RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. Honours in Chemistry
Fourth Year - Semester I Examination – January / February 2021

CHE 4204 – ADVANCED INORGANIC CHEMISTRY II

Time: Two (02) hours

Answer only four (04) questions.

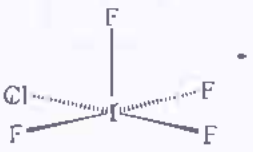
Use of a non-programmable calculator is permitted.

1. a) Illustrate the addition of vinyl functionality in siloxane. (15 marks)
   b) Suggest a suitable siloxane which can be used to terminate polymerization of linear chain silicones. (10 marks)
   c) Silicone polymers can be vulcanized at room temperature; Justify. (25 marks)
   d) Account for the Nuclear Quadrupole Resonance spectroscopy (NQR). (20 marks)
   e) Tyrosinases oxidize phenol 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 [^{2}D (I=1), ^{19}F (I=1/2), ^{14}N (I=1), ^{31}P (I=1/2), ^{35}Cl (I=3/2), ^{127}I (I=5/2)].
   Assume all the compounds are consisted with only the isotopes indicated here.
   hint: You do not have to draw the spectra.

   i. CHDClF - ^{1}H NMR

   ii. PFI_2 - ^{31}P NMR

   iii.  - ^{19}F NMR

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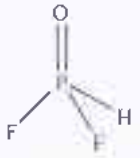
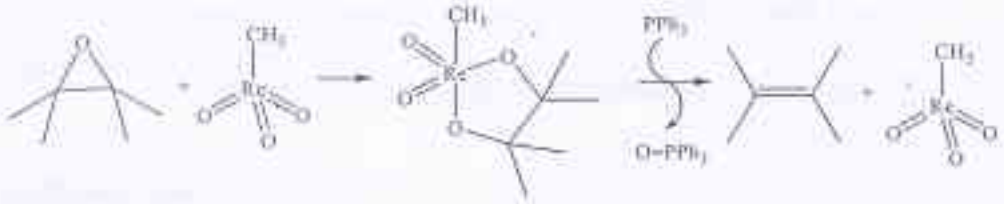
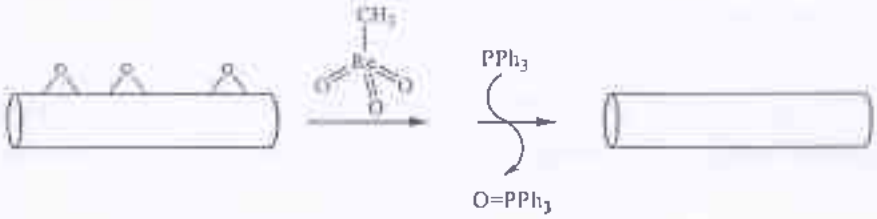
iv.  - ^{19}F NMR

(20 marks)

b) 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.

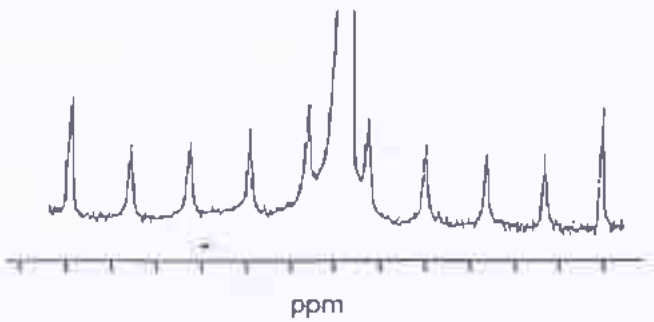


Discuss, how to use ^{31}P NMR to determine the amount of epoxide on carbon nanotubes.

(Hint: use known amount of PPh_3 for your thought experiment)

(20 marks)

c) ^{1}H NMR of GeH_4 sample is given below. For Germanium two isotopes present namely ^{73}Ge and ^{71}Ge. Calculate the spin quantum number I for each isotope, comment about the abundance of each isotope in the sample.



