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Total Pages: 33

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ENTRANCE EXAMINATION, 2012

Pre-Ph.D./Ph.D.
CHEMICAL SCIENCES

[Field of Study Code : CHEP (162)]

Time Allowed : 3 hours

Maximum Marks : 75

Weighted : 70

INSTRUCTIONS FOR CANDIDATES

(i) All questions are compulsory.

(ii) Answers should be written in the box given in **page 3**.

(iii) Each correct answer carries 3 marks. Wrong answers carry (–1) mark.

(iv) Rough work should be done in the space given below the questions.

(v) If additional space is required, three extra sheets provided at the end of the paper can be utilized for rough work.

(vi) Use of calculator is permitted.

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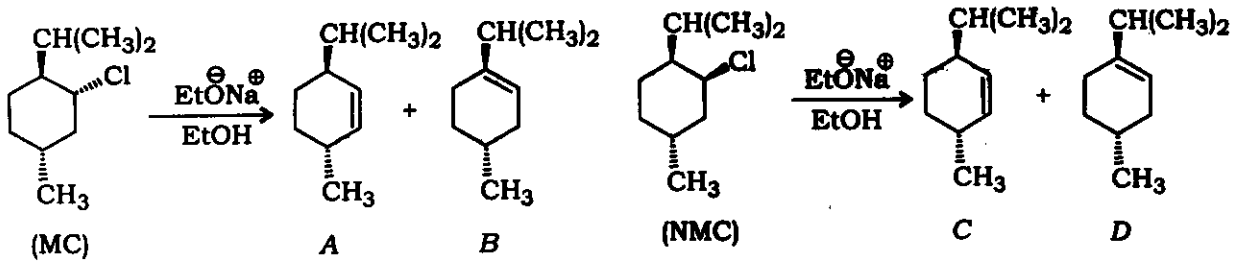
Fundamental Constants	Values
Speed of light (c)	$2{\cdot}99792558\times10^{8}$ m s^{-1}
Elementary charge (e)	$1{\cdot}602176\times10^{-19}$ C
Faraday's constant ($F = N_A e$)	$9{\cdot}64853\times10^{4}$ C mol^{-1}
Boltzmann's constant (k)	$1{\cdot}38065\times10^{-23}$ JK^{-1}
Gas constant ($R = N_A k$)	$8{\cdot}31447$ JK^{-1} mol^{-1}
Planck's constant (h)	$6{\cdot}62608\times10^{-34}$ J-s
Avogadro's constant (N_A)	$6{\cdot}02214\times10^{23}$ mol^{-1}
Atomic mass unit (u)	$1{\cdot}66054\times10^{-27}$ kg
Electron mass (m_e)	$9{\cdot}10938\times10^{-31}$ kg
Electron charge (e)	$4{\cdot}8\times10^{-10}$ esu
Proton mass (m_p)	$1{\cdot}67262\times10^{-27}$ kg
Neutron mass (m_n)	$1{\cdot}67493\times10^{-27}$ kg
Vacuum permittivity ($\varepsilon_0 = 1/c^2\mu_0$)	$8{\cdot}85419\times10^{-12}$ J^{-1}C^{2}m^{-1}
$4\pi\varepsilon_0$	$1{\cdot}11265\times10^{-10}$J^{-1}C^{2}m^{-1}
Vacuum permeability (μ_0)	$4\pi\times10^{-7}$J-s^{2}C^{-2}m^{-1}
Bohr magneton ($\mu_B = e\hbar/2m_e$)	$9{\cdot}27401\times10^{-24}$ JT^{-1}
Nuclear magneton ($\mu_N = e\hbar/2m_p$)	$5{\cdot}05078\times10^{-27}$ JT^{-1}
Bohr radius ($a_0 = 4\pi\varepsilon_0\hbar^2/m_e e^2$)	$5{\cdot}29177\times10^{-11}$ m
Fine-structure constant ($\alpha = \mu_0 e^2 c/2h$)	$7{\cdot}29735\times10^{-3}$
Inverse of fine-structure constant (α^{-1})	$1{\cdot}37036\times10^{2}$
Second radiation constant ($c_2 = hc/k$)	$1{\cdot}43878\times10^{-2}$ m-K
Standard acceleration of free fall (g)	$9{\cdot}80665$ m s^{-2}

1. Menthyl chloride (MC) and neomenthyl chloride (NMC) upon reaction with sodium ethoxide in ethanol would produce the following products, respectively :



