

**CORK INSTITUTE OF TECHNOLOGY
INSTITIÚID TEICNEOLAÍOCHTA CHORCAÍ**

Semester 2 Examinations 2010/11

Module Title: Physical Chemistry 1

Module Code: CHEM 6004

School : Science

Programme Title: Bachelor of Science in Analytical & Pharmaceutical Chemistry – Year 1
Bachelor of Science in Analytical Chemistry with Quality Assurance – Stage 1

Programme Code: **SCHEM_7_Y1**
SCHQA_8_Y1

External Examiner(s): Dr. G. Keaveney

Internal Examiner(s): Dr. M. Sheahan

Instructions: Answer any **FOUR** questions

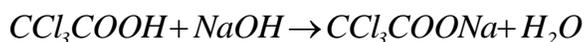
Duration: 2 Hours

Sitting: Summer 2011

Requirements for this examination: Periodic Table

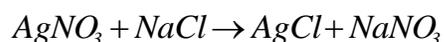
Note to Candidates: Please check the Programme Title and the Module Title to ensure that you have received the correct examination paper.
If in doubt please contact an Invigilator.

Q1. A 20 cm³ aliquot of a solution of trichloroethanoic acid (CCl₃COOH) was titrated with a 0.1 mol dm⁻³ solution of sodium hydroxide. The titer obtained was 24.9 cm³ (titration 1). A second 20cm³ aliquot of the trichloroethanoic acid solution was extracted with 20cm³ of diethyl ether. The extracted aqueous layer was then titrated with the 0.1 mol dm⁻³ NaOH solution. The titer obtained was 5.3cm³ (titration 2). The equation for the neutralization reaction is:



- (a) Calculate the number of moles of NaOH used in the titration 1. Hence deduce the moles of CCl₃COOH in 20 cm³ aliquot of acid solution. (2 Marks)
- (b) Calculate the number of moles of NaOH used in the titration 2. Hence deduce the moles of CCl₃COOH remaining in the 20 cm³ aliquot after the extraction. (2 Marks)
- (c) Calculate the moles of trichloroethanoic acid that extracted into the diethyl ether layer (2 Marks)
- (d) Determine a value for the partition coefficient, K_D for the extraction. (4 Marks)
- (e) Describe how a liquid-liquid extraction procedure may be carried out in the laboratory. Include in your answer the measures which must be taken to ensure the best extraction efficiency and state the precautions which must be observed for the safe conduct of the experiment (10 Marks)
- (f) If a third 20cm³ aliquot of the CCl₃COOH solution was doubly extracted (e.g. 2 x 10cm³) with diethyl ether and then titrated with the NaOH solution, how would you expect the titer and the K_D value to compare with the results obtained for the single (1 x 20cm³) extraction? Explain your answer. (5 Marks)

- Q2. (a) Name each term in the expression, $\Delta E = q + w$. Use the expression to calculate the energy change for a system which absorbs 6.48kJ of heat while expanding by 45L against a pressure of 1.5atm. Assumes the temperature remains constant at 25°C. Express your answer in J (1L.atm = 101J) (7 Marks)
- (b) Differentiate between the terms *specific heat capacity* and *molar heat capacity*. If the specific heat capacity of iron is 0.45J g⁻¹K⁻¹ at 25C, what is the value of its molar heat capacity? (5 Marks)
- (c) The reaction between silver nitrate (AgNO₃) and sodium chloride is as shown:

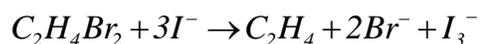


In a laboratory experiment, 10cm³ of 1M AgNO₃ were added to 10cm³ of a 1M NaCl solution at 25°C in a calorimeter. The calorimeter absorbs a negligible amount of heat while the temperature of the reaction mixture increased to 32.6°C.

