系所組別：化學工程學系乙組

考試科目：無機化學及分析化學　　　　　　　　　　　　考試日期：0222，節次：2

※ 考生請注意：本試題可使用計算機。　　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Inorganic Chemistry (50 points)

(1) (a) Does the integral $\int (3d_z^2)x(3dxy)d\tau$ vanish in a tetrahedral molecule? Explain. (5 points)

   (b) Does the integral $\int (2p_x)(2p_y)(2p_z)d\tau$ necessarily vanish in an octahedral environment? Explain. (5 points)

(2) Consider the C_{2v} molecule NO_2. The combination $p_x(A)$-$p_x(B)$ of the two O atoms (with x perpendicular to the plane) spans A_2. Is there any orbital of the central N atom that can have a non-zero overlap with that combination of O orbitals? What would be the case in SO_2, where $3d$ orbitals might be available? (20 points)

(3) Explain how the facts that $(\eta^6\text{-}C_6H_5CO_2H)Cr(CO)_3$ is a stronger acid than benzoic acid and that $(\eta^6\text{-}C_6H_5NH_2)Cr(CO)_3$ is a weaker base than aniline show that the $Cr(CO)_3$ group withdraws electrons from the aromatic ring. (10 points)

(4) $HNi[P(OEt)_3]_4^+$ is known to be a catalyst for olefin isomerization. Write a catalytic cycle for isomerization of 1-butene catalyzed by this species. Keep in mind the 16- and 18-electron rule. How would you formulate in the most reasonable way the electronic structure of the Ni cation? (10 points)

Analytical Chemistry (50 points)

(5) A 4.476-g sample of a petroleum product was burned in a tube furnace, and the produced SO_2 was collected in 3% H_2O_2.　Reaction:

$SO_2(g) + H_2O_2 \rightarrow H_2SO_4$

A 25.00-mL portion of 0.00923M NaOH was introduced into the solution of H_2SO_4, following which the excess based was back-titrated with 13.33 mL of 0.01007 M HCl.　Calculate the parts per million of sulfur in the sample.　(15 points)

(6) Calculate pH change when 0.05 M CH_3COONa (with $Ka = 1.75 \times 10^{-5}$) is diluted with water by ten folds. (15 points)

(7) The $KClO_3$ in 0.1342-g sample of an explosive was determined by reaction with 50.00 mL of 0.09601 M Fe^{+2}:

$ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 3H_2O + 6Fe^{3+}$

When the reaction was complete, the excess Fe^{+2} was back-titrated with 12.99 mL of 0.08362 M Ce^{+4}. Calculate the percentage of $KClO_3$ in the sample.　(20 points)