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ENTRANCE EXAMINATION, 2014

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

[Field of Study Code : CHEP (162)]

Time Allowed : 3 hours

Maximum Marks : 70

INSTRUCTIONS FOR CANDIDATES

(i) All questions in Part—A are compulsory.

(ii) In Part—A, each correct answer carries 1·5 marks and wrong answers carry (–0·5) mark.

(iii) The answers for Part—A must be written in the box provided on Page 3.

(iv) Answer only 8 questions from Part—B.

(v) Answer for Part—B must be done in the space provided along with the question.

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

(vii) Use of calculator is permitted.

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ENTRANCE EXAMINATION, 2014

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

SUBJECT . . . . . .

FIELD OF STUDY CODE . . . . . .

NAME OF THE CANDIDATE . . . . . .

. . . . . .

REGISTRATION NO. | | | | | |

CENTRE OF EXAMINATION. . . . . .

. . . . . .

DATE. . . . . .

.....
(Signature of Candidate)

.....
(Signature of Invigilator)

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(Signature and Seal of Presiding Officer)

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Write down the answers for the multiple choice answers given in Part—A :

Question No.	Answer	Question No.	Answer
A1		**A11**	
A2		**A12**	
A3		**A13**	
A4		**A14**	
A5		**A15**	
A6		**A16**	
A7		**A17**	
A8		**A18**	
A9		**A19**	
A10		**A20**	

Fundamental Constants :	**Value**
Speed of light (c)	$2{\cdot}99792558 \times 10^{8}$ m s^{-1}.
Elementary charge (e)	$1{\cdot}602176 \times 10^{-19}$ C
Boltzmann constant (k)	$1{\cdot}38065 \times 10^{-23}$ J K^{-1}
Gas constant ($R = N_A k$)	8·31 J K^{-1} mol^{-1}
Planck constant (h)	$6{\cdot}62608 \times 10^{-34}$ J s
Avogadro's constant (N_A)	$6{\cdot}02214 \times 10^{23}$ mol^{-1}
Electron mass (m_e)	$9{\cdot}11 \times 10^{-31}$ kg
Proton mass (m_p)	$1{\cdot}67 \times 10^{-27}$ kg
Neutron mass (m_n)	$1{\cdot}67 \times 10^{-27}$ kg
Bohr radius ($a_0 = 4\pi\varepsilon_0\hbar^2 / m_e e^2$)	$5{\cdot}3 \times 10^{-11}$ m

PART—A

Important Note : Each wrong answer carries (–0·5) mark

Multiple Choice Questions : 1·5×20=30

A1. The number of unpaired electrons in the metal *d*-orbitals for the coordination complex anion $[CoF_6]^{3-}$ is

(a) 4

(b) 3

(c) 0

(d) 6

A2. In active site of the metalloenzyme, carbonic anhydrase is associated with the metal

(a) Ni

(b) Mo

(c) Zn

(d) V

A3. The *R-S* ground state term symbols for Cr^{3+} ion and Co^{2+} ion respectively are

(a) $^2D_{3/2}$ and $^5D_0$

(b) $^3F_2$ and $^3F_4$

(c) $^4F_{9/2}$ and $^4F_{3/2}$

(d) $^4F_{3/2}$ and $^4F_{9/2}$

A4. A crown ether receptor would prefer to encapsulate (by coordinate covalent bond) the metal ion

(a) Cu^+

(b) Ag^+

(c) Mn^{2+}

(d) K^+

A5. The general formula of closo-boranes is generally described by

(a) $[B_nH_n]^{2-}$

(b) B_nH_{n+4}

(c) B_nH_{n+6}

(d) B_nH_{n+8}

A6. The reduction potential for the conversion of Tl^{3+} to Tl, from the Latimer diagram

$$Tl^{3+} \xrightarrow{+1{\cdot}25\ V} Tl^{+} \xrightarrow{-0{\cdot}34\ V} Tl$$

is

(a) $-0{\cdot}72$ V

(b) $0{\cdot}38$ V

(c) $+0{\cdot}72$ V

(d) $+0{\cdot}94$ V

A7. The correct sequence of increasing order of C—O bond strength among the following is

(a) $[Mn(CO)_6]^+ > [Cr(CO)_6] > [V(CO)_6]^- > [Ti(CO)_6]^{2-}$

(b) $[Ti(CO)_6]^{2-} > [V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+$

(c) $[Cr(CO)_6] > [Mn(CO)_6]^+ > [Ti(CO)_6]^{2-} > [V(CO)_6]^-$

(d) $[V(CO)_6]^- > [Cr(CO)_6] > [Mn(CO)_6]^+ > [Ti(CO)_6]^{2-}$

A8. Facts and related answer are given in codes. Which one of the following codes is correct?

