The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/ B. Ed Degree Programme

Department	**: Chemistry**
Level	**: 03**
Name of the Examination	**: Final Examination**
Course Title and - Code	**: CYU3201 - Basic Principles of Chemistry II - *(PART B)***
Academic Year	**: 2019/2020**
Date	**: 15.02.2021**
Time	**: 9.30 am- 11.30 am**
Duration	**: 2 hours**

1. Read all instructions carefully before answering the questions.
2. This question paper *(Part B)* consists of **three** questions in **four** pages.
3. Answer all the questions. All questions carry equal marks.
4. Answer for each question should commence from a new page.
5. Draw fully labelled diagrams where necessary.
6. The use of a non-programmable electronic calculator is permitted.
7. Involvement in any activity that is considered as an exam offense will lead to punishment
8. Use blue or black ink to answer the questions.
9. Clearly state your index number in your answer script
10. Submit the answer scripts of ***Part A and Part B*** attached together.

Gas constant (R) $= 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

Avogadro constant $= 6.023 \times 10^{23}\ \text{mol}^{-1}$

Faraday constant (F) $= 96{,}500\ \text{C mol}^{-1}$

Planck's constant (h) $= 6.63 \times 10^{-34}\ \text{J s}$

Velocity of light (c) $= 3.0 \times 10^{8}\ \text{m s}^{-1}$

Standard Atmospheric pressure $= 10^{5}$ Pa (N m^{-2})

Mass of an electron $= 9.1 \times 10^{-31}\text{kg}$

$$\Delta G = -nFE \qquad I = 0.5 \times \sum_j c_j Z_j^2 \qquad \log(\gamma_\pm) = -\frac{A Z^2 \sqrt{I}}{1 + aB\sqrt{I}} \qquad E = E^0 - \frac{RT}{nF}\ln(Q)$$

Data: $A = 0.509\ \text{dm}^{3/2}\ \text{mol}^{-1/2}$ $\quad aB = 1.25\ \text{dm}^{3/2}\ \text{mol}^{-1/2}$

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Part B

(Recommended time 1 hour 30 min)

1. Answer **all** parts (a), (b), and (c).

a) Write down the mathematical expression for the 2nd law of thermodynamics?

(10 Marks)

b) Define the following terms

i) Open system ii) Isothermal process iii) Intensive properties

iv) State function v) Isolated system

(20 Marks)

c) Helium gas (2.0 g) undergoes a reversible isobaric expansion from 30 L to 60 L at 0.7 atm followed by a reversible isochoric heating till pressure reaches 1.0 atm. Depict the change of state on P-V diagram and calculate q, W, ΔU and ΔH.

(Hint for a mono atomic gas $C_v = \frac{3R}{2}$).

(50 marks)

d) Show the variation of PV/nRT *vs* P (pressure) at constant temperature (T) for one mole of the gases; CO_2, H_2 and O_2.

(20 marks)

2. (a) What do you understand by the following used in the study of Kinetics?

(i) Rate determining step

(ii) Under what conditions, the elementary reaction $A + B \rightarrow P$ could be made a pseudo first order reaction?

(10 marks)

(b) A hypothetical elementary reaction is of the form

$$2A + B \longrightarrow \text{products}$$

(i) Write down the rate expression for the above reaction using the standard symbols

(ii) Determine the **SI units** of the rate constant, ***k***.

(iii) Assuming that this reaction is carried out with an excess amount of B relative to A, **derive** an expression **(integrated form)** for the **pseudo** rate constant (k^*) of the reaction in term of the concentration of A, [A] at time, t and its initial concentration $[A_o]$

(iv) Derive the expression for time (t) when 20% of A has reacted and hence, calculate the corresponding time taken if the rate constant for the above reaction = 4.0×10^{-5} mol^{-1} dm^{3} min^{-1} and the initial concentration of A = 1.0 mol dm^{-3}.

