RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
Fourth Year - Semester I Examination – September / October 2019

CHE 4204 – ADVANCED INORGANIC CHEMISTRY II

Time: Two (02) hours

Answer **only four (04)** questions.

Use of a non-programmable calculator is permitted.

---

1. a) State four applications of silicone oils. (10 marks)

   b) Suggest a suitable siloxane which can be used to terminate polymerization of linear chain silicones. (10 marks)

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

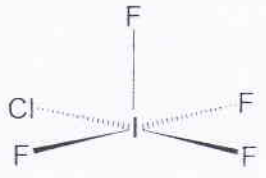
   e) Tyrosinases oxidize phenole to *o*-quinone. Draw the catalytic cycle. (30 marks)

2. a) Predict the number of peaks and the splitting patterns for the compounds given below [^{19}F (I=1/2), ^{14}N (I=1), ^{31}P (I=1/2), ^{35}Cl (I=3/2), ^{127}I (I=5/2)].

   i. CD_2F_2 - ^{19}F NMR

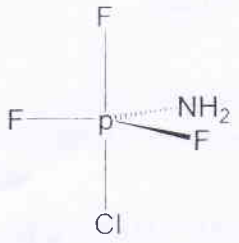
   ii. $PFCl_2$ - ^{31}P NMR

iii.



- ^{127}I NMR

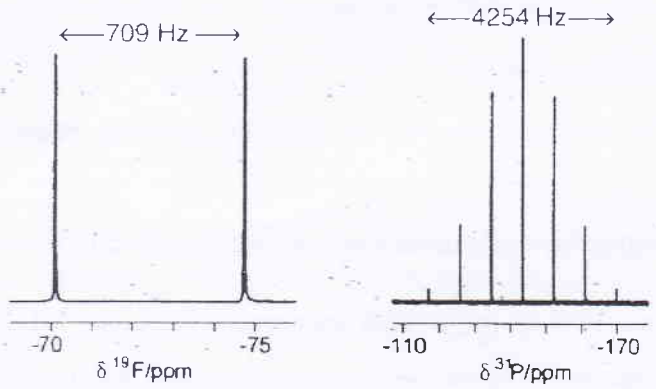
iv.



- ^{19}F NMR

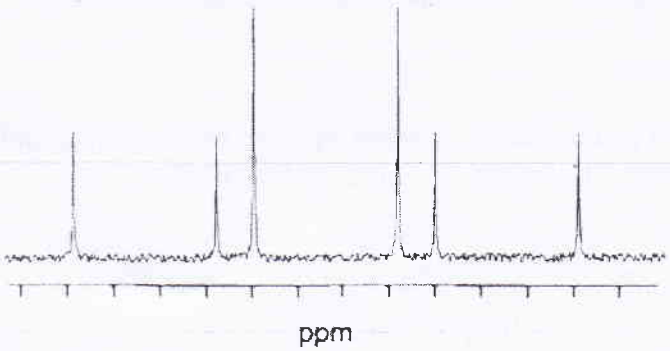
(20 marks)

b) ^{19}F NMR and ^{31}P NMR spectra of $[P_xF_y]^-$ ion are given below. Identify the ion.



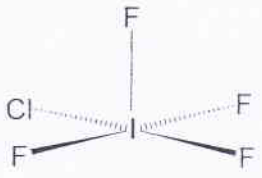
(30 marks)

c) ^{31}P NMR of POF_2H is given below. Give the splitting pattern for the spectrum.



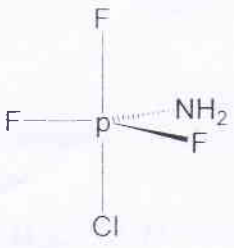
(25 marks)

iii.



