_{2h}$ ;  $3\mathbf{C}_2$ ,  $\sigma_d$  and  $\mathbf{B}$  :  $\mathbf{D}_3$ ;  $\mathbf{C}_5$ ,  $5\mathbf{C}_2$ ,  $\sigma_h$
- 12. The stepwise synthesis to saccharin is given below. Predict the correct reactants **A**, **B** and **C**:

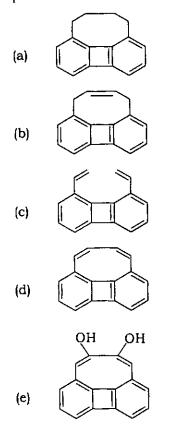


- (a)  $\mathbf{A}$  : SOCl<sub>2</sub>;  $\mathbf{B}$  : NH<sub>4</sub>OH;  $\mathbf{C}$  : Na<sub>2</sub>CO<sub>3</sub>
- (b)  $\mathbf{A}$  : SOCl<sub>2</sub>;  $\mathbf{B}$  : NH<sub>3</sub>;  $\mathbf{C}$  : Na<sub>2</sub>CO<sub>3</sub>
- (c)  $\mathbf{A}$  : CISO<sub>3</sub>H;  $\mathbf{B}$  : NH<sub>3</sub>;  $\mathbf{C}$  : KMnO<sub>4</sub>
- (d)  $\mathbf{A}$  : SOCl<sub>2</sub>;  $\mathbf{B}$  : NH<sub>4</sub>OH;  $\mathbf{C}$  : KMnO<sub>4</sub>
- (e)  $\mathbf{A}$  : CISO<sub>3</sub>H;  $\mathbf{B}$  : NH<sub>4</sub>OH;  $\mathbf{C}$  : KMnO<sub>4</sub>

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 :

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

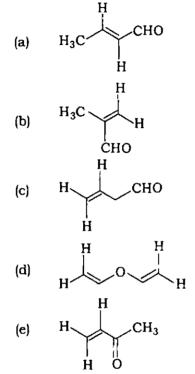
- (a) **D** : Ethylene; **E** : N,N-Dimethyl-hydroxylamine
- (b) **D** : Propylene; **E** : N,N-Dimethyl-hydroxylamine
- (c) **D** : Propyne; **E** : Dimethylamine
- (d) **D** : Propylene; **E** : Dimethylamine
- (e) **D** : Propyne; **E** : *N*,*N*-Dimethyl-hydroxylamine

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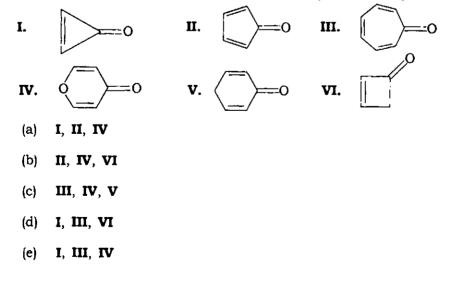
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- 15. A compound  $C_4H_6O$  has the following spectral data :
  - (a) Electronic absorption at  $\lambda_{max} = 213 \text{ nm}$ ,  $\varepsilon_{max} = 7100$  and  $\lambda_{max} = 320 \text{ nm}$ ,  $\varepsilon_{max} = 27$
  - (b) Infrared bands at 3000 cm<sup>-1</sup>, 2900 cm<sup>-1</sup>, 1675 cm<sup>-1</sup> and 1602 cm<sup>-1</sup>
  - (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

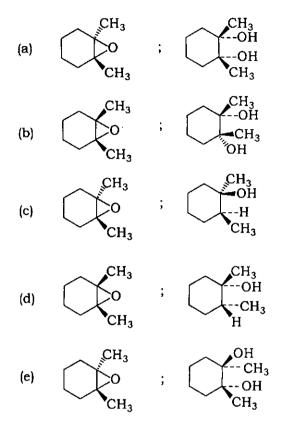


16. Protonation of a carbonyl group forms a cation with significant charge on the carbon atom. Which of the following carbonyl compounds form an aromatic cation on protonation? Select the correct answer using the codes given below :



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) NiAl<sub>2</sub>O<sub>4</sub>
- (ii) Fe<sub>3</sub>0<sub>4</sub>
- (iii) ZnMn<sub>2</sub>O<sub>4</sub>
- (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<sup>-</sup> and NH<sub>3</sub>
- (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 <sub>2</sub>	I. V-shaped, one
Q. XeOF <sub>4</sub>	II. Square planar, two
R. BrF <sub>4</sub>	III. T-shaped, two
S. SO <sub>2</sub>	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)<sub>4</sub> 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 SnCl<sub>2</sub> reagent. If the resulting solution is titrated with 0.112 (N) KMnO<sub>4</sub> 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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