Facts

(I) *meta*-benzyne is bicyclo[3, 1, 0]hexa-1,3,5-triene

(II) *para*-benzyne is bicyclo[2, 2, 0]hexa-1,3,5-triene

Codes

(a) (I) is correct and (II) is incorrect

(b) (II) is correct and (I) is incorrect

(c) Both (I) and (II) are correct

(d) Both (I) and (II) are incorrect

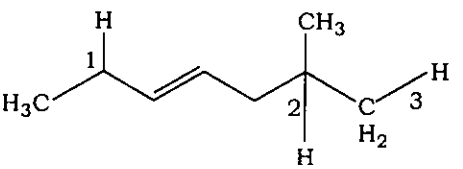
A9. Match List—I (Name of reaction) and List—II (Substrate) and select the correct answer using codes given below :

	List—I (Name of reaction)		*List—II (Substrate)*
A.	Chugaev reaction	1.	Amine oxide
B.	Cope elimination	2.	Xanthate
C.	E1cb reaction	3.	$Ph—CH_2—CH_2—F$
D.	Hoffmann elimination, E_2 reaction	4.	$CH_3CH_2—CH(F)—CH_3$

Codes :

(a)	A	B	C	D
	2	1	4	3
(b)	A	B	C	D
	1	2	4	3
(c)	A	B	C	D
	2	1	3	4
(d)	A	B	C	D
	3	2	1	4

A10. Pick the correct order of decreasing C—H bond energy of bonds shown in the given compound :



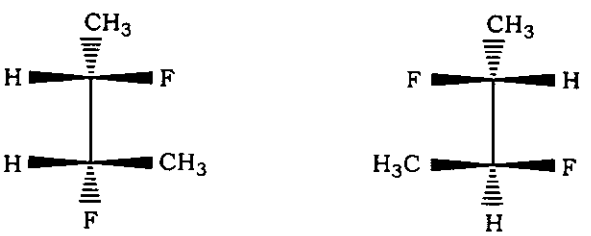
(a) 2 > 1 > 3

(b) 1 > 2 > 3

(c) 3 > 2 > 1

(d) 2 > 3 > 1

A11. Which statement is correct for the following two molecules?



(a) They have same melting point

(b) They have different melting points

(c) They have equal but opposite optical rotations

(d) None of the above

A12. ^{1}H-NMR spectra of $(CH_3)_2O$, CH_3F and RCOOH show chemical shift (δ) in ppm at

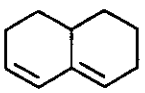
(a) 3·27, 4·30 and 10·8 respectively

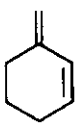
(b) 4·30, 3·27 and 10·8 respectively

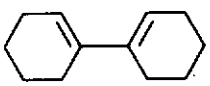
(c) 3·27, 10·8 and 4·3 respectively

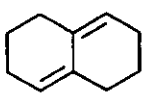
(d) 10·8, 4·30 and 3·27 respectively

A13. The diene which reacts in Diels-Alder reaction is

(a) 

(b) 

(c) 

(d) 

A14. Increasing order of the stability of carbocations $C(Ph)_3^+$, $C(CH_3)_3^+$, $C(CD_3)_3^+$, $PhCH_2^+$ is

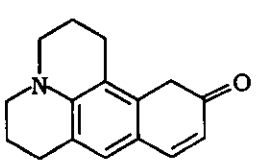
(a) $C(Ph)_3^+ < C(CH_3)_3^+ < C(CD_3)_3^+ < PhCH_2^+$

(b) $PhCH_2^+ < C(CH_3)_3^+ < C(CD_3)_3^+ < C(Ph)_3^+$

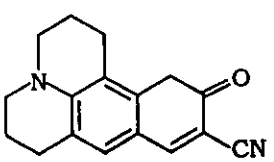
(c) $C(Ph)_3^+ < PhCH_2^+ < C(CH_3)_3^+ < C(CD_3)_3^+$

(d) $C(CD_3)_3^+ < C(CH_3)_3^+ < PhCH_2^+ < C(Ph)_3^+$

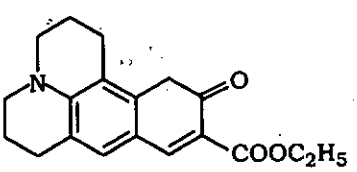
A15. The order of high-to-low dipole moments (μ) for the following coumarin molecules is



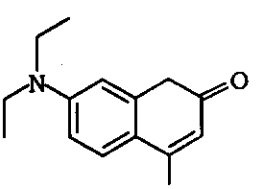
M-1



M-2



M-3



M-4

(a) M-2 > M-3 > M-1 > M-4

(b) M-1 > M-2 > M-3 > M-4

(c) M-2 > M-4 > M-3 > M-1

(d) M-1 > M-4 > M-2 > M-3

A16. If the characteristic absorption of O—H stretch for water is 3300 cm^{-1}, then with excitation at 400 nm the (Stokes) Raman-band would appear at