(MC) *A* *B* (NMC) *C* *D*

(a) Only *B*; *C* (minor) and *D* (major)

(b) Only *A*; *C* (minor) and *D* (major)

(c) *A* (major), *B* (minor); *C* (major) and *D* (minor)

(d) *A* (minor), *B* (major); only *C*

2. The basicity of $EtNH_2$ (*I*), $HN{=}C(NH_2)_2$ (*II*) and $CH_3C(=NH)NH_2$ (*III*) would follow the following order :

(a) *II* > *III* > *I*

(b) *III* > *II* > *I*

(c) *I* > *II* > *III*

(d) *I* > *III* > *II*

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3. The conversions of cyclohexanone oxime to Nylon-6 and cyclic ketones to lactones involve, respectively

(a) Curtius rearrangement and Wolff rearrangement

(b) Wolff rearrangement and Lossen rearrangement

(c) Beckmann rearrangement and Baeyer-Villiger oxidation

(d) Curtius rearrangement and Baeyer-Villiger oxidation

4. The following is true for Cope reaction :

(a) Occurs at low temperature, tertiary amines are reactants, proceeds through SYN pathway

(b) Occurs at low temperature, tertiary amine oxides are reactants, proceeds through SYN pathway

(c) Occurs at high temperature, tertiary amine oxides are reactants, proceeds through ANTI pathway

(d) Occurs at low temperature, tertiary amine oxides are reactants, proceeds through ANTI pathway

5. Match the structure of the eight-membered ring compounds (*A-D*) with the following ^{1}H-NMR chemical shifts (in ppm) :

A *B* *C* *D*

(a) *A*: δ 5·74 (*s*); *B*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *C*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *D*: δ 1·54 (*s*)

(b) *A*: δ 1·54 (*s*); *B*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *C*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *D*: δ 5·74 (*s*)

(c) *A*: δ 1·54 (*s*); *B*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *C*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *D*: δ 5·74 (*s*)

(d) *A*: δ 5·74 (*s*); *B*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *C*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *D*: δ 1·54 (*s*)

6. The underlined H atoms in molecules *A*, *B* and *C* are, respectively

A *B* *C*

(a) Enantiotopic, homotopic and diastereotopic

(b) Diastereotopic, enantiotopic and homotopic

(c) Homotopic, enantiotopic and diastereotopic

(d) Enantiotopic, diastereotopic and homotopic

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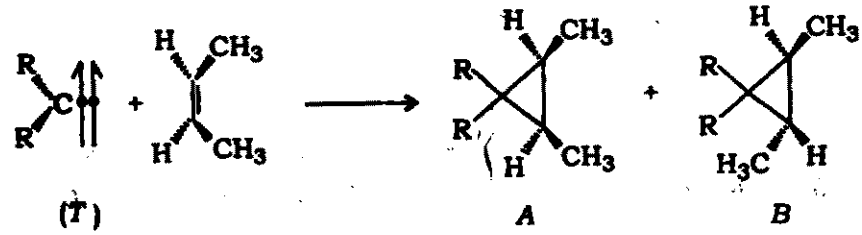
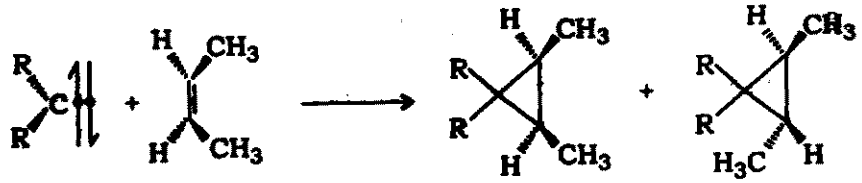
7. Addition of a triplet (*T*) carbene to an alkene and a singlet (*S*) carbene to an alkene would produce, respectively



(*T*) *A* *B*



(*S*) *C* *D*

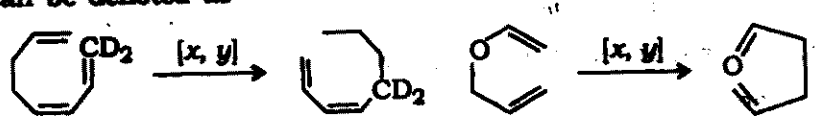
(a) Only *A* and only *D*

(b) Only *B* and only *C*

(c) *A* and *B* and only *D*

(d) *A* and *B* and only *C*

8. The reactions of *A* to *B* and *C* to *D* are examples of [*x*, *y*] type of sigmatropic shifts, which can be denoted as



