4-67

ENTRANCE EXAMINATION – 2020

Ph. D. Chemistry – 2020

TIME: 2 HOURS

MAXIMUM MARKS: 70

HALL TICKET NUMBER:	

INSTRUCTIONS

- 1. Write your HALL TICKET NUMBER in the space provided above and also on the OMR ANSWER SHEET given to you.
- 2. Make sure that pages numbered from 1 20 are present (excluding 4 pages assigned for rough work).
- 3. There are eighty (80) multiple-choice questions in this paper (20 in Part-A and 60 in Part-B). You are required to answer all questions of Part-A and a maximum of 20 questions of Part-B. If more than the required number of questions are answered in Part-B, only the first 20 questions will be evaluated.
- 4. Each question in Part-A and Part-B carries **1.75 marks**
- 5. There is negative marking for both Part-A and Part-B. Each wrong answer carries -0.50 mark
- 6. Answers are to be marked on the OMR answer sheet following the instructions provided on it.
- 7. Handover the OMR answer sheet to the invigilator at the end of the examination.
- 8. In case of a tie, the marks obtained in the first 20 questions (**Part-A**) will be used to determine the order of merit.
- 8. No additional sheets will be provided. Rough work can be done in the space provided at the end of the booklet.
- 9. Calculators are allowed. Cell phones are not allowed.
- 10. Useful constants are provided just above Part-A in the question paper.
- 11. OMR without hall ticket number will not be evaluated and University shall not be held responsible.

Useful Constants:

Rydberg constant = 109737 cm^{-1} ; Faraday constant = 96500 C; Planck constant = $6.625 \times 10^{-34} \text{ J}$ s; Speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$; Boltzmann constant = $1.380 \times 10^{-23} \text{ J} \text{ K}^{-1}$; Gas constant = $8.314 \text{ J} \text{ K}^{-1} \text{ mol}^{-1} = 0.082 \text{ L}$ atm K⁻¹ mol⁻¹ = $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$; Mass of electron = $9.109 \times 10^{-31} \text{ kg}$; Mass of proton = $1.672 \times 10^{-27} \text{ kg}$; Charge of electron = $1.6 \times 10^{-19} \text{ C}$; 1 bar = $10^5 \text{ N} \text{ m}^{-2}$; RT/F (at 298.15 K) = 0.0257 V; Avogadro number = 6.022×10^{23}

Part-A

- 1. The correct order for energy of the d-orbitals in trigonal prism geometry is:
 - $[A] \quad d_{xz}, d_{yz} > d_{z^2} > d_{xy}, d_{x^2-y^2} \qquad [B] \quad d_{z^2} > d_{xz}, d_{yz} > d_{xy}, d_{x^2-y^2}$
 - [C] $d_{z^2} > d_{xy}, d_{x^2-y^2} > d_{xz}, d_{yz}$ [D] $d_{xz}, d_{yz} > d_{xy}, d_{x^2-y^2} > d_{z^2}$
- 2. Consider the two molecules, N₂F₂ and O₂F₂. The correct statement among the following regarding them (at 25 °C) is:
 - [A] Both of them show geometrical isomerism.
 - [B] Neither of them shows geometrical isomerism.
 - [C] O₂F₂ shows geometrical isomerism while N₂F₂ does not.
 - [D] N_2F_2 shows geometrical isomerism while O_2F_2 does not.
- A similar rate constant for the displacement of Cl⁻ by H₂O in complexes, [PtCl₃²⁻, [PtCl₃(NH₃)]⁻, [PtCl₂(NH₃)₂] and [PtCl(NH₃)₃]⁺ indicates that
 - [A] the reaction is associative. [B] the reaction is dissociative.
 - [C] the activation energy is high. [D] the activation energy is low.
- 4. In the presence of an external magnetic field, the number of Balmer H_{α} lines observed is:

