## BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI - K.K. BIRLA GOA CAMPUS FIRST SEMESTER 2019-2020, Comprehensive Examination (Closed Book) COURSE NO: CHEM F111, COURSE TITLE: GENERAL CHEMISTRY TOTAL MARKS: 135 Duration: 3.0 hours Date: 03/12/2019

*Instructions:* Write the <u>final</u> <u>answers only</u> in the <u>templated answer sheet provided</u>; <u>the main answer book may be</u> <u>used for rough work only.</u> Do not write anything on the question paper. *Useful Information:*  $m_{electron} = 9.11 \times 10^{-31}$  kg,  $m_{neutron} = 1.67 \times 10^{-27}$  kg,  $h = 6.626 \times 10^{-34}$  Js,  $c = 2.998 \times 10^8$  m/s,  $1 \text{ eV} = 1.602 \times 10^{-19}$  J, R = 8.314 JK<sup>-1</sup>mol<sup>-1</sup>, Bohr Radius (a<sub>0</sub>) = 0.529 Å, 1 kcal = 4.18 kJ, 1 kJ mol<sup>-1</sup> = 83.7 cm<sup>-1</sup>,  $R_{\rm H} = 1.097 \times 10^5$  cm<sup>-1</sup>, 1 amu =  $1.66 \times 10^{-27}$  kg,  $N_{\rm A} = 6.022 \times 10^{23}$  mol<sup>-1</sup>,  $\psi_n(x) = Nsin(\frac{n\pi x}{L})$ ,  $\psi_{1s} = \pi^{-1/2}(Z/a_0)^{3/2}e^{-Zr/a_0}$ ;  $\int \sin^2 bx \, dx = x/2 - \sin(2bx)/4b$  1 °C = 273.15 K, At. No. of Cr = 24, V = 23, Fe = 26, Ni = 28, Cu = 29, Co = 27, Pt = 78, Zn = 30.

1) One mole of water vapor initially at 200 °C and 1 bar undergoes a cyclic process for which  $W = 145 \text{ J K}^{-1}$ . What are the values of (i) q and (ii)  $\Delta S$  for the process respectively? [1+1=2]

2) The standard reaction entropy for  $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$  is -198.7 J K<sup>-1</sup> mol<sup>-1</sup>. What is the change in entropy (in JK<sup>-1</sup> mol<sup>-1</sup>) when 4 moles of hydrogen react? [3]

3) 149 J of heat is evolved on solidification of 1g of napthalene ( $C_{10}H_8$ ). What is the enthalpy of fusion of naphthalene (in kJmol<sup>-1</sup>)? [3]

4) For the reaction  $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g), \Delta_r G^\circ = +1.7 \times 10^3 \text{ Jmol}^{-1}$  at 30 °C. Find the value of the equilibrium constant. [3]

5) 1 m<sup>3</sup> of Neon gas (molar mass = 10g mol<sup>-1</sup>) with  $C_{V, m} = (3/2) R$  at 10 atm and 273.2 K undergoes an isothermal reversible expansion to a final pressure of 1 atm. What is the work done during the process (in kJ) (take R = 0.082 L atm K<sup>-1</sup>). [3]

6) What is  $\Delta_{\text{fus}}$ S (in J K<sup>-1</sup>) for the melting of 5.00 g of ice (heat of fusion = 79.7 cal g<sup>-1</sup>) at 0°C and 1 atm? [3]

7) If we want the heat engine to be operating at 90% efficiency, and the cold reservoir is working at 10°C, then what should be the minimum temperature (in K) of the hot reservoir? [2]

8) The standard enthalpy of formation of carbon dioxide (g) and water (l) are -394 kJ mol<sup>-1</sup> and -286 kJ mol<sup>-1</sup> respectively. If the standard enthalpy change of combustion of propyne,  $C_3H_4$  (g) is -1938 kJ mol<sup>-1</sup>, what is the standard enthalpy of its formation (kJ mol<sup>-1</sup>)? [3]

9) Ultraviolet radiation of wavelength 200 nm strikes a metal surface having a work function of 1.5 eV. Calculate (i) the momentum (in kg m s<sup>-1</sup>) of the electron ejected and (ii) the de Broglie wavelength (in Å) of the ejected electron assuming free particle. [2+2=4]

10) A conjugated polyene has its lowest energy electronic transition of energy difference 1.001 eV. Consider that the electrons in conjugated polyene can be approximated to particle in 1-dimensional (1d) box with a box dimension of 2.94 nm. Assuming that Pauli's exclusion principle is followed while filling each electronic energy level in 1d box, answer the following: (i) Find the principal quantum number (rounded to the nearest integer) of the energy level from which the lowest energy electronic transition takes place. (ii) How many carbon atoms are in conjugation? [2+2=4]

11) An electron is confined in a two-dimensional (2d) square box of dimension  $L_x = L_y = 2$  nm. Answer the following questions. (i) Write down the normalized wavefunction ( $\psi_{1,1}$ ) for the ground state. (Use box dimension in nm unit only for writing normalization constant of  $\psi_{1,1}$ ); (ii) Calculate the energy ( $\Delta E$  in eV) associated with the electronic transition from the ground state to the first excited level for the above electron in 2d square box. [2+2=4]

