RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester I Examination – Oct / Nov 2017

CHE 4204 –ADVANCED INORGANIC CHEMISTRY II

Time: Two (2) hours

Answer the first question (question number 1 – **Part A**) and select any **three (03)** questions from **Part B**. Answer **only four** questions. Only first four answers will be graded.

Part A

1.

a) State four applications of silicone oils (10 Marks)

b) Explain why the room temperature vulcanization is possible with silicone polymers. (30 Marks)

c) State two advantages of silicone polymers over organic polymers. (10 Marks)

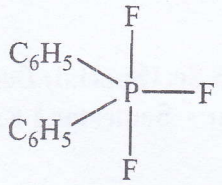
d) Metastable crystalline phase PCl_5 shows a NQR spectrum with three ^{35}Cl resonances with intensities 1:1:3. Explain the observed spectrum correlating with the structure of the metastable crystalline phase. (20 Marks)

e) Account for the major different functions of zinc (Zn) in biological systems giving examples. (Marks 30)

Part B

2.

a) The structure of $PF_3(C_6H_5)_2$ is trigonal bipyramidal with one equatorial and two axial F atoms as shown in figure. The F atoms interchange the positions at elevated temperatures. Draw NMR spectra of $PF_3(C_6H_5)_2$ under the conditions indicated below. Show the coupling constants in your spectra. (Assume that $J_{P\text{-}F} \gg J_{F\text{-}F}$, P and F do not couple to H and axial F atoms interact more strongly with P than equatorial F atoms.) (^{31}P(I=1/2), ^{19}F (I=1/2)).

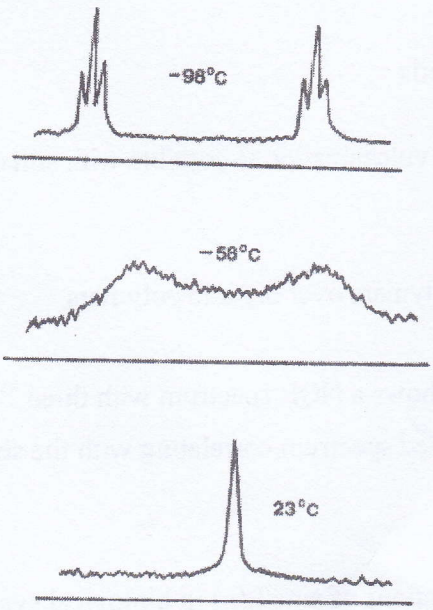


i) High temperature ^{31}P NMR spectrum
ii) Low temperature ^{31}P NMR spectrum
iii) High temperature ^{19}F NMR spectrum
iv) Low temperature ^{19}F NMR spectrum

(Marks 40)

b) Variable temperature ^{19}F NMR spectrum of SF_4 is given below. Explain the observed spectra according to the structural changes at different temperatures (^{19}F (I=1/2)).

(Marks 20)

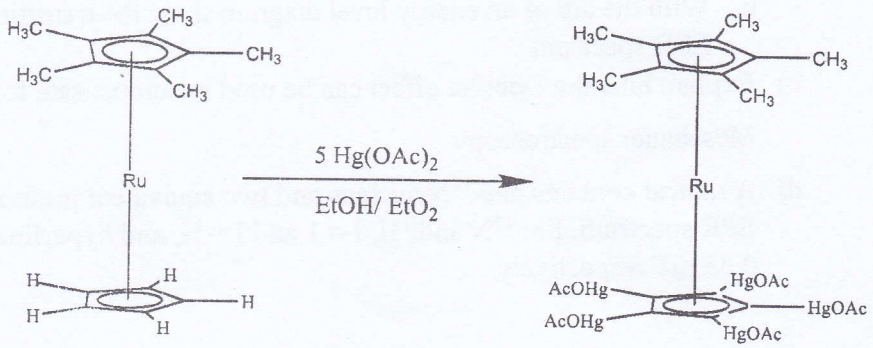


c) Account for the nuclear hyperfine structure in ESR spectroscopy.