- (i) Assuming the density of the reaction solution is 1g cm⁻³, what is the mass of the contents of the calorimeter? (2 Marks)
- (ii) Use the specific heat capacity of water 4.18 kJ kg⁻¹K⁻¹ to calculate the heat (in J) change involved in the reaction. (3 Marks)
- (iii) If the reaction was repeated using 100cm³ of each reactant, what heat change would be take place? (2 Marks)
- (iv) How many moles of AgNO₃ are present in the 10cm³ aliquot? Hence calculate the heat change (kJ mol⁻¹) which would accompany the formation of one mole of AgCl. Indicate if the process is endothermic or exothermic by assigning the appropriate sign to your answer. (6 Marks)

Q3. (a) Differentiate between homogenous and heterogeneous catalysis. Describe how a catalyst can influence the rate of a reaction. List three other factors which influence the rates of chemical reactions. (9 Marks)

(b) The initial rates listed in the table were measured in methanol solution for the reaction



Experiment	Initial [C ₂ H ₄ Br ₂]	Initial [I ⁻]	Initial Rate of Formation I ₃ ⁻ (Ms ⁻¹)
1	0.127M	0.102M	6.45 x 10 ⁻⁵
2	0.381M	0.102M	1.93 x 10 ⁻⁴
3	0.127M	0.408M	2.58 x 10 ⁻⁴

Perform and show the appropriate calculations in each of the following answers.

(i) Determine the order in both reactants; hence write the rate law for the reaction. (4 Marks)

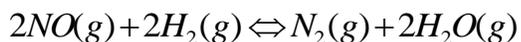
(ii) Calculate the value of the rate constant (*k*)? Assign units to *k*. (5 Marks)

(iii) What is the reaction rate when both reactant concentrations are 0.15M? (3 Marks)

(iv) Based on the reaction equation, at what rate is the iodide ion (I⁻) being consumed in experiment 1? Is the C₂H₄Br₂ reacting at the same rate as the iodide ion? Explain.

(4 Marks)

- Q4. (a) A mixture of 0.10 moles of NO, 0.05 moles of H₂ and 0.10 moles of H₂O is placed in a 1.0L vessel at 300K. Equilibrium was established according to the equation given below and the equilibrium concentration of NO was found to be 0.062M:



Calculate the equilibrium concentrations of H₂, N₂ and H₂O. Hence determine a value for K_c at 300K (5 Marks)

- (b) The oxidation of sulfur dioxide is an exothermic reaction which proceeds according to the equation: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Write the expression for the equilibrium constant K_c. What does the magnitude of K_c indicate about the reaction at this temperature? (5 Marks)

- (c) State *Le Chatelier's Principle* and use this principle to discuss the effects of the following on the equilibrium involved in the oxidation of sulfur dioxide. Give reasons for your answers in each case
- (i) The pressure on the reaction mixture is decreased
 - (ii) The volume of the reaction mixture is decreased
 - (iii) The temperature is decreased
 - (iv) SO₃ is removed from the equilibrium mixture as it is generated
 - (v) A catalyst is added to the reaction

(15 Marks)

- Q5. (a) Differentiate between a strong acid and a weak acid. Write a balanced equation showing the ionization of each of the following acids in aqueous solution: HCl, C₂H₅COOH, and HSO₄⁻. Identify the conjugate base in each case. (8 Marks)
- (b) Explain the effect (increase or decrease) on the pH of a weak acid when
- a small volume of HCl is added to it
 - a small volume of NaOH is added. (4 Marks)
- (c) Calculate the H₃O⁺ concentration in the following solutions:
- 0.05M NaOH (3 Marks)
 - A strong acid solution which has a pH of 3.2 (2 Marks)
- (d) A 625cm³ sample of an aqueous solution containing 0.275 moles propionic acid (C₂H₅COOH) has a hydronium ion concentration of 0.00239M.
- Calculate the molar concentration of the propionic acid solution. (2 Marks)
 - Write a balanced equation showing the ionization of the acid in aqueous solution. (2 Marks)
 - Hence determine a value for K_a for propionic acid? (4 Marks)
- Q6. (a) For the galvanic cell represented by the following:
 $\text{Pb}(s) | \text{Pb}^{2+}(aq) || \text{Br}_2(l) | \text{Br}^-(aq) | \text{Pt}(s)$
- Sketch the experimental set up for the cell. Label the anode and the cathode, identify the sign of each electrode and indicate the direction of electron flow. (10 Marks)
 - Write an equation for the half-cell reactions. Identify the oxidizing and reducing agents respectively. (4 Marks)
- (b) Sodium metal is produced by electrolysis of a molten mixture of sodium chloride (NaCl) and calcium chloride (CaCl₂).
- What do you understand by the term *electrolysis*? (2 Marks)
 - If a current of 50A is passed through molten NaCl for 2.5hrs, calculate the respective weights of Na and Cl₂ that are produced? (6 Marks)
 - What products would be obtained if the electrolysis was carried out in an aqueous solution of sodium chloride (3 Marks)