(40 marks)

(c) A student prepared a Galvanic cell by inserting a rod of metal P in an aqueous solution of $P(NO_3)_2$ in a beaker, inserting a rod of metal Q in an aqueous solution of $Q(NO_3)_3$ in a beaker and making an electrical contact between the two solutions using a salt bridge. The student observed that the electrons flow from Q to P when they are connected to a load. The emf of the cell was found to be 1.24V at 25^{0}C. It is known that

$[P(NO_3)_2] = 0.50$ mol dm^{-3} and $[Q(NO_3)_3] = 0.25$ mol dm^{-3}.

The student found out that the electrode potential of the $Q_{(s)}|Q^{3+}(aq)$ electrode is 0.74 V.

(i) Define the electrode potential of an electrode.

(ii) Draw the cell diagram for the cell prepared by the student.

(iii) Write down the anode reaction, cathode reaction and the cell reaction for the cell diagram you have drawn in part (ii) above.

(iv) What is the charge number of the cell reaction you have written?

(v) Giving reasons, state whether the cell reaction you have written in part (iii) above is spontaneous or not.

(50 marks)

3. Answer any **TWO (02)** parts out of (a), (b) and (c).

(a) Consider an aqueous solution of $CaCl_2$ with a concentration of 0.001 mol dm^{-3}.

(i) Calculate, the ionic strength of the $CaCl_2$ solution

(ii) Using the Debye-Huckel limiting law at 298K, Calculate the following in this solution,

- The activity coefficients of Ca^{2+} and Cl^{-} ions
- The mean activity coefficient of $CaCl_2$

(iii) Explain qualitatively why log $\gamma_{\pm}$ should tend to zero as the ionic strength goes to zero.

(50 marks)

(b) (i) Define the terms energy capacity and energy density, indicating the units.

(ii) Consider the following cell diagram,

$$Pt(s)|Fe^{3+}(aq), Fe^{2+}(aq)||Br^{-}(aq), Br_2(l)|Pt(s)$$

E^0 of $Pt(s)|Br^{-}(aq), Br_2(l)$ = 1.065V and $Pt(s)|Fe^{3+}(aq), Fe^{2+}(aq)$ = 0.771 V at 298 K.

- Write down the anode reaction, cathode reaction and cell reaction

- Calculate the standard emf of the cell reaction at 298 K
- Write down the Nernst equation corresponding to the above cell reaction
- Calculate the emf when the activities of $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ are 0.05 and 0.01 respectively and activity of $Br^{-}(aq)$ is 0.02. Assume the activity of $Br_2(l)$ is 1.

(iii) Calculate the thermodynamic equilibrium constant for the reaction,

$$Fe^{2+}(aq) + Ce^{4+}(aq) \rightarrow Fe^{3+}(aq) + Ce^{3+}(aq)$$

$E^0(Ce^{4+}(aq)|\, Ce^{3+}(aq)) = 1.44\ V$, $E^0(Fe^{3+}(aq)|\, Fe^{2+}(aq)) = 0.68\ V$, at 298 K

(50 marks)

(c) (i) At 298 K calculate the emf assigned to the cell diagram,

$Zn(s)|ZnCl_2(aq)), |AgCl(s)|Ag(s),$

if the standard electrode potentials at 298 K are; $E^0(Zn^{2+}(aq)|Zn(s)) = -0.763\ V$,

$E^0(Cl^-(aq), AgCl(s)|Ag(s)) = 0.222V$ and the activity of aqueous $ZnCl_2 = 0.5$

(ii) At 298K, a potentiometric titration of Ti^{3+} was carried out using an acidic solution of MnO_4^- as the titrant. The experimental setup used to determine the $Ti^{3+}(aq)$ potentiometrically consists of a platinum rod immersed in the titrand, the potential of which is measured relative to a standard calomel electrode.

Using the following data,

$E^0_{Pt|Ti^{4+},Ti^{3+}} = 0.07\ V$

$E^0_{Pt|MnO_4^-,Mn^{2+},H^+} = 1.51\ V$

$E^0_{Hg|Hg_2Cl_2|Cl^-} = 0.268\ V$

(α) Sketch the variation of the potential E, (in volts) of the Platinum rod immersed in the titrand as a function of the volume V of titrant during the titration. Label the sketch.

(β) Explain the observed variation of the potential of the platinum rod at the end point (observed in the sketch you have made in part (α) above). (50 marks)