÷.,

- [A] 3 [B] 6 [C] 9 [D] 12
- 5. The mRNA sequence that is complementary to the DNA sequence 5'-CGAGCATTCGAT-3' is:

[A] 5'-AUCGAAUGCUCG-3'	[C] 5'-ATCGAATGCTCG-3'
[B] 3'- AUCGAAUGCUCG-5'	[D] 3'-ATCGAATGCTCG-5'

- 6. The ³¹P NMR spectrum of $P_4S_3[^{31}P; I = \frac{1}{2}]$ has:
 - [A] Two sets of peaks, a doublet and a quartet, in the intensity ratio of 3:1
 - [B] Two sets of two triplets each
 - [C] A singlet
 - [D] Two singlets and a triplet

7. Given the following data,

 $O_{2}(g) + 4H^{+}(aq) + 4e^{-} \rightleftharpoons 2H_{2}O(l); E^{o} = 1.23 \text{ V (pH = 0)}$ $O_{2}(g) + 2H_{2}O(l) + 4e^{-} \rightleftharpoons 4OH^{-}(aq); E^{o} = 0.80 \text{ V (pH = 7)}$ $Mn^{3+} + e^{-} \rightleftharpoons Mn^{2+}; E^{o} = 1.54 \text{ V (pH = 0)}$ $Fe^{2+} + 2e^{-} \rightleftharpoons Fe; E^{o} = -0.44 \text{ V (pH = 7)}$

the incorrect statement among the following is:

- [A] Dioxygen is a better oxidizing agent in acidic medium than in neutral medium.
- [B] Dissolved oxygen can oxidize iron at neutral pH.
- [C] Mn³⁺ can reduce dioxygen in acidic medium.
- [D] The change in E° value for dioxygen reduction can be determined by using the Nernst equation.
- 8. If the source (⁵⁷Co) of ⁵⁷Fe* is moving at a speed of 2 mm s⁻¹, then the frequency shift is γ -ray frequency = 3.5 × 10¹⁸ Hz, v = 3 × 10⁸ m s⁻¹]:

[A]	23.3 MHz	[B]	20.2 MHz
[C]	46.6 MHz	[D]	11.7 MHz

The concentration (in g L⁻¹) at which the solution of a non-electrolyte of molar mass 100 would be isotonic with 0.1 N NaCl solution is (degree of dissociation of NaCl is 0.9):

[A]	9.5	[B]	38
[C]	29	[D]	19

10. The molar heat capacity (in J K⁻¹) at constant pressure of a perfect gas varies with temperature as, $C_p = 20.17 + 0.4T$. The change in internal energy (in kJ) of 1 mol of the gas on increase of temperature from 0 to 100 °C is close to:

[A]	7.45	[B]	7.05
[C]	14.9	, [D]	14.1

Page 3 of 24

- Y-67
- 11. The X-ray diffraction peak corresponding to the (1 1 1) plane of a crystal with a primitive cubic lattice shifts from $2\theta = 30^{\circ}$ to $2\theta = 20^{\circ}$ when the temperature is increased from 100 to 300 K. Ratio of the densities of the crystal at the two temperatures, $\frac{\rho_{300}}{\rho_{100}}$ is:

[A]	0.13	[B]	0.30
[C]	0.50	[D]	0.67

12. The characters of the irreducible representations (Γ) of the C_{2h} point group are given below. The correct Mulliken symbols for the Γ_2 and Γ_3 are respectively:

C _{2h}	Ê	C ₂	i	$\sigma_{\rm h}$
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ3	1	1	-1	-1
Γ4	1	-1	-1	1

[A]	A_1 and B_2	[B]	B_1 and A_2
[C]	B_g and A_g	[D]	B_g and A_u

13. For a two-level system, the excited state lies at 600 cm⁻¹ above the ground state. If both states are non-degenerate, then the temperature (in K) at which 10% of the population will be in the upper state is close to (1 cm⁻¹ \equiv 1.4 K):