12) Calculate the (i) reduced mass ( $\mu$ ) (in kg) and (ii) force constant (k) (in Nm<sup>-1</sup>), of <sup>1</sup>H <sup>81</sup>Br, if it absorbs at 2630 cm<sup>-1</sup> in IR spectrum. [2+2=4]

13) In  $H_2^+$  molecule ion, the overlap integral (S) is equal to 0.75. Calculate the normalization constants,  $N_+$  and  $N_-$  for molecular orbitals  $\Psi_+$  (bonding) and  $\Psi_-$  (antibonding), respectively. [2+2=4]

14) Write down the bond orders of the following species:  $N_2^+$ ,  $O_2^+$  and  $O_2^{2-}$ . [1+1+1=3]

15) State *true* or *false* for the following statements (i) The rate law of overall reaction for a hypothetical process  $A+B\rightarrow$ Products must be always; rate = k [A][B]; (ii) Homogeneous reaction rate have the dimensions of concentration divided by time; (iii) The activation energy is positive for all reactions. [1+1+1=3]

16) The rate of formation of C in the reaction A + 2 B  $\rightarrow$  4 C + 3 D is 10.0 mol dm<sup>-3</sup> s<sup>-1</sup>. Find the rate of formation of D and rates of consumption of A & B. [1+1+1=3]

17) A reaction 3 A  $\rightarrow$  P has a second-order rate law with rate constant 0.5 dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>. Calculate the time required for the concentration of A to change from 0.200 mol dm<sup>-3</sup> to 0.01 mol dm<sup>-3</sup>. [3]

18) The Arrhenius parameters for a reaction  $\log(A/s^{-1}) = 10$  and  $E_a = 100$  kJ mol<sup>-1</sup>. (i) What is the rate constant of the reaction at 25°C? (ii) Find the temperature (in K) at which the rate constant of the reaction of the above process will be tripled than that of the rate constant at 25 °C? [2+2=4]

19) A hypothetical overall process  $A + B \rightarrow P$  proceeds through the following mechanism. Write the final rate equation for the formation of P using steady state approximation to the appropriate species.

 $A + B \xrightarrow{k_1} C$   $C \xrightarrow{k_2} P$  [3]

20) The fundamental  $(0 \rightarrow 1)$  and first overtone  $(0 \rightarrow 2)$  vibrational bands of HCl are observed at 2885 cm<sup>-1</sup> and 5664 cm<sup>-1</sup> respectively. Calculate the anharmonicity constant. [4]

21) In atmospheric chemistry, the OH radical is an important gas phase species. The radical <sup>16</sup>OH has an OH stretching vibration observed at 3546 cm<sup>-1</sup>. Calculate the wavenumber (in cm<sup>-1</sup>) that you expect for the OH stretch of the radical <sup>18</sup>OH ( $^{16}O = 15.9994$  amu,  $^{18}O = 17.999160$  amu, H =1.00784 amu). Assume the bond vibration is harmonic and the force constant remains unchanged on isotope substitution. [3]

22) An aqueous solution of methylene blue (dye) has absorption maximum at 660 nm with molar absorption coefficient of  $1.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ . The absorption of 50 mg dm<sup>-3</sup> of methylene blue solution is 0.5 when it is measured in a cell of path length 1 cm. A methylene blue solution of unknown concentration absorbs to the same extent when it is measured in a cell of path length 2 mm. Calculate the concentration (in mg dm<sup>-3</sup>) of methylene blue in this solution? [3]

23) A solution mixture consisting of two absorbing dyes A & B. The light intensity is dropped to 20 % at  $\lambda_1$  and to 10 % at  $\lambda_2$  of its initial value, when measured in a cell of path length 2 cm. Given that  $\varepsilon_A(\lambda_1) = 22 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\varepsilon_A(\lambda_2) = 25 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\varepsilon_B(\lambda_1) = 10 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ ,  $\varepsilon_B(\lambda_2) = 15 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . Calculate the ratio of concentrations of A and B present in the mixture. [3]

24) The IR spectrum of the Haber-Bosch process ( $N_2 + 3 H_2 \rightarrow 2 NH_3$ ) at time t = 0 sec and also upon completion of the reaction was recorded. How many vibration bands one can expect in the **initial** and **final** IR spectrum? [2+2=4]

25) Which of the following complexes in each series has the minimum  $\Delta_0$  value? (i)  $[Cr(NH_3)_6]^{3+}$ ,  $[Cr(H_2O)_6]^{3+}$ ,  $[CrCl_6]^{3-}$ ,  $[Cr(CN)_6]^{3-}$ ; (ii)  $[Fe(H_2O)_6]^{2+}$ ,  $[Fe(CN)_6]^{4+}$ ,  $[Fe(H_2O)_6]^{3+}$ . [2]

