THE UNIVERSITY OF ZAMBIA
SCHOOL OF NATURAL SCIENCES
2012 SEMESTER I EXAMINATIONS

C 205: ANALYTICAL AND INORGANIC CHEMISTRY
TIME: THREE HOURS.

INSTRUCTIONS:
1. **THIS PAPER CONTAINS FIVE QUESTIONS**
2. **ANSWER ANY FOUR QUESTIONS**
3. **EACH QUESTION CARRIES 15 MARKS**
4. **SHOW ALL YOUR WORKING CLEARLY**
5. **ESSENTIAL DATA TABLES ARE ATTACHED TO THE QUESTION PAPER.**

Question 1.

(a). In 1964, a new compound composed of potassium, molybdenum and cyanide, with formula $K_xMo_y(CN)_z$ was reported. Chemical analyses showed the presence of 25.51% K and 31.54% Mo. Determine the empirical formula of the compound.

(b). Ethylene diamminetetraacetic acid (EDTA, H_4Y) has the following dissociation constants $pK_{a1} = 2.008$; $pK_{a2} = 2.683$; $pK_{a3} = 6.098$; and $pK_{a4} = 10.181$.
(i) Write down equilibrium constant expressions for the second dissociation of the acid.
(ii) Calculate the K_a value for the acid.

(c). The use of octane enhancing additives leads to the accumulation of metals such as lead, on the leaves of plant growing by the road-side. The lead content of leaf samples was measured spectrophotometrically by reaction with dithizone. The standard deviation for a triplicate analysis was 2.3ppm. What is the 90% confidence limit?

(d). Deduce the structures of the complexes $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ using Valence bond theory.

Question 2.

(a). Lead iodate, $Pb(IO_3)_2$, is an example of a sparingly soluble salt with a solubility product of 2.6×10^{-13} in aqueous medium.
(i) What is meant by the term 'sparingly soluble'
(ii) When 35ml of a 0.150 M lead nitrate, $Pb(NO_3)_2$ solution was added to 15ml of a solution of 0.0800 M potassium iodate, KIO_3, a precipitate was formed. What precipitate is it?
(iii) What is the concentration of Pb^{+2} ions in the equilibrium mixture?

(b). Using M.O diagram indicate paramagnetic nature of B_2 and non existence of He_2.

(c). In the nuclear industry, detailed records are kept of the quality of plutonium received, transported or used. Each shipment of plutonium pellets received is carefully analyzed to check that the purity and hence the total quantity is as the supplier claims. A particular shipment is analyzed with the following results: 99.93, 99.87, 99.91 and 99.86%. The listed purity as received from the supplier is 99.95%. Is the shipment acceptable with 95% confidence?

Question 2(Continued).

(d). (i) Describe the ingredients you would use to prepare a buffer solution that can be used at values less than pH 7.

(ii) Calculate the pH of a buffer solution prepared by adding 10.0 ml of 0.20 M acetic acid to 40.0 ml of 0.50 M sodium acetate.

Question 3.

(a). What is Inorganic benzene? Comment on its reactivity.

(b). A batch of cough mixture was weighed to determine if they fell within acceptable standard control guidelines. The individual weights were: 127.2; 128.4; 127.1, 129.0 and 131.1g.

(i) Determine whether the last weight is an outlier datum at 99% confidence level.

(ii) Compute the standard deviation of the mean.

(c). An iron ore is analysed for iron content by dissolving in acid, converting the iron to Fe^{2+}, then titrating with standard potassium dichromate (0.0150 M) solution. If 35.6 mL titrant is required to titrate the iron in 1.85 g of an ore sample, how much iron is in the sample expressed as milligrams of Fe_2O_3 correct to 3 significant figures?

(d). If 5.82 g of $KHC_2O_4.H_2C_2O_4$ (three ionisable protons) having 10% inert impurities, and 3.02 g of $KHC_8H_4O_4$ (one ionisable proton) are dissolved in water and diluted to 500 cm^3, what is the normality of the solution assuming a complete ionisation.

Question 4.

(a) When the strong cleaning agent "trisodium phosphate" is mixed with household vinegar, which contains acetic acid, the following equilibrium is established:

$PO_4^{3-}{}_{(aq)} + HC_2H_3O_{2(aq)} \rightarrow HPO_4^{2-}{}_{(aq)} + C_2H_3O_{2(aq)}$. Identify the pairs of conjugate acids and bases involved.

(b) Classify, with justification, the following reactions as either redox or not redox

(i) $2Ag + Cl_2 \rightarrow 2AgCl$

(ii) $2H_2 + O_2 \rightarrow 2H_2O$

(iii) $Ag^+ + 2NH_3 \rightarrow Ag(NH_3)_2^+$

(c) Compare the ionization energy of Ca to that of Zn. Explain the difference in terms of balance between shielding with increasing number of d electrons and effect of increasing nuclear charge.

(d). A new method of determining oxyphen butazone gave 99.35% recovery (variance 0.185). The standard method gave 99.53% recovery (variance 0.152). In each case three replicate measurements were made. Test whether the two *means* differ significantly at the 95% confidence level.

Question 5.

(a) Complete and balance the following redox reactions which occur in acid aqueous solution:

(i) $Cr_2O_7^{2-} + BrO_4^- + H_2O \rightarrow Br_2 + Cr^{+3} + H_2O$ given that E^0 for $Cr_2O_7^{2-}/Cr^{3+} = 1.33v$; and, E^0 for $BrO_4^- / Br_2 = 1.52v$.

(ii). $NO_3^- + Cu \rightarrow NO_2 + Cu^{2+} + H_2O$

Question 5 (Continued).

(b). Phthalic acid is a diprotic acid (generally represented as H_2A). The acid constants are given as $K_{a1} = 1.13 \times 10^{-3}$, and $K_{a2} = 3.90 \times 10^{-6}$, determine the following:

(i) All types of dissociation species present at equilibrium.
(ii) The equilibrium expression constant for the loss of two protons.
(iii) The value of pK_a for phthalic acid.

(b) The complex $K_2[Ni(CN)_4]$ has a magnetic moment $\mu_s \approx 0.01$ BM. Using Crystal field theory discuss the shape and bonding of the complex. (Do not use quadratic equations to solve this).

(d). Analytical results are usually expressed as concentration in various units. DDT, a chlorinated insecticide used in the past but banned now from being used in aerial spraying, known to accumulate in the food chain. In Lake Kariba, 0.014ppm DDT has been found in the mud and 5.0ppm DDT in the fish. Express these concentration found in fish, in units of %wt/wt.

END OF EXAMINATION