UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL II)
SEMESTER (I) EXAMINATIONS
July 2016

SUBJECT: Chemistry

COURSE UNIT: **CHE 4473** TIME: **Two (02)** hours

Answer **three (03)** questions only.

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01. Answer **all** parts.

(a)(i) Define the following terms.

(I) Carbonaceous biochemical oxygen demand (CBOD)

(II) Nitrogenous biochemical oxygen demand (NBOD)

(04x2 marks)

(ii) Write balanced chemical equations pertaining to carbonaceous biochemical oxygen demand and nitrogenous biochemical oxygen demand of a solution containing alanine.

(07 marks)

(iii) Calculate the theoretical CBOD, NBOD and total BOD (in mg L^{-1}) of a water sample contaminated with 267 mg L^{-1} alanine.

(05x3 marks)

Note: Chemical formula of alanine is $C_3H_7NO_2$ and its relative molar mass is 89.

(b) (i) $K_2Cr_2O_7$ is normally used as the oxidizing agent in the determination of chemical oxygen demand (COD) and COD is reported as oxygen equivalent.

(I) Derive the oxygen equivalence between $Cr_2O_7^{2-}$ and O_2.

(05 marks)

(II) Theoretical amount of $Cr_2O_7^{2-}$ required (in mols) to oxidize one mole of $C_aH_bO_cN_d$ to CO_2, H_2O and NH_4^+ is $\frac{2a}{3} + \frac{b}{6} + \frac{c}{3} + \frac{d}{2}$.

Calculate the theoretical COD of a water sample containing 376 mg L^{-1} of phenol.

(10 marks)

Note: Relative molar mass of O_2 and C_6H_5OH are 32 and 94 respectively.

(ii) A student was provided with a water sample to determine the alkalinity. Titration of 100.00 mL of water sample with 0.04 M H_2SO_4 acid required 5.00 mL of the acid for phenolphthalein end point. Titration of another 100.00 mL of water sample with 0.04 M H_2SO_4 acid required 5.00 mL acid for methyl orange end point.

(I) Giving reasons state the species responsible for alkalinity of the above water sample. (10 marks)

(II) Calculate the alkalinity (as $CaCO_3$ g L^{-1}) of the water sample. (10 marks)

(Note: relative molar mass of $CaCO_3$ is 100)

(c) Reduction of oxygen gas and reduction of $H^+_{(aq)}$ ions are considered as the upper and lower thermodynamic stability limits of water in it's pE-pH diagram. E° values for the above two processes are 1.229 V and 0.00 V. Answer the following questions by considering the activity of water as 1 and partial pressure of O_2 and H_2 as 1atm.

(I) Write the half reaction for reduction of $O_{2(g)}$.

(II) Write the half reaction for reduction of $H^+_{(aq)}$.

(III) State the relationship between pE and E at 25 °C.

(IV) Derive the pE-pH relationship at 25 °C for the following;

(A) Reduction of $O_{2(g)}$.

(B) Reduction of $H^+_{(aq)}$.

(35 marks)

02. Answer **all** parts.

(a) (i) Define the following terms relevant to atmospheric chemistry;

(A) Number density (n_X) (05 marks)

(B) Mixing ratio (C_x) (05 marks)

(ii) Show that $n_X = \frac{A_v P}{RT} C_X$, where A_v is the Avogadro number, R is universal gas constant, P is pressure and T is temperature. (15 marks)

(iii) Calculate the number density of CO_2 at sea level for P = 1 atm, T = 0 °C and the mixing ratio of CO_2 is 380 X 10^{-6}.

Note: $Av = 6.023X10^{23}$ R= 8.0134 J mol^{-1} K^{-1}

8.314 (10 marks)

(b) (i) $HO^{\cdot}_x$ radicals catalyze ozone destruction in the stratosphere but support ozone production in the troposphere. Explain this statement.

(10 marks)

(ii) Consider the following reactions. Rate constants

$$CO + {}^{\cdot}OH \longrightarrow CO_2 + H^{\cdot} \qquad k_1$$

$$CH_4 + {}^{\cdot}OH \longrightarrow {}^{\cdot}CH_3 + H_2O \qquad k_2$$

$$HCHO + {}^{\cdot}OH \longrightarrow CHO^{\cdot} + H_2O \qquad k_3$$

The following data was obtained in an industrial area during a field experiment.

Rate constant/ $cm^3 molecule^{-1} s^{-1}$	Concentration/ molecule cm^{-3}
$k_1 = 1.5 X10^{-13}$	$[CO] = 1x10^{13}$
$k_2 = 6.3 X10^{-15}$	$[CH_4] = 5.3X10^{13}$
$k_3 = 9.4 X10^{-12}$	$[HCHO] = 1.4x10^{10}$

(A) Calculate the life time (τ) of the ${}^{\cdot}OH$ radicals in this area.