26) Against each of the following metal ion d-electronic configuration, write the extent of tetragonal distortion possible in octahedral complexes of corresponding metal ions as NIL / weak /strong: (i)  $d^3$  in strong field; (ii)  $d^4$  in weak field (iii)  $d^5$  in strong field; (iv)  $d^8$  in weak field. [4]

27) Enthalpy of hydration of  $Cr^{2+}$  is -460 kcal/ mol, whereas the predicted enthalpy in the absence of CFSE is -435 kcal/ mol. What is the value of crystal field splitting ( $\Delta_0$ ) for [Cr(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> expressed in cm<sup>-1</sup>? [2]

28) The UV visible spectrum of  $[VCl_6]^{2-}$  gives a broad peak for the d-d transition with a maximum at 15,400 cm<sup>-1</sup>. Calculate the CFSE (in kJ/mol). [3]

29) Predict the hybridization of following complexes with the number of unpaired electrons in brackets. (i)  $[Fe(CN)_6]^{4-}$ (0), (ii)  $[Ni(dmg)_2]$  (0), (iii)  $[Ni(CN)_4]^{2-}$ (0), (iv)  $[Mn(NO_2)_6]^{3-}$ (2). [4]

30)  $[Cu(NH_3)_6]^{2+}$  has four Cu-N bonds of length 2.07 Å and two Cu-N bonds of 2.62 Å. Write the d-orbital electronic configurations of Cu<sup>2+</sup> in the complex according to crystal field theory, in the increasing order of energy (with correct labeling and electron occupancy of each d orbital) separating with = or < symbol wherever appropriate. [3]

31) Predict if the following complexes will show tetragonal distortion? (Write YES/NO).  $[Cr(H_2O)_6]^{2+}$ ,  $[Co(NH_3)_6]^{2+}$ ,  $[Cr(NH_3)_6]^{3+}$ . [3]

32) Calculate effective atomic number (EAN) for the following complexes. (i)  $[Pt(NH_3)_6]^{4+}$ , (ii)  $[Fe(CN)_6]^{3-}$ , (iii)  $[Cr(NH_3)_6]^{3+}$ . [3]

33) Which one among the following cationic complexes has the highest spin only magnetic moment value:  $[Cr(H_2O)_6]^{3+}$ ,  $[Fe(H_2O)_6]^{2+}$ ,  $[Zn(H_2O)_6]^{2+}$ ? Also calculate the value in BM for that complex. [1+1=2]

34) Predict the structure and magnetic behavior (paramagmetic/diamagnetic) of the following complexes: (i)  $[PtCl_4]^{2-}$ , (ii)  $[Ni(CO)_4]$ . [2+2=4]

35) Label the given pair of molecules as identical/ enantiomers/diastereoisomers.

36) Assign R/S descriptors for the numbered chiral centers of the following molecules:



37) Convert the following molecule in correct Fischer projection formula using the skeleton structure given and assign the R/S descriptors for the chiral centers. [1+1=2]



38) The bromo compound shown below on treatment with NaOEt in refluxing ethanol gives predominantly product X. Write down the structure of X with correct stereochemistry. [3]

39) Write down the major product Y for the following reaction.

 $\begin{array}{c} \text{Me} & \begin{array}{c} \text{Ph} \\ \text{H} \end{array} \xrightarrow{\text{conc. } H_2 \text{SO}_4,} \\ \text{OH} \end{array} Y$ 

40) Write down the structure of the major product Z for the following reaction with suitable stereochemistry. [2]

$$\frac{1. \text{ BH}_{3}, \text{ THF}}{2. \text{ H}_{2}\text{O}_{2}, \text{ NaOH}} \textbf{Z}$$

41) Oxymercuration-demercuration of 1-methylcyclopentene using Hg(OAc)<sub>2</sub>/EtOH and then reduction with NaBD<sub>4</sub> gives the following stereoisomer as the only product. Is it true or false? [2]

[3]

[2]

[2+4=6]

42) Identify the most stable conformation of the compound (X) in gas phase from the given ones (A, B, C, D).

[1]

[2]



43) Identify the elimination reaction from the list below (a, b, c, d) will give 1-butene as the major product.

$$(a) \xrightarrow{OH} \qquad \underbrace{H_2SO_4}_{\bigtriangleup} ?$$

$$(b) \xrightarrow{+} \qquad \underbrace{KOH/EtOH}_{\bigtriangleup} ?$$

$$(c) \xrightarrow{+} \qquad \underbrace{NMe_3}_{\Box} \qquad \underbrace{NaOEt/EtOH}_{\bigtriangleup} ?$$

$$(d) \xrightarrow{Br} \qquad \underbrace{NaNH_2/NH_3}_{\bigtriangleup} ?$$

44) Identify the nucleophiles among the given ones which will exclusively give a substitution product and no elimination product upon reaction with secondary alkyl bromides at 50 °C in DMF: OEt, CN, OH, AcO, OTs, SMe. [3]

45) In E2 elimination with potassium tert-butoxide, the Hoffman product formation arises due to the formation of the most stable carbocation and then removal of the less hindered  $\beta$ -hydrogen. Is this statement true or false? [1]

## End