Ollscoil na hÉireann, Gaillimh

National University of Ireland, Galway

SUMMER EXAMINATIONS 1999

THIRD UNIVERSITY B.Sc. EXAMINATION IN SCIENCE

(INCLUDING DENOMINATED DEGREES)

CHEMISTRY

Second Paper

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Time allowed: *Three* hours

(Answer Question 1 and *four* more questions)

1. See accompanying sheet for multiple choice question.

2. Answer **(a)** and **(b)**

(a) Outline the type of metal complexes to which the "18 electron rule" applies and those to which it does not.

(b) Give valence electron counts for the following systems and indicate those which are likely to be stable and those which are not; $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^5\text{-}C_5H_5)Mo(CO)_2$, $Mo(CO)_3(PPh_3)I_2$, $(\eta^4\text{-butadiene})Mo(CO)_5$, $(\eta^4\text{-Butadiene})Rh(CO)_2Br$ and $(\eta^3\text{-allyl})(\eta^5\text{-}C_5H_5)Mo(CO)_2$.

3. Describe what is meant by the term oxidative addition. Describe Vaska's complex and some of its oxidative addition reactions. Describe the mechanism of one type of oxidative addition. What factors involving the metal and its ligands can be altered to favour oxidative addition ?

more on the next page....

4. Describe some selected examples of biomolecules which illustrate the variety of roles played by metals in biological systems.

5. Account for the following observations.
"The spectra of octahedral complexes of Co(II) usually consist of one band in the near infrared and a double band in the visible region. Thus the complex ion $[Co(H_2O)_6]^{2+}$ has absoptions at 8100, 16,000 and 19,400 cm^{-1}". "Addition of chloride to the above *aquo* complex changes the colour from pale pink to deep blue. "

6. Answer **(a)** and **(b)**

(a) Show with the assistance of a diagram that the operations C_3 and C_3^2 of the D_{3h} point group belong to the same class [8 marks].

(b) List the symmetry elements and symmetry operations of the following molecules and assign them to the correct point group [12 marks]:

CH_2Cl_2, NCl_3, PF_5, $SnCl_2$, $POCl_3$, ICl_4^-

[You **must** use the correct structures for the species in **(b)**]

7. Answer **(a)** and **(b)**

(a) Describe the Eigen-Wilkins-Tamm mechanism for complex formation by nickel(II) in aqueous solution. Show how the mechanism is consistent with experimental data.

(b) Describe the mechanism(s) by which electron transfer reactions take place in transition metal complexes in solution..

8. Answer **(a)** and **(b)**.

(a) Write brief notes on crystal systems and Bravais lattices. Provide a diagram showing all of the possible Bravais lattices for the orthorhombic system and indicate how they can be distinguished by analysis of X-ray diffraction data. In the case of any one Bravais lattice include the (1,2,4) Miller plane. If the two opposing (parallel) faces cutting the c-axis are sections of neighbouring planes of an infinite set of planes, what are the Miller indices for this set of planes? If other planes are added to the set of planes such that the interplanar spacing is halved, what will be the Miller indices for the new set of planes?

(b) A pyrophosphate of zirconium (the pyrophosphate anion contains two phosphorus and seven oxygen atoms) crystallises in the cubic system. The first two expected reflections are removed from its diffraction pattern on account of a special absence condition and the first six recorded d-spacings (Å) are :4.78, 4.12, 3.70. 3.37, 2.92 and 2.75. Index the data. Given that the density of the pyrophosphate is 4.22 $g.cm^{-3}$ and that there are eight zirconium atoms per unit cell, deduce the formula of the pyrophosphate and the oxidation state of zirconium. (atomic masses are: O,16.0; P, 30.97; Zr, 91.22. Avogadro's constant is 6.022×10^{23} mol^{-1}).