(a) 435 nm

(b) 461 nm

(c) 353 nm

(d) 408 nm

A17. If λ_1 is the wavelength associated to a dog of 20 kg running with a velocity of 20 km/hour, and λ_2 is the wavelength for an electron of velocity 10^7 m/s, then the ratio, λ_2 / λ_1 would be

(a) $1{\cdot}22 \times 10^{25}$

(b) $8{\cdot}17 \times 10^{-25}$

(c) $2{\cdot}44 \times 10^{-25}$

(d) $4{\cdot}09 \times 10^{25}$

A18. If the change in enthalpy and entropy is negative for a chemical reaction, then which of the following statements is true?

(a) Reaction is spontaneous at any condition

(b) Reaction is non-spontaneous at any condition

(c) Reaction is non-spontaneous at low temperature and spontaneous at high temperature

(d) Reaction is spontaneous at low temperature and non-spontaneous at high temperature

A19. Equivalent conductivity of 0·07 *N* solution of a monobasic acid is 15·8 mho cm^2 eq^{-1}. If the equivalent conductivity of the acid at infinite dilution is 350 mho cm^2 eq^{-1}, then the dissociation constant of the acid is

(a) infinite

(b) $2{\cdot}988 \times 10^{-4}$

(c) $2{\cdot}988 \times 10^{-5}$

(d) $1{\cdot}494 \times 10^{-4}$

A20. For a simple diatomic molecule, the functional form of the potential energy can be expressed (with usual terms) as

(a) $V(r) = D_e\left(1 - e^{-a(r-r_e)^2}\right)$

(b) $V(r) = D_e\left(1 - e^{-a(r-r_e)}\right)^2$

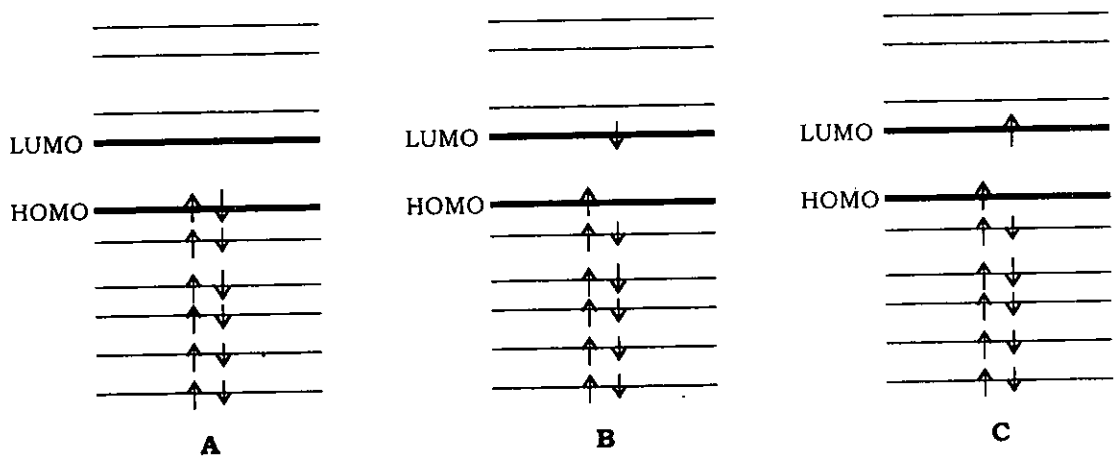
(c) $V(r) = D_e\left(e^{-a(r-r_e)^2} - 1\right)$

(d) $V(r) = D_e\left(e^{-a(r-r_e)^2} - 1\right)^2$

PART—B

Answer *any* **eight** questions (Descriptive) : 5×8=40

B1. The molecular orbital electronic level description of a molecule is shown below :



(a) Write down the spin multiplicities of the molecule in these three descriptions.

(b) Identify the electronic states for the molecule in the three descriptions.

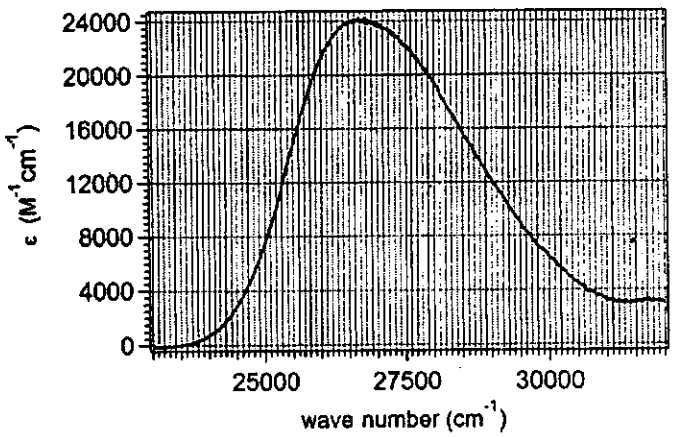
(c) Explain how the molecule can undergo transitions

$$\mathbf{A} \rightarrow \mathbf{B},\ \mathbf{B} \rightarrow \mathbf{C},\ \mathbf{B} \rightarrow \mathbf{A} \text{ and } \mathbf{C} \rightarrow \mathbf{A}$$

(d) Arrange the total energy of the molecule in the three descriptions from highest to lowest energy value.