[A]	273	[B]	323
[C]	363	[D]	393

14. The major product formed in the following reaction is:



Page 4 of 24

15. The correct set of reagents, X and Y, in the following scheme are:



16. The correct set of reagents, X and Y, in the following scheme are:

 $[A] X = NaOH/H_2O \qquad Y = H_3O^+$ $[B] X = H_3O^+ \qquad Y = NaOMe$

[C] $X = n-Bu_4NF$ $Y = NaB(OH)_4$ [D] $X = H_3O^*$ $Y = n-Bu_4NF, H_3O^*$

17. The most appropriate products, X and Y, in the following reaction are:



Page 5 of 24

18. The major product formed in the following reaction is:



19. The molecules having (\mathbf{R}, \mathbf{R}) configuration from the following compounds are:



20. The mass spectrum of an ether is given below. Based on the fragmentation pattern, the most likely compound is:



[A] diisopropyl ether [B] ethyl *t*-butyl ether [C] di-*n*-propyl ether[D] ethyl isobutyl ether

Page 6 of 24

Part-B

21. The 'glucose tolerance factor' in humans can be managed by the controlled uptake of:

- [A] Cr^{3+} ion. [B] Fe^{3+} ion.
- C] V^{4+} ion. [D] Na⁺ ion.

22. LiCoO₂ is used in Li-ion batteries as:

- [A] cathode since it has a layered structure.
- [B] anode since it contains oxygen.
- [C] cathode since the reduction potential of Li is very high.
- [D] electrolyte because of the variable oxidation state of Co.
- 23. Among the following ions whose shapes are different from that predicted by VSEPR theory are:

(i) $SbCl_6^{3-}$	(ii) $SbCl_6^-$	(iii) $PtCl_4^{2-}$
(.) 555.6	(1) 50016	(11) I IC 14

- [A] (i) and (ii) [B] (i) and (iii)
- [C] (ii) and (iii) [D] (iii) only
- 24. The number of triangular faces, edges and angle $(\angle X_{eq}$ -E-X_{eq}) in EX7 with pentagonal bipyramidal structure are respectively:

[A]	10, 15, 72°	[B]	15, 15, 72°
[C]	15, 10, 60°	[D]	10, 15, 60°

25. The electronic spectrum of CrO_4^{2-} displays two strong absorption bands at 375 and 280 nm. An approximate value of the crystal field splitting Δ_{td} (in cm⁻¹) is:

[A]	9,000	[B]	10,500
[C]	16,700	[D]	25,600

26. The number of microstates for a d³ metal ion is:

[A] 15 [B] 45 [C] 120 [D] 210

27. The correct statements among the following are:

(i) In dissociative interchange (I_d) mechanism, bond breaking dominates over bond formation.

(ii) In associative interchange (I_a) mechanism, bond formation dominates over bond breaking.

(iii) Associative interchange (I_a) is a concerted process in which the reaction rate depends on the entering group.

.

[A]	(i) and (ii) only	[B]	(1) and (111) only
[C]	(ii) and (iii) only	[D]	(i), (ii) and (iii)

28. In Taube's classic demonstration of inner-sphere electron transfer reaction,

- [A] the reduced forms were substitutionally labile and the oxidized forms were substitutionally inert.
- [B] the reduced forms were substitutionally inert and the oxidized forms were substitutionally labile.
- [C] both the reduced and oxidized forms were substitutionally labile.
- [D] both the reduced and oxidized forms were substitutionally inert.

29. The correct statement/s with regard to Eigen-Wilkins mechanism is/are:

- (i) It applies to substitution reactions of octahedral complexes
- (ii) It applies to substitution reactions of square planar complexes.

(iii) It assumes that an encounter complex is formed between the substrate and entering ligand in a pre-equilibrium step.