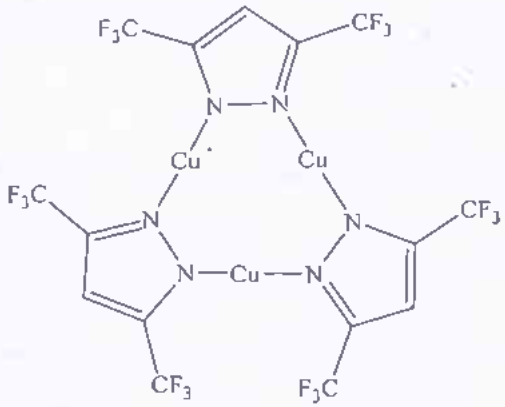
(30 marks)

d) Draw ^{19}F NMR for the following compounds. Indicate the peak intensities. Consider coupling of nuclei only up to three bonds.
[^{19}F (I=1/2), ^{14}N (I=1)]
Assume all the compounds are consisted with only the isotopes indicated here.

i. SF_4

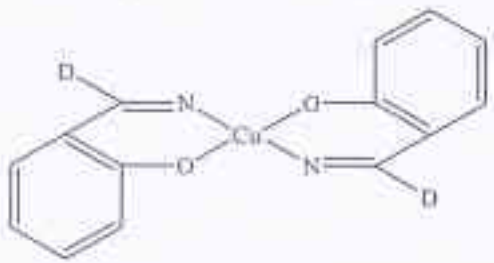
ii. $[PhSiF_6]^{2-}$

iii.



(30 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 isotopes present are the ^{14}N and ^{63}Cu isotopes for nitrogen and copper respectively [^{2}D (I=1), ^{14}N (I=1), ^{63}Cu (I=3/2)]. If the real spectrum would give you only 68 peaks, explain the observation with the use of a splitting pattern diagram.



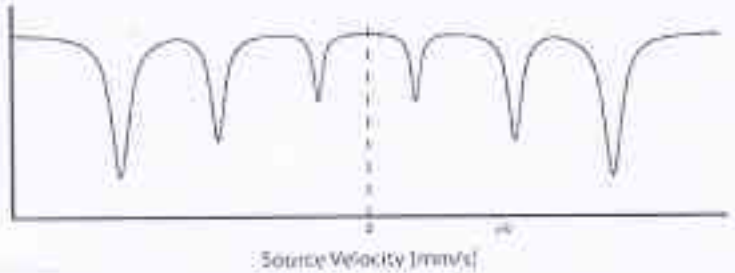
(30 marks)

b) Account for the zero-field splitting and Krammers theorem relevant to ESR spectroscopy.

(20 marks)

c) Consider the D_2^+ ion. With the aid of an energy level diagram, show the transitions corresponding to the ESR spectrum of the D_2^+ ion. (20 marks)

d) Account for the given Mossbauer spectrum corresponding to ^{57}Fe nuclei using an energy level diagram and showing the transitions relevant to the spectrum.
[^{57}Fe, I=1/2 - ground state and ^{57}Fe, I=3/2 - excited state]



(30 marks)

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

b) Iron-sulphur proteins are crucial component in biological electron transfer reactions. Support the statement with suitable examples. (25 marks)

c) Execute HSAB theory to account on "poisoning" in biological systems giving examples. (25 marks)

d) Illustrate the function of enzyme carboxy peptidase, and propose a mechanism to explicate the activity. (30 marks)

5. a) Brief speciation of iron in biological systems. (20 marks)

b) Illustrate the oxygen binding in Hemoglobin and Hemocyanine. (25 marks)

c) Describe the active site of the corresponding enzyme for the reaction given below.

$$2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2$$

(25 marks)

d) Explain the active site of Vitamin B_{12} Coenzyme and describe its catalytic activity. (30 marks)

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