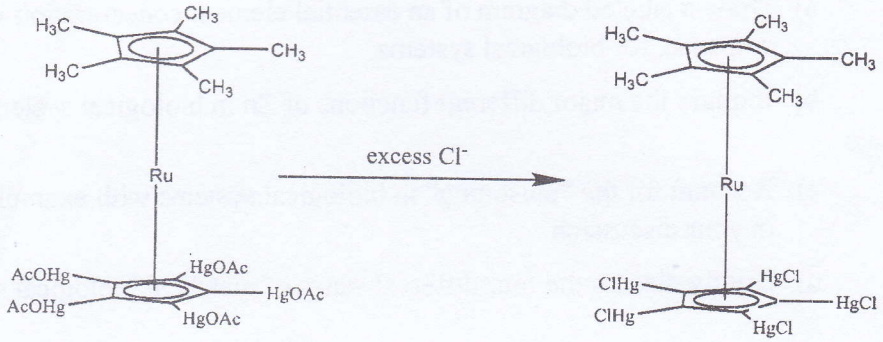
(Marks 20)

d) Describe, how to determine the completion of below reactions by the given spectroscopic method.

i. By means of 1H NMR



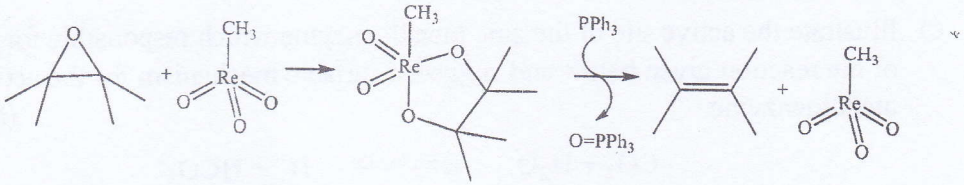
ii. By means of IR spectroscopy



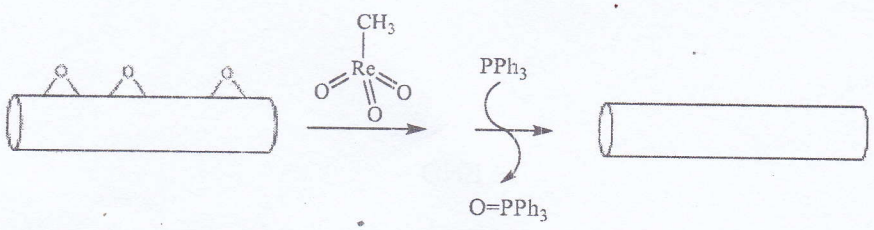
(Marks 20)

3.

a) An epoxide can transfer its oxygen atom to a PPh_3 molecule by means of the catalyst methyltrioxorhenium (CH_3ReO_3), which illustrated in the reaction below.



This reaction occurs on the carbon nanotubes in which epoxide oxygens are present.



Discuss, how to use ^{31}P NMR to determine the amount of epoxide on carbon nanotubes. (Hint: use known amount of PPh_3 for your thought experiment)

(30 Marks)

b) Consider a system with one unpaired electron coupled to a nucleus with nuclear spin (I) = 1.
   i. Draw the ESR spectrum of this system.
   ii. With the aid of an energy level diagram show the transitions responsible for the ESR spectrum. (20 Marks)

c) Explain how the Doppler effect can be used to compensate for the recoil energy loss in Mossbauer spectroscopy. (30 Marks)

d) A radical contains one ^{14}N nucleus and two equivalent protons. Predict the form of EPR spectrum. For ^{14}N and ^{1}H, I = 1 and I = ½, and hyperfine constants 1.61 mT and 0.35 mT respectively. (20 Marks)

4.

a) Draw a labeled diagram of an essential element concentration vs physiological response, for biological systems. (Marks 20)

b) Explain the major different functions of Zn in biological systems giving examples. (Marks 30)

c) Account for the "poisoning" in biological systems with examples. Use HSAB theory in your discussion. (Marks 30)

d) Briefly discuss the four different states of metals in biological systems. (Marks 20)

5.

a) Draw and name the forms of hemoglobin. (Marks 10)

b) Describe the active sites of hemocyanine and hemoerythrine. (Marks 30)

c) Illustrate the active site of the zinc metalloenzyme which responsible for the catalysis of the reaction given below and suggest a suitable mechanism for the action of the metalloenzyme. (Marks 30)

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$$

d) Write a short note on "Macrocylic antibiotics". (Marks 30)

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