[A] (i) and (ii)	[B]	(ii) and (iii)
------------------	-----	----------------

- [C] (i) and (iii) [D] (i) only.
- 30. The metal ion substitution which facilitates the characterization of carbonic anhydrase by optical and EPR spectroscopy techniques is:
 - [A] Fe^{2*} [B] Co^{2*} [C] Mg^{2*} [D] Zn^{2*}

31. The point group of cis-[Co(en)₂Cl₂]⁺ (en = 1,2-diaminoethane) is:

[A] D_{2h} [B] C_{2v} [C] C_2 [D] C_{2h}

32. The potential (in V) of a concentration cell constructed by dipping two identical Cu electrodes in Cu²⁺ solutions of concentrations 1 M and 0.002 M at 25 °C is:

[A] 0.05 [B] 0.08 [C] 0.94 [D] 1.12

33. When ⁵⁹Cu undergoes a positron emission the immediate product is:

[A] ⁵⁸Ni [B] ⁵⁸Cu [C] ⁵⁹Ni [D] ⁵⁹Zn

34. A blue copper protein shows intense absorption at around 600 nm. This is due to

- [A] oxygen to copper charge transfer transition.
- [B] nitrogen to copper charge transfer transition.
- [C] d-d transition of Cu²⁺ ion.
- [D] sulfur to copper charge transfer transition.

35. A sample weighing 0.70 g contains 25% of Fe₂O₃. The volume (in mL) of ammonia (density 0.99 g/mL, 2.3% W/V) required to precipitate Fe³⁺ completely as Fe(OH)₃ is:

[A]	0.55	[B]	2,46
[C]	0.49	[D]	4.92

36. The product formed by treating graphite with a mixture of sulfuric acid and nitric acid is:

[A] $(C_{24})^{+}(NO_{3})^{-}$ [B] $(C_{24})^{+}(HSO_{4})^{-}$ [C] $(C_{24})^{2+}(SO_{4})^{2-}$ [D] $(C_{24})^{2+}[(NO)_{3}^{-}]_{2}$

37. The moiety which is NOT isolobal with Mn(CO)₄ is:

[A]	Co(CO)3	[B]	$Cr(CO)_{2}(\eta^{5}-C_{5}H_{5})$
[C]	Fe(CO) ₃	[D]	Р

Page 9 of 24

38. The bond angle of the following hydrides decreases as:

- $[A] NH_3 > PH_3 > AsH_3 > SbH_3$ $[C] SbH_3 > AsH_3 > PH_3 > NH_3$ $[D] AsH_3 > SbH_3 > PH_3 > NH_3$
- 39. The number of spectral lines for a high spin Co^{2+} ion considering the zero field splitting + and Kramers degeneracy is:
 - [A] 3 [B] 4
 - [C] 2 [D] 1

40. The ground state term symbol and effective magnetic moment (in BM) of Nd³⁺ ion is:

[A]	⁴ l _{9/2} and 3.62	[B]	⁴ H _{9/2} and 3.80
[C]	⁴ F _{9/2} and 3.42	[D]	${}^{4}G_{9/2}$ and 4.12

- 41. The Dulong-Petit law of molar heat capacity fails in the case of diamond at ambient temperature because:
 - [A] it is an electrical insulator with no free electrons
 - [B] it is an elemental solid
 - [C] of its high vibrational frequencies
 - [D] of lack of mobile ions in the material
- 42. According to Hückel theory, the spin density in *cis*-butadiene cation radical is predominantly localized on:
 - [A] atoms 1 and 2 [B] atom 1 and 3
 - [C] atoms 1 and 4 [D] atom 2 and 3
- 43. The expectation value of the Hamiltonian, $\langle E \rangle$, of a particle-in-a-box of length a in the state, $\psi(x) = \left(\frac{30}{a^5}\right)^{1/2} x(a-x)$, is (h = Planck's constant, m = mass of electron):

[A]
$$\frac{5h^2}{4\pi^2 ma^2}$$
 [B] $\frac{6h^2}{4\pi^2 ma^2}$
[C] $\frac{3h^2}{2\pi^2 ma^2}$ [D] $\frac{7h^2}{3\pi^2 ma^2}$

