I.F.S. EXAM-(M) 2018

FSI-P-CHM

CHEMISTRY

Paper – I

Time Allowed : **Three Hours**

Maximum Marks : **200**

Question Paper Specific Instructions

Please read each of the following instructions carefully before attempting questions :

*There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.*

*Questions no. **1** and **5** are **compulsory**. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two Sections A and B.*

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

*Answers must be written in **ENGLISH** only.*

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

$h = 6{\cdot}626 \times 10^{-34}$ Js	$k_B = 1{\cdot}38 \times 10^{-23}$ JK^{-1}
$R = 8{\cdot}314$ JK^{-1} mol^{-1}	$\pi = 3{\cdot}14$
$c = 3 \times 10^{8}$ ms^{-1}	$F = 96500$ C mol^{-1}
$N_A = 6{\cdot}023 \times 10^{23}$ mol^{-1}	1 atm = 101325 Pa
$m_e = 9{\cdot}1 \times 10^{-31}$ kg	

SECTION A

Q1. (a) Is the function, $\psi(x) = Be^{-mx}$ an eigenfunction for the operator $\hat{A} = \frac{d^2}{dx^2}$? If so, what is the eigenvalue ? *8*

(b) Estimate the ratio of the electric dipole moments of *ortho* and *meta* dichlorobenzenes. *8*

(c) For an ideal gas : $\left(\frac{\partial U}{\partial V}\right)_{T,\, n} = 0$. Show that $\left(\frac{\partial C_v}{\partial V}\right)_{T,\, n} = 0$. *8*

(d) Sulphur exists in four different (solid rhombic, solid monoclinic, liquid, and gaseous) phases under different conditions. Any two or three phases of sulphur may coexist in equilibrium, but all four phases do not coexist in equilibrium. Give reasons. *8*

(e) A certain chemical reaction completes 20% in 15 min at 27°C and in 5 min at 37°C. Calculate the activation energy (in SI units) of the reaction. *8*

Q2. (a) Using de Broglie wave-particle dual relationship, $\lambda \times p = h$; calculate the wavelength (in SI units) of (i) an electron travelling 1·00% of the speed of light, and (ii) a baseball (mass = 140 g) travelling at 40 ms^{-1}. Comment on your findings. *15*

(b) (i) A non-ideal gas is used in a Carnot engine. Find the values of ΔU, ΔH, ΔS_{univ}, ΔA, ΔG for a cycle. Give reason/s.

(ii) At constant pressure, for fixed amount of a substance, with increase of temperature enthalpy (H) of the substance increases but Gibbs free energy (G) decreases. Give reasons.

(iii) At constant pressure and temperature, adsorption of gas on solid surface occurs spontaneously. What will be the signs of ΔH, ΔS and ΔG of this process ? *5+5+5=15*

(c) Calculate the number of photons in 1·0 kcal of light of wavelength 350 nm. *10*

Q3. (a) At 27°C, for fixed amount of (i) ideal gas, (ii) hydrogen gas, (iii) ammonia gas; show the plots of 'Z' (compressibility factor) against P (pressure) on the same diagram. *10*

(b) Derive the expression of half-life period ($t_{1/2}$) of a first order chemical reaction from its integrated rate equation. Does this value depend on the temperature of the reaction ? Give reason in support of your answer. *15*

(c) (i) Using Stirling's approximation, we write

$ln(n!) \cong (n)\, ln(n) - (n)$.

Calculate the % of error when (A) n = 10 and (B) n = 69. Comment on your results.

(ii) Calculate the interplanar distance between two successive 123-Miller planes of an orthorhombic crystal with unit cell lengths a = 0·82 nm, b = 0·94 nm, and c = 0·75 nm. *7+8=15*

Q4. (a) The equilibrium constant, K_p of a certain gas-phase reaction, varies with temperature (T in K) as $ln\ K_p = -\ 1{\cdot}04 - \dfrac{1088K}{T} + \dfrac{1{\cdot}51 \times 10^5 K^2}{T^2}$, in the temperature range of 300 to 500 K.

Calculate the standard entropy change of the reaction ($\Delta_r S°$) at 400 K.

Given : $\Delta_r G° = -\ RT\ ln\ K_p$ and $\Delta_r S° = -\left[\dfrac{\partial(\Delta_r G°)}{\partial T}\right]_P$ *15*

(b) Phosphorescence emission rate is slower than fluorescence emission rate. Explain with Jablonski diagram. *10*

(c) What are the respective electrode reactions and cell reaction of the following galvanic cell ?

$Pt(s) \mid H_2(g) \mid H^+(aq) \mid\mid Ag^+(aq) \mid Ag(s)$.