B2. *(a)* What is oscillator strength of an electronic transition?

(b) If the area of a spectrum is expressed as the product of peak molar extinction coefficient and full-width-at-half-maximum, then calculate the oscillator strength for the molecule whose spectrum is shown below. (Given the oscillator strength of simple harmonic oscillator is $2 \cdot 3 \times 10^{8}$)



B3. *(a)* Calculate the percentage ionic character in HCl molecule if the observed dipole moment is 1·08 D and bond length is 1·2746 Å.

(b) What is the pH of a buffer solution containing 0·2 *M* hydrofluoric acid (pK_a is 3·2) and 1 *M* sodium fluoride? Calculate also the final pH if the buffer is half-diluted.

B4. *(a)* Define Gibbs free energy for a chemical reaction. Show that for a reaction; $A + B \rightleftharpoons C + D$ to be spontaneous at room temperature, the Gibbs free energy change must be negative if the backward reaction-rate ($k\_$) is lower than the forward reaction-rate (k_+).

(b) Calculate the equilibrium constant (K) for the following reaction, if $\Delta G° = -10$ kJ at 298 K :

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

B5. *(a)* The magnetic moment values of lanthanides (Ln^{3+}) are determined solely by the ground state except for Sm^{3+} and Eu^{3+}.Comment on this statement.

(b) Derive the ground state term symbols for Ce^{3+} and Gd^{3+} ions.

B6. *(a)* $[Cu(H_2O)_6]^{2+}$ complex has two 2·45 Å axial and four 2·00 Å equatorial Cu—O distances. Why are two different Cu—O distances observed? Draw the *d*-orbital splitting pattern and show the electron distribution in them for this complex.

(b) The magnetic moment of $[Fe(H_2O)_5(NO)]SO_4$ is ~ $3 \cdot 9\,\mu_B$. What oxidation state and which spin state for iron can be expected from this given value?

B7. The power of the 18-electron rule for predicting structures of complexes involving unsaturated ligands can be illustrated with $W(CO)_2(C_5H_5)_2$. How do you prove this? Square planar d^8 complexes (that show 16-electron rule) are consistent exceptions to the 18-electron rule. How do you justify this statement?

B8. The electronic spectrum of $[V(H_2O)_6]^{2+}$ displays three bands at 12300 cm^{-1}, 18500 cm^{-1} and 27900 cm^{-1}. Assign these bands and calculate the values of 10Dq, B and β. (B_0 for V^{2+} ion is 755 cm^{-1})

B9. Elucidate the molecular structure from the following spectroscopic data :

Molecular formula : C_9H_8O

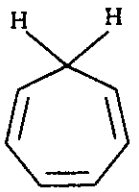
UV : λ_{max} 285 nm

IR (cm^{-1}) : 3090–3000, 1680, 1630, 1610–1455

NMR : δ 6·62, doublet of doublet, 1*H*, J = 16·3 and 7·4 Hz
δ 7·41, doublet, 1*H*, J = 16·3
δ 7·40, multiplet, 5*H*
δ 9·66, doublet, 1*H*, J = 7·4 Hz

Mass (m/z) : 132, 131, 103, 91, 77, 51

B10. *(a)* Which one of the following two compounds has aromatic character? Explain why :



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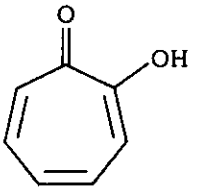
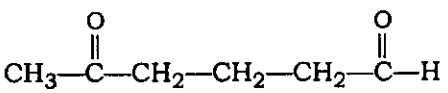


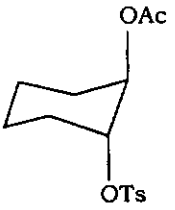
II

(b) In the ozonolysis reaction of the following, an olefin product could be isolated :

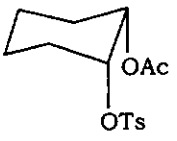


Draw the molecular structure of the olefin.

B11. Consider the following two compounds. Explain why the *trans*-isomer (I) undergoes acetolysis 670 times faster than the *cis*-isomer (II) and that the product has same (*cis*) stereochemistry in both the cases :



(I)



(II)

B12. Write the structures of *A*, *B* and *C* in the following reactions and provide mechanisms for the product formation :