Page 10 of 24

44. In a non-stoichiometric metal oxide having formula MO_{1.04}, the metal is present in different oxidation states in the mole ratio:

[A]	$M^{2+}: M^{3+} = 11.5:1$	[B]	$M^{2+}: M^{3+} = 5: 1$
[C]	$M^{2+}: M^{1+} = 11.5:1$	[D]	$M^{2+}: M^{1+} = 1:5$

45. In the rotational spectrum of HBr ($B = 8.46 \text{ cm}^{-1}$), the transition corresponding to J = 4 to J = 5 is the most intense. The temperature (in K) at which the spectrum recorded is close to:

[A]	173	[B]	493
[C]	363	[D]	29 3

46. A system has three energy levels at 0, ε and 2ε with degeneracies 1, 1 and 2, respectively. The canonical partition function of the system is:

[A]	$e^{-3\epsilon/k_BT}$	[B]	$1 + e^{-3\epsilon/k_BT}$
[C]	$1 + e^{-\epsilon/k_BT} + e^{-2\epsilon/k_BT}$	[D]	$1 + e^{-\epsilon/k_BT} + 2e^{-2\epsilon/k_BT}$

47. A porous nanomaterial was subjected to N_2 gas adsorption experiment. The slope and intercept of linear BET plot obtained from this experiment are 0.003 and 0.002, respectively. The surface area (cm² g⁻¹) of the nanomaterial is close to (Area occupied by N_2 gas is 16.2 Å²):

[A]	250×10^{4}	[B]_	$560 imes 10^3$
[C]	320×10^{5}	[D]	870×10^4

48. The vibrational frequency of a diatomic molecule A-B is v. If another molecule C-D has the same force constant, and the mass of C and D are, respectively, twice that of A and B, the vibrational frequency of C-D is:

[A]	(1/2)v	[B]	2ν	
[C]	(1/√2)v	[D]	√ 2ν	

49. If the chemical shift (δ) of the methyl protons is 2 ppm with reference to tetramethylsilane in an NMR spectrometer operating at 100 MHz, the separation (in Hz) between these protons and those in TMS is:

[A]	2×10^{6}	[B]	·2 ×	10 ⁸
[C]	2×10^{10}	• [D]	2 ×	10 ¹²

50. A symmetry element that a normal crystal cannot have, but a quasicrystal can have is:

- [A] glide plane [B] 10-fold rotation
- [C] centre of inversion [D] 3-fold screw axis
- 51. The EMF of a concentration cell without liquid junction is -0.1 V. The liquid junction potential for this cell is 0.05 V. If the cell is reversible with respect to anion, then the transport number of the anion is:

[A]	0.5	[B]	0.05
[C]	0.25	[D]	0.75

52. For the sublimation process, HNO₃·2H₂O → HNO₃ (g) + 2H₂O (g), the free energy and enthalpy changes at 220 K are 69.4 and 188 kJ mol⁻¹, respectively. The free energy change (in kJ mol⁻¹) at 190 K for this process is closest to:

[A]	105.6	[B]	95.6
[C]	15.6	[D]	85.6

- 53. Domains in a ferromagnet arise from the competition between:
 - [A] ferro and antiferromagnetic interactions
 - [B] electron repulsion and nuclear attraction
 - [C] mechanical and frictional forces
 - [D] exchange and dipolar interactions
- 54. A metal crystallizes in FCC lattice. The closest distance between the metal atoms in the crystal lattice is close to (density and atomic weight of the metal are 2.6 g cm⁻³ and 26, respectively):

[A]	3.3 Å	[B]	2.9 Å	
[C]	4.6 Å	[D]	5.6 Å	

55. A liquid of density 0.5 g cm⁻³ and surface tension 50 dynes cm⁻¹ is filled in a U-tube with limbs having internal diameters of 1 and 2 mm. The difference in height of the liquid in the two limbs is close to:

[A]	0.4 cm	[B]	1 cm
[C]	4 cm	[D]	2 cm

Page 12 of 24

56. For the bi-molecular gas phase chemical reaction, $H_2 + I_2 \rightarrow 2HI$, the rate constants at 373 K and 473 K are, respectively, 8.74×10^{-15} and 9.53×10^{-10} L mol⁻¹ s⁻¹. Ratio of the fraction of collisions at 373 K to that at 473 K, within the hard sphere collision theory, is:

[A]	1.033×10^{-2}	[B]	1.033×10^{-5}
[C]	1.330×10^{-2}	[D]	1.330×10^{-5}

57. The change in entropy (in J K⁻¹) when 1 mol of a perfect gas ($C_{v,m} = 1.5 \text{ R}$) changes from the initial state (T = 600 K, p = 1.00 bar) to the final state (T = 250 K, p = 4.5 bar) is:

[A]	-30.7	[B]	-23.4
[C]	-5.7	[D]	1.6

58. Thermal expansion of solids is strongly influenced by the:

[A]	presence of free electrons	[B]	magnetic moment of the ions
[C]	anharmonicity of lattice vibrations	[D]	size of unit cells

59. In the fluorite structure with the general formula MX₂, M occupies the FCC lattice sites and X, the tetrahedral sites within. If two of the tetrahedral sites are vacant in all the unit cells, formula of the defective crystal will be:

[A]	М	[B]	MX
ICI	M ₄ X ₃	[D]	M_2X

60. Among the following, the intersystem crossing is enabled by:

[A] hyperfine coupling[B] spin-orbit coupling[C] vibronic coupling[D] electronic coupling

61. The increasing order of reactivity of the following compounds towards cyclopentadiene is:

Page 13 of 24

1



62. Identify X and Y in the following synthetic scheme:

63. The major product formed in the following reaction is:







.

Page 14 of 24

64. The major product formed in the following transformation is:



65. The major product formed in the following reaction is:



66. The products, X and Y, in the following reactions are:



Page 15 of 24



67. The most appropriate products, X and Y, in the following reaction are:

соон

68. The increasing order of carbanion stability of the following compounds is:



69. The major product formed in the following reaction is:



Page 16 of 24

70. The correct matching of the reagents (I to IV) with the name reactions (P to S) is:

- P Petasis olefination
- Q Horner-Emmons olefination
- R Peterson olefination
- S Julia olefination
- [A] P-(III); Q-(I); R-(II); S-(IV)
- [B] P-(IV); Q-(I); R-(II); S-(III)
- [C] P-(II); Q-(III); R-(I); S-(IV)
- [D] P-(II); Q-(I); R-(IV); S-(III)

71. The most suitable reagents sequence to effect the following transformation is:



[A] (i) CH₃MgBr (2 equiv.)/H⁺ (ii) CrO₃·2 Py



- [B] (i) CH₃MgBr, CuI & CH₃I (ii) KMnO₄
- [D] (i) LDA, CH₃I (2 equiv.) (ii) CrO₃
- 72. The most stable conformations of 2-(methylthio)cyclohexan-1-one and 2-methoxycyclohexan-1-one in CDCl₃ are:







Page 17 of 24

Y-67

73. The major product of the following reaction is:



74. The major product formed in the following reaction is:



75. The major product formed in the following reaction is:



Page 18 of 24

76. The appropriate product in the following reaction is:



77. The major product formed in the following reaction is:



78. The order of increasing stability of the following fully-conjugated hydrocarbons is:



Page 19 of 24

79. Assign the peaks appearing at chemical shifts δ 0.85, 1.27 and 1.63 ppm to the corresponding methyl groups labelled as x, y and z in the following structure.



ť.

80. In a single strand of DNA, two nucleotides are linked by a:

- [A] nitrogeneous base
- [B] diphosphate unit
- [C] phosphate unit
- [D] glycosidic bond