Calculate the equilibrium constant value of the cell reaction at 25°C. Given : $E°_{cell} = +\ 0{\cdot}7996$ V at 25°C. *15*

SECTION B

Q5. (a) How many isomers are possible for $[Co(NH_3)_5(NO_2)]Cl_2$? Draw their structures and mention their names. *8*

(b) What are labile and non-labile complexes ? Identify labile and non-labile complexes from the following : *8*

(i) $[Ni(H_2O)_6]^{2+}$

(ii) $[Co(NH_3)_5(H_2O)]^{3+}$

(c) Identify the intermediate and the product in the following reaction sequence : *8*

$$W(CO)_6 \xrightarrow{\text{PhLi}} \text{Intermediate} \xrightarrow[\downarrow\ LiBF_4,\ Me_2O]{[Me_3O]^+\ BF_4^-} \text{Product}$$

(d) Although N_2 is available in atmosphere in plenty (~ 78% by volume), it does not react with some of the reactive metals easily. Give three reasons for inert nature of N_2 towards the metals mentioned above. *8*

(e) What is a super acid ? How can one prepare super acid ? The super acid upon reaction with neopentane gives an intermediate that on further decomposition afforded $Me_3C^{\oplus}$ and CH_4. Identify the intermediate. *8*

Q6. (a) The magnetic moment of a certain Co(II) octahedral complex is 4·0 μ_B. What is its *d*-electron configuration ? *15*

(b) Explain the variation in ν_{CO} (cm^{-1}) of the following isoelectronic metal carbonyls : *15*

Compound	ν_{CO} (cm^{-1})
$Ni(CO)_4$	2060
$[Co(CO)_4]^-$	1890
$[Fe(CO)_4]^{2-}$	1790

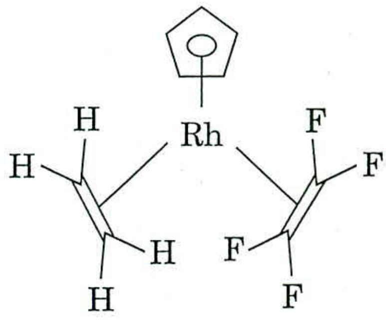
(c) How many geometrical isomers are possible for $[Ru(H_2O)_3Cl_3]$? Draw their structures and indicate their names. *10*

Q7. (a) Draw the structures of the following metal carbonyls and show electron counting for each one of the complexes : *15*

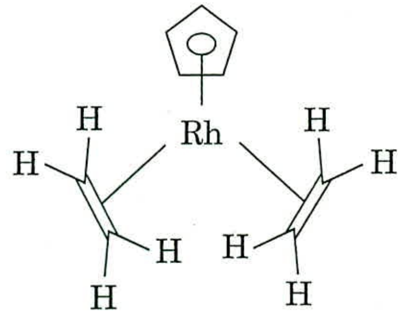
(i) $Co_2(CO)_8$

(ii) $Mn_2(CO)_{10}$

(b) Draw two resonance structures (A and B) for metal olefin complex, $L_nM(C_2X_4)$. In which of the following complexes does the resonance structure A or B dominate and why ? *15*



(i)



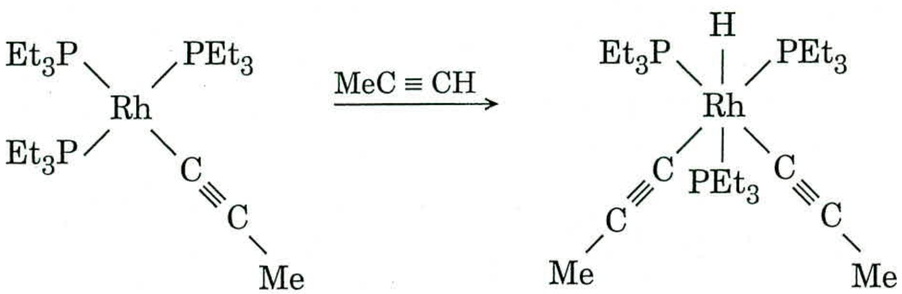
(ii)

(c) Consider the following equations and explain the observed trend in log K values. en refers to ethylenediamine, $H_2NCH_2CH_2NH_2$. *10*

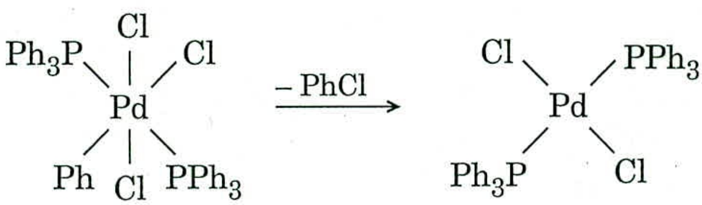
$[Cd(H_2O)_6]^{2+} + en \rightleftharpoons [Cd(en)(H_2O)_4]^{2+} + 2H_2O, \; \log K = 5{\cdot}84$

$[Cd(H_2O)_6]^{2+} + 2NH_3 \rightleftharpoons [Cd(NH_3)_2(H_2O)_4]^{2+} + 2H_2O, \; \log K = 4{\cdot}95.$

Q8. (a) What are the key points invoked for oxidative addition (OA) and reductive elimination (RE) ? In the given two equations below, which one corresponds to OA and which one corresponds to RE and why ? *15*



(i)



(ii)

(b) The magnetic moment of La^{3+} (f^0), Gd^{3+} (f^7) and Lu^{3+} (f^{14}) can be calculated using $\mu_{spin\ only}$ formula. However, for the other lanthanides $\mu_{spin\ only}$ formula fails. Explain why. Write down the formula to calculate magnetic moment for those lanthanides other than La^{3+}, Gd^{3+} and Lu^{3+}. *15*

(c) Explain the spin state and electronic configuration of iron(II) in myoglobin and O_2 bound myoglobin. How does the geometry of iron(II) in these metalloproteins vary subtly ? *10*