NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS – APRIL/MAY 2014
PHYSICAL CHEMISTRY II – SCH 2204

TIME – 3 HOURS

INSTRUCTIONS TO CANDIDATES:

1. ANSWER **ALL** QUESTIONS FROM SECTION A AND **ANY THREE** FROM SECTION B. SECTION A CARRIES 40 MARKS AND EACH QUESTION IN SECTION B CARRIES 20 MARKS. MARKS ARE ALLOCATED IS INDICATED IN BRACKET [ ]

2. START ANSWERING EACH QUESTION ON A NEW PAGE. (NOT EACH PART OF A QUESTION)

INFORMATION TO CANDIDATES

1. YOU ARE REMINDED FOR THE NEED TO USE CLEAR PRESENTATION AND GOOD ENGLISH

TOTAL MARKS = 100

THIS QUESTION PAPER CONSISTS OF **FIVE (5)** PRINTED PAGES (ON ONE SIDE ONLY) INCLUDING THE TOP PAGE WITH THE INSTRUCTIONS.

SECTION A:

1)

a) Phosphine decomposes according to the following stoichiometric equation

$$4PH_3(g) \longrightarrow P_4(g) + 6H_2(g)$$

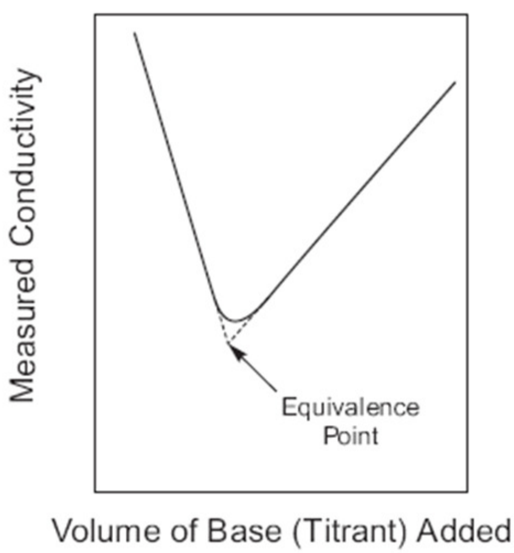
Let the rate of disappearance of phosphine, $(r_{PH_3}) = 1 \times 10^{-5}$ Ms^{-1}.

Compute the rates of appearance of phosphorus (P_4) and Hydrogen [4 marks]

b) Consider the general reaction $2A \rightarrow A_2$ with a rate constant (k) = 5×10^{-5} $dm^3\ mol^{-1}\ s^{-1}$ at 400 K. At the start of the reaction, the concentration of A was 0.7 M and no A_2 was present. Calculate the time in which the concentration of A_2 will increase to 0.1 M.

[6 marks]

2) Discuss the diagram below which shows results for a titration of $HCl_{(aq)}$ against $KOH_{(aq)}$



[10 marks]

3)

a) For the reaction $Br_2(g) + 2NO(g) \longrightarrow 2BrNO(g)$.A mechanism has been proposed which involves the following 2 steps.

Step 1: $Br_2(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Br_2NO(g)$ Fast equilibrium

Step 2: $Br_2NO(g) + NO \xrightarrow{k_2} 2BrNO(g)$ Slow

Given that the experimentally determined rate equation is: $rate = k_{obs}[NO]^2[Br_2]$.
Is the above mechanism valid? [5 marks]

b) Calculate the conductivity, (κ), for pure water given that the ionic conductivities at infinite dilution (λ^0) are $\lambda^0_{(H_3O^+)}$ = 349.85 S cm^2 mol^{-1} and $\lambda^0_{(OH^-)}$ = 197.6 S cm^2 mol^{-1} Values are quoted at 298 K, the pH of pure water is 7. [5 marks]

4) Compare and contrast Chemisorption and Physisorption. Discuss procedures that you need to carry out to distinguish chemisorption from Physisorption. [10 marks]

SECTION B:

1) The reaction given below was investigated at 25 ^oC.

   $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$.

   Given that the starting concentrations of ethyl acetate and NaOH were the same and equal to 0.01 M. Some of the results of the experiment are given in the table below.

t (min)	5	9	13	20	25	33	37
concentration	0.00755	0.00633	0.00541	0.00434	0.00385	0.00320	0.00296

   On the basis of these data, determine the order of the reaction and the rate constant

   [20 marks]

2) The following reaction scheme has been proposed as a mechanism for the decomposition of N_2O_5, which decomposes according to the following equation.

   $$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g),$$

   Step 1 (equilibrium reaction) $N_2O_5(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2(g) + NO_3(g)$

   Step 2 $NO_2(g) + NO_3^*(g) \overset{k_2}{\longrightarrow} NO_2(g) + NO(g) + O_2(g)$

   Step 3 $NO^*(g) + N_2O_5(g) \overset{k_3}{\longrightarrow} 3NO_2(g)$

   Use steady state approximation to show that the rate of reaction obtainable from the scheme is consistent with and can explain the observed first order decomposition of N_2O_5, and hence show that the overall rate can be obtained from any of the species in the stoichiometric equation [20 marks]

3)

   a) The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650°C than at 500^{o}C? [6 marks]

   b) Calcium iodate dissolves in water as follows

   $$Ca(IO_3)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2IO_3^-(aq)$$

Given that an approximate expression for the solubility product constant for the dissolution is as follows:

$$K_{sp} = [Ca^{2+}][IO_3^-]^2$$

Show that the accurate expression is as given below

$$K_{sp} = \gamma_{\pm}^3[Ca^{2+}][IO_3^-]^2$$ [5 marks]

c) Discuss what you understand by model fitting procedures and using example(s) explain their importance in chemistry. [9 marks]

4)

a) For the reaction given below, comment on the equilibrium constant. [5 marks]

$$Fe(s) + Cd^{2+}(aq) \rightleftharpoons Fe^{2+}(aq) + Cd(s)$$

Half-Reaction	E^0(V)
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.440
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.403

b) A voltaic cell is set up with copper and hydrogen half-cells. Standard conditions are employed in the copper half-cell. The hydrogen gas pressure is 1.00 bar, and the hydrogen ions concentration in the hydrogen half-cell is unknown. The E_{cell}recorded at 298 K has a value of 0.490 V. Draw the line diagram for the cell and determine the pH of the solution.

$$Cu^{2+}_{(aq)} + 2^{e-} \rightarrow Cu_{(s)} \qquad E^0 = +0.34\ V$$

[7 marks]

c) A cell is constructed by combining a ½ cell with the reduction reaction given by

$Fe(OH)_2(s) + 2e^-$ ⟶ $Fe(s) + 2\ OH^-$ $E^0 = -0.887$ V, with a ½ cell for which the reduction reaction is given by the following:

i) $Al^{3+}_{(aq)} + 3e^-$ ⟶ $Al_{(s)}$ $E^0 = -1.66$ V

ii) $AgBr_{(s)} + e^-$ ⟶ $Ag_{(s)} + Br^-_{(aq)}$ $E^0 = +0.071$ V

For the above 2 cases, for an overall reaction in the direction of spontaneous change, is Fe reduced or oxidized? [8 marks]

END OF QUESTION PAPER