(10 marks)

(B) The main source of OH radicals in this area is the reaction,

$${}^{\cdot}HO_2 + NO \longrightarrow {}^{\cdot}OH + NO_2 \qquad \text{(Rate constant -}k_4\text{)}$$

Show that OH radical concentration is given by the expression,

$$[{}^{\cdot}OH] = \tau_{OH}\, k_4[HO_2^{\cdot}][NO].$$

(10 marks)

(c) Consider the box model for a chemical species X emitted by a chemical industry operating only during the first nine months of the year. The industry emits the pollutant X at a rate E kg $month^{-1}$ during the operating season and zero during non-operating season. The pollutant is removed from the atmosphere with a constant life time τ. Let m(t) be the mass of the pollutant in the box at time t.

(i) Write the mass balance equation for the pollutant X inside the box.

(05 marks)

(ii) Solve the above equation in (i) to show that $\mathbf{m(t) = m(0)e^{(-t/\tau)} + E\tau(1-e^{[-t/\tau]})}$

(20 marks)

(iii) Derive an equation to determine m(t) for the non-operating season.

(10 marks)

03. Answer **all** parts.

(a) (i) What are the factors affecting dissolved oxygen content in a water body?

(05 marks)

(ii) An industrial effluent containing $[CH_2O]$ and NH_4^+ ions has been subjected to aerobic digestion. Give balanced chemical equations for following processes.

(I) degradation of $[CH_2O]$

(II) nitrification of NH_4^+ ions

(10 marks)

(b) (i) A dairy industry in Ambewela involves processing of raw milk into consumer milk, yogurt and ice cream. Total hardness and total alkalinity of water available in the site are 192 mg L^{-1} (as $CaCO_3$) and 103 mg L^{-1} (as $CaCO_3$) respectively. A water soften plant reduces noncarbonate hardness of that water by using Na_2CO_3, before using in the above production processes. Calculate the amount of Na_2CO_3 (mg L^{-1}) required to soften above water. Assume that the noncarbonated hardness is due to $CaSO_4$.

Note: Relative molar mass of $CaCO_3$ and Na_2CO_3 are 100 and 106 respectively.

(15 marks)

(ii) The effluent of the above industry is originated from the following sections of the industry: milk receiving station, bottling plant, yogurt plant, ice cream plant, water softening plant and bottle and can-washing plants. This dairy industry generates an average of 2.5- 3.0 L of effluent per liter of milk processed and contains water mixed with spilled milk which consists of fat, casein, and lactose; inorganic salts and detergents. The effluent has a bad smell. Certain other qualities of the effluent and recommended levels for release of diary effluents into surface water are given in the following table.

parameter	Observed value	Recommended level
pH	10.5	5.5-9.0
Total dissolved solids(mg/L)	1600	< 2100
Total Suspended solids(mg/L)	760	< 30
BOD_5 (mg/L)	1240	< 30
COD (mg/L)	84	< 250
PO_4^{3-} (mg/L)	38	< 5
Oil and grease (mg/L)	290	< 10
Chloride (mg/L)	105	< 600

(I) Suggest suitable treatment methods for the above effluent.

(15 marks)

(II) Based on the given data, recommend three cleaner production options for the above industry.

(05 marks)

(c) Briefly discuss the following;

(i) The essential ingredients found in a typical paint formulation and their specific role.

(15 marks)

(ii) The basic ingredients in a typical shampoo formulation.

(15 marks)

(iii) Drying mechanisms which take place soon after the application of a paint on to a surface.

(10 marks)

(iv) Interaction between surfactant(s) and hair is a physicochemical phenomenon; describe briefly the adsorption mechanisms involved.

(10 marks)

04. Answer **all** parts.

(a) What are the major types of classification of metals with respect to their biogeochemical behaviour.

(20 marks)

(b) You have given below are some of the metal catios presence in muddy soil and their ionic radii. Giving reasons identify each metal ion is "toxic", "possibly toxic" or "non-toxic".

Metal ion	Ionic radius (A)
Li^{+}	0.74
Mg^{2+}	0.72
Fe^{3+}	0.65
Hg^{2+}	1.02
Ba^{2+}	1.36
Cr^{3+}	0.62
Cr^{6+}	0.35

(25 marks)

(c) What is the chemistry underline with above classification of the metal toxicity?

(05 marks)

(d) Define the following terms used in soil chemistry

(i) cation exchange capacity (CEC)

(ii) Base saturation

(10 marks)

(e) Acid sulphate soil is a problem in Godagama area. Acidity can be reduced by applying $MgCO_3$. Soil analysis carried out Godagama area has revealed that the CEC and pH are 40 meq/100 g and 4.3 respectively. Base saturation at pH 4.3 and 6.0 are 20% and 85%. Calculate the amount of $MgCO_3$ (80% effective) needed per acre of land to a depth of 8" inches to raise the pH from 4.3 to 6.0.

(**Note:** 1 acre = 43560 ft^2, density of soil = 45 kg/ft^3)

(25 marks)

(f) (i) State the Jackson–Sherman soil weathering stages. Give one example for each.

(ii) Give chemical equations for following processes which occur at the final stage of Jackson–Sherman soil weathering process.

(I) The weathering of albite to kaolinite

(II) Albite complexation with oxalate.

(**Note:** albite $NaAlSi_3O_8$, kaolinite $Si_4Al_4O_{10}(OH)_8$)

(15 marks)

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