A *B* *C* *D*

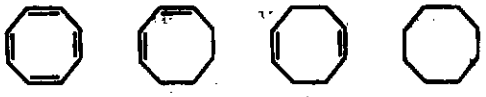
(a) [1, 8] and [1, 3]

(b) [3, 5] and [1, 3]

(c) [3, 5] and [3, 3]

(d) [1, 8] and [3, 3]

5. Match the structure of the eight-membered ring compounds (*A-D*) with the following ^{1}H-NMR chemical shifts (in ppm):



A *B* *C* *D*

(a) *A*: δ 5·74 (s); *B*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *C*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *D*: δ 1·54 (s)

(b) *A*: δ 1·54 (s); *B*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *C*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *D*: δ 5·74 (s)

(c) *A*: δ 1·54 (s); *B*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *C*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *D*: δ 5·74 (s)

(d) *A*: δ 5·74 (s); *B*: δ 2·39 (*m*, 8*H*), 5·60 (*m*, 4*H*); *C*: δ 1·20 – 1·70 (*m*, 4*H*), 1·85 – 2·50 (*m*, 4*H*), 5·35 – 5·94 (*m*, 4*H*); *D*: δ 1·54 (s)

6. The underlined H atoms in molecules *A*, *B* and *C* are, respectively

A *B* *C*

(a) Enantiotopic, homotopic and diastereotopic

(b) Diastereotopic, enantiotopic and homotopic

(c) Homotopic, enantiotopic and diastereotopic

(d) Enantiotopic, diastereotopic and homotopic

9. The following is true for the complex of [18] crown-6 and $KMnO_4$:

(a) Ion-dipole interaction, phase transfer catalyst, turns benzene purple

(b) π-π interaction, acid catalyst, turns benzene purple

(c) π-π interaction, phase transfer catalyst, turns benzene yellow

(d) Ion-dipole interaction, acid catalyst, turns benzene yellow

10. XeF_2, $[XeF_5]^-$, SF_4, $[BBr_4]^-$ have the following molecular shapes, respectively :

(a) Tetrahedral, pentagonal planar, trigonal bipyramid, linear

(b) Linear, trigonal bipyramid, pentagonal planar, tetrahedral

(c) Trigonal bipyramid, pentagonal planar, tetrahedral, linear

(d) Linear, pentagonal planar, trigonal bipyramid, tetrahedral

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11. Symmetry operators that are lost in going from NH_3 to NH_2Cl are

(a) C_3 and two σ_v

(b) C_2 and two σ_v

(c) C_3 and one σ_v

(d) C_2 and one σ_v

12. How many degrees of vibrational freedom do $SiCl_4$, BrF_3 and $POCl_3$ possess?

(a) 9, 6 and 9, respectively

(b) 6, 9 and 6, respectively

(c) 4, 3 and 4, respectively

(d) 5, 4 and 5, respectively

13. The number of framework electrons in the closo, nido and arachno series would equal to

(a) $2n + 2$, $2n + 4$ and $2n + 6$, respectively

(b) $2n + 6$, $2n + 4$ and $2n + 2$, respectively

(c) $2n + 4$, $2n + 2$ and $2n + 6$, respectively

(d) $2n + 6$, $2n + 2$ and $2n + 4$, respectively

14. The spin only magnetic moment, (μ_s) for Co(III) octahedral complex with weak field ligand and Co(II) in a tetrahedral would be

(a) 3·87 BM and 1·73 BM

(b) 0 BM and 1·73 BM

(c) 1·73 BM and 3·87 BM

(d) 4·90 BM and 3·87 BM

15. Jahn-Teller distortion would be exhibited by the following :

(a) Cr(II) and Mn(III) in weak ligand field

(b) Co(III) and Fe(II) in strong ligand field

(c) Cr(III) in weak ligand field

(d) Ni(II) and Fe(III) in weak ligand field

16. Which of the following is a haem iron protein?

(a) Rubredoxin

(b) Transferrin

(c) Haemerythrin

(d) Cytochrome c

17. The ground state terms for Ti(III) and Mn(II) would, respectively, be

(a) ${}^3F$ and ${}^4F$

(b) ${}^2D$ and ${}^6S$

(c) ${}^4F$ and ${}^5D$

(d) ${}^2D$ and ${}^4F$

18. In computational chemistry, one calculates the lowest energy structure of molecule through variation principle using Hartree-Fock equation, $\boldsymbol{F}_i\Phi_i = \varepsilon\Phi_i$. In this equation, the Fock operator ($\boldsymbol{F}_i$) is expressed as