- ^{127}I NMR

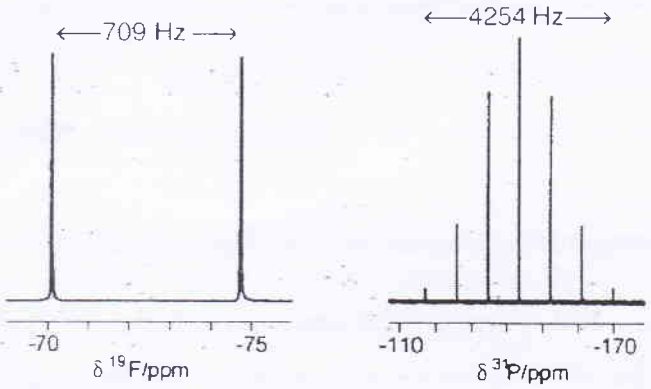
iv.



- ^{19}F NMR

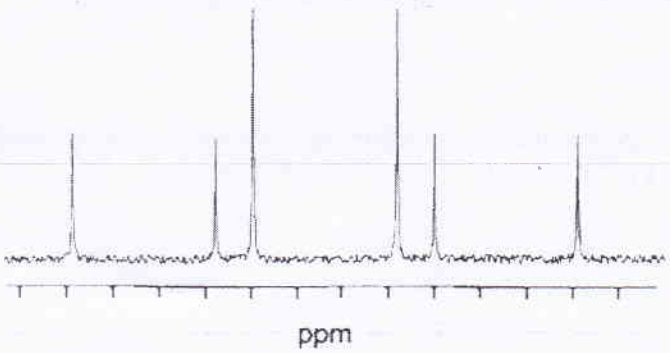
(20 marks)

b) ^{19}F NMR and ^{31}P NMR spectra of $[P_xF_y]^-$ ion are given below. Identify the ion.



(30 marks)

c) ^{31}P NMR of POF_2H is given below. Give the splitting pattern for the spectrum.



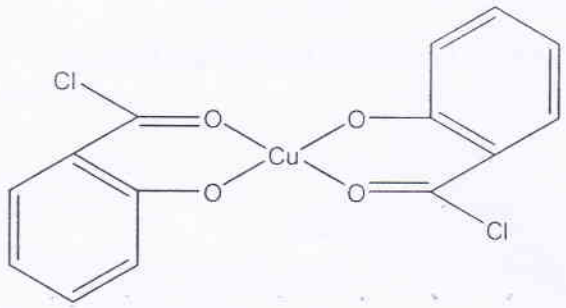
(25 marks)

d) Following reaction gives a mixture of products. ^{31}P NMR spectrum of the products yields a septet as the only peak. Identify the product which contains phosphorus.

$$P(SiH_3)_3 + MeLi \rightarrow \text{Products}$$

(25 marks)

3. a) Draw the ESR spectrum you expect for the ^{63}Cu complex given below considering the interaction of the unpaired electron up to four bonds. The only isotope present is the ^{35}Cl isotope [^{35}Cl (I=3/2)]. If the real spectrum would give you only 60 peaks, explain the observation with the use of a splitting pattern diagram.

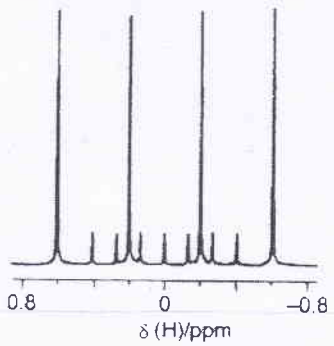


(40 marks)

b) Describe how you would apply Doppler effect in Mössbauer spectroscopy. (30 marks)

c) 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)

d) BH_4 shows ^1H NMR spectrum given below. Explain the splitting patterns and intensities observed.



(10 marks)

4. a) Illustrate the active site of the enzyme responsible for the conversion of dinitrogen to ammonia. Propose a mechanism for this process. (40 marks)

b) Write a brief account on "poisoning" in biological systems with examples. Use HSAB theory in your discussion. (30 marks)

c) Describe the active sites of hemocyanine and hemoerythrine. (30 marks)

5. a) Discuss the role of iron-sulphur proteins involved in electron transfer reactions. (Marks 30)

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

c) Brief the roles of following enzymes giving suitable examples

i. Hydrolases
ii. Two electron reductases
iii. Multipair oxidoreductases (Marks 30)

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

— END —