※ 考生請注意 本試題 ☑可 □不可 使用計算機

Part I: Inorganic Chemistry (total points: 50)

(1)(a) The rate of reaction of O_2 with trans-$[IrX(CO)(PPh_3)_2]$ in benzene decreases in the order X = NO_2 > I > ONO_2 > Br > Cl > N_3 > F Explain this observation. (5 pts)

   (b) A pink solid has the empirical formula $CoCl_3 \cdot 5NH_3 \cdot H_2O$ A solution of this salt is also pink and rapidly gives 3 mol AgCl on titration with $AgNO_3$ solution When the pink solid is heated, it loses 1 mol H_2O to give a purple solid with the same ratio of $NH_3:Cl:Co$ (recall that Co(III) complexes are inert). Deduce the structures of the two octahedral complexes and draw and name them (5 pts)

(2) List the symmetry elements of the following molecules and name the point groups to which they belong (a) staggered CH_3CH_3, (b) chair and boat cyclohexane, (c) B_2H_6, (d) $[Co(en)_3]^{3+}$ where en is ethylenediamine (ignore its detailed structure, and (e) crown-shaped S_8 (10 pts)

(3) Suppose that a methane molecule became distorted to (a) C_{3v} symmetry by lengthening of one bond, (b) C_{2v}, symmetry, by a kind of scissors action in which one bond angle opened and another closed slightly Would more d orbitals become available for bonding? (10 pts)

(4) The Lewis structure for CO_2 shows four lone pairs of electrons on the oxygen. There are two nonbonding pairs in the MO description. How can you reconcile the two descriptions? (10 pts)

(5) Use the Hückel approximation to find the energies of the π orbitals of cyclobutadiene, and estimate the delocalization energy (10 pts)

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Part II: Analytical Chemistry (Total points: 50)

(6) Lord Rayleigh prepared nitrogen samples by several different methods The density of each sample was measured as the mass of gas required to fill a particular flask at a certain temperature and pressure. Masses of nitrogen samples prepared by decomposition of various nitrogen compounds were 2.29280 g, 2.29940 g, and 2.30054 g. Masses of "nitrogen" prepared by removing oxygen from air in various ways were 2.31001 g, 2.31163 g, and 2.31028 g. Is the density of nitrogen prepared from nitrogen compounds significantly different from that prepared from air? (10 pts) (*t = 2.78 for four degrees of freedom and the 95% confidence level*)

(7) A nitrate-ion electrode in 1 64×10⁻⁴ M KNO₃ has an electrode potential of 0.017 V Enough potassium nitrite is added to the solution to make its concentration 4 76×10⁻² M, without change the volume The new electrode potential is -0.049 V Calculate the selectivity of the electrode for nitrate over nitrite ions (10 pts)

(8) Briefly describe or define (10 pts)
      (a) resonance fluorescence
      (b) vibrational relaxation
      (c) quantum yield
      (d) Stokes shift
      (e) internal conversion

(9) (a) In NMR spectroscopy, what are the advantages of using a magnet with as large a field strength as possible? (2 pts)
    (b) What is the difference between longitudinal and transverse relaxation in NMR spectroscopy? (2 pts)
    (c) Sketch the appearance, including chemical shifts, J-coupling patterns, and integrals, of the high-resolution ^{1}H NMR spectrum of (i) cyclohxane, (ii) ethyl benzene, and (iii) 1,2-dimethoxyethane (6 pts)

(10) The relative retention for two compounds in GC is 1 068 on a column with a plate height of 0.520 mm The capacity factor for compound 1 is 5 16
    (a) Find the separation factor (γ) for the two compounds (2 pts)
    (b) What length of column will separate the compounds with a resolution of 1 00? (2 pts)
    (c) The retention time for air (t_m) is 2.00 min If the number of plates is the same for both compounds, find t_r and $w_{1/2}$ for each peak. (3 pts)
    (d) If the ratio of stationary phase to mobile phase is 0.30, find the partition coefficient for compound 1 (3 pts)