(a) $\boldsymbol{F}_i = \boldsymbol{h}_j + \Sigma_j(\boldsymbol{J}_j - \boldsymbol{K}_j)$, with $\boldsymbol{h}_j = -(\hbar^2/2m_e)\nabla_j^2 - \Sigma_n(Z_n e/|\boldsymbol{R}_n - \boldsymbol{r}_e|)$, and $\boldsymbol{J}$ as Coulomb operator and $\boldsymbol{K}$ as exchange operator, where i and j are indices for different electrons

(b) $\boldsymbol{F}_i = \boldsymbol{h}_i + \Sigma_i(\boldsymbol{J}_i - \boldsymbol{K}_i)$, with $\boldsymbol{h}_i = -(\hbar^2/2m_e)\nabla_i^2 - \Sigma_n(Z_n e/|\boldsymbol{R}_n - \boldsymbol{r}_e|)$, and $\boldsymbol{J}$ as Coulomb operator and $\boldsymbol{K}$ as exchange operator, where i and j are indices for different electrons

(c) $\boldsymbol{F}_i = \boldsymbol{h}_i + \Sigma_j(\boldsymbol{J}_j - \boldsymbol{K}_j)$, with $\boldsymbol{h}_i = -(\hbar^2/2m_e)\nabla_i^2 - \Sigma_n(Z_n e/|\boldsymbol{R}_n - \boldsymbol{r}_e|)$, and $\boldsymbol{J}$ as Coulomb operator and $\boldsymbol{K}$ as exchange operator, where i and j are indices for different electrons

(d) $\boldsymbol{F}_i = \boldsymbol{h}_i + \Sigma_i(\boldsymbol{J}_i - \boldsymbol{K}_i)$, with $\boldsymbol{h}_i = -(\hbar^2/2m_e)\nabla_j^2 - \Sigma_n(Z_n e/|\boldsymbol{R}_n - \boldsymbol{r}_e|)$, and $\boldsymbol{J}$ as exchange operator and $\boldsymbol{K}$ as Coulomb operator, where i and j are indices for different electrons

19. If the estimated dipole moment and bond length of HCl are 1·1 D and 1·28 Å, respectively, the percentage ionic character in HCl molecule is

(a) 12·8%

(b) 86·3%

(c) 85·9%

(d) 17·9%

20. Maximum entropy of a mixture of hexane and heptane occur when they are mixed in a proportion of

(a) 86 gm and 100 gm

(b) 86 gm and 1 gm

(c) 1 gm and 100 gm

(d) 8·6 gm and 10 gm

17. The ground state terms for Ti(III) and Mn(II) would, respectively, be

(a) ^3F and ^4F

(b) ^2D and ^6S

(c) ^4F and ^5D

(d) ^2D and ^4F

18. In computational chemistry, one calculates the lowest energy structure of molecule through variation principle using Hartree-Fock equation, $F_i\Phi_i = \varepsilon\Phi_i$. In this equation, the Fock operator (F_i) is expressed as

(a) $F_i = h_j + \Sigma_j(J_j - K_j)$, with $h_j = -(\hbar^2/2m_e)\nabla_j^2 - \Sigma_n(Z_n e/|R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons

(b) $F_i = h_i + \Sigma_i(J_i - K_i)$, with $h_i = -(\hbar^2/2m_e)\nabla_i^2 - \Sigma_n(Z_n e/|R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons

(c) $F_i = h_i + \Sigma_j(J_j - K_j)$, with $h_i = -(\hbar^2/2m_e)\nabla_i^2 - \Sigma_n(Z_n e/|R_n - r_e|)$, and J as Coulomb operator and K as exchange operator, where i and j are indices for different electrons

(d) $F_i = h_i + \Sigma_i(J_i - K_i)$, with $h_i = -(\hbar^2/2m_e)\nabla_j^2 - \Sigma_n(Z_n e/|R_n - r_e|)$, and J as exchange operator and K as Coulomb operator, where i and j are indices for different electrons

21. If at a given temperature, the equilibrium constant (K) of the reaction $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ is $(K) = 4 \times 10^{-3}$, then the equilibrium constant (K') for the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ is

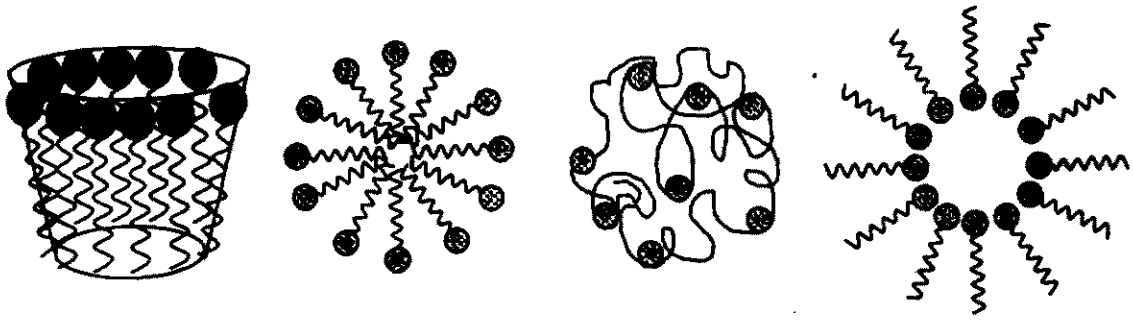
(a) 4×10^{-3}

(b) 16×10^{3}

(c) $6{\cdot}25 \times 10^{4}$

(d) $1{\cdot}6 \times 10^{-4}$

22. Which of the following pictures is the most appropriate for reverse-micelle structure?



(a) (b) (c) (d)

23. The wave function of a quantum particle is given by $\psi(x) = e^{-ax}$. The expectation value, $< x >$ in the range $x = -1$ to 1 is given by

(a) $(1/a)\, e^{-2a}$

(b) e^{-2a}

(c) $(1/a^2)\, e^{-2a}$

(d) $(1/a)\, e^{-a}$

24. A substance, when dissolved in water at 10^{-3} M concentration, absorbs 10% of an incident radiation in a path of 1 cm length. In order to absorb 90% of same radiation, the concentration of the solution should be

(a) $21{\cdot}8 \times 10^{-3}$ M

(b) $9{\cdot}5 \times 10^{-3}$ M

(c) $27{\cdot}4 \times 10^{-3}$ M

(d) 18×10^{-3} M

21. If at a given temperature, the equilibrium constant (K) of the reaction $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ is $(K) = 4 \times 10^{-3}$, then the equilibrium constant (K') for the reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ is

(a) 4×10^{-3}

(b) 16×10^{3}

(c) $6{\cdot}25 \times 10^{4}$

(d) $1{\cdot}6 \times 10^{-4}$

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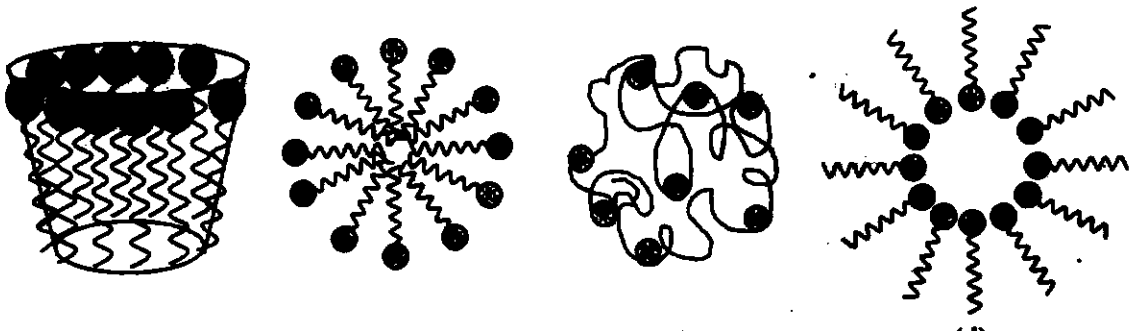

(a) (b) (c) (d)

25. HCl molecule is well described by the Morse potential ($V = hcD_e[1 - e^{-a(R - Re)}]^2$) with $D_e = 42940 \cdot 6\,cm^{-1}$, $\nu = 2990\,cm^{-1}$ and $x_e\nu = 52\,cm^{-1}$ (x_e is the anharmonicity constant). The dissociation energy of HCl molecule is

(a) $39950 \cdot 6\,cm^{-1}$

(b) $41458 \cdot 6\,cm^{-1}$

(c) $42940 \cdot 6\,cm^{-1}$

(d) $40002 \cdot 6\,cm^{-1}$