UNIVERSITY OF KELANIYA - SRI LANKA
FACULTY OF SCIENCE

Bachelor of Science General Degree Examination – May 2023
Academic Year 2020/2021– Semester II

CHEMISTRY

CHEMB 12642, CHEM 12642(R) - Physical Chemistry I

Number of Questions: Four (04)
Number of pages: Three (03)

Time: Two (02) hours
Answer all four (04) questions.

Planck's constant (h)	= 6.626×10^{-34} J s
Speed of light (c)	= 2.98×10^{8} m s^{-1}
Charge of an electron (e)	= 1.602×10^{-19} C
Mass of an electron (m_e)	= 9.10908×10^{-31} kg
Avogadro's number (L)	= 6.022×10^{23} mol^{-1}
Faraday's constant (F)	= 96487 C mol^{-1}
Universal gas constant (R)	= 8.314 J k^{-1} mol^{-1}
Permittivity of free space (ε_o)	= 8.84×10^{-12} C^2 N^{-1} m^{-2}
1 atm	= 1.01×10^{5} N m^{-2}

(1) Answer all parts

(a) (i) Write the rate expression for the decomposition of hydrogen peroxide as given in the following reaction.

H_2O_2 (aq) → H_2O (aq) + ½ O_2(g)

(ii) If the above reaction follows first order kinetics, derive an expression for the integrated rate law.

(iii) The rate constant for the above reaction at 25 °C is 0.041 min^{-1}. A commercially available bottle of hydrogen peroxide contains 7.5% of H_2O_2 by weight. Calculate the percentage of H_2O_2 left, if the bottle was left open to decompose for 10 minutes.

(40 marks)

(b) (i) State Arrhenius equation and define all the terms of it.

(ii) Rate constants for the decomposition of nitrogen dioxide was measured at different temperatures were given below. Make Arrhenius plot of above data and find the activation energy of the reaction.

$2NO_2$ (g) → 2NO (g) +O_2 (g)

T(K)	Rate constant (s^{-1})
350	0.0068
370	0.0410
380	0.1300
400	0.5000

(iii) If the reaction enthalpy is -474 kJ/mol calculate the energy required for the reverse reaction.

(40 marks)

(c) Peroxyacetyl nitrate (PAN) is a photochemical pollutant that could adversely affect human health, especially with relation to effects on lung function. The main removal process for PAN is thermal decay according to first order kinetics as given in the following reaction.

$$CH_3CO_3NO_2\,(g) \rightarrow CH_3CO_3^{\cdot}\,(g) + NO_2\,(g)$$

If it took 10.0 hrs to reduce the initial PAN concentration of 2.7×10^{15} molecules/L in air to 1.4×10^{14} molecules/L. Calculate the half-life for this reaction. (20 marks)

(2). Answer all parts

(a) At 298 K, the limiting molar conductivities of KCl (aq), HCl(aq) and CH_3COOK (aq) solutions are 149 S cm^2 mol^{-1}, 369.3 S cm^2 mol^{-1} and 81 S cm^2 mol^{-1} respectively. If the molar conductivity of 0.0010 mol/L solution of CH_3COOH at 298 K is 105 S cm^2 mol^{-1}, calculate the acid dissociation constant (K_a) (30 marks)

$K_a = \frac{c\alpha^2}{1-\alpha}$

(b) Plot the conductometric titration curve for the titration of equimolar mixture of hydrochloric and formic acid against a standard NaOH solution. All important points and axes should be labeled properly. (20 marks)

(c) (i) Explain briefly why the activity coefficient ($\gamma_\pm$)of 5 mol/L LiBr solution is 2.7 whereas 0.001 mol/L solution of LiBr is 0.965. $\log \gamma_\pm = |z_+ z_-| A\sqrt{I}$ $I = \frac{1}{2}\sum z^2 \frac{b}{b^\ominus}$

(ii) Calculate the pH of 0.010 mol/kg H_2SO_4 (aq) solution containing 0.010 mol/kg K_2SO_4. (Hint: $pH = -\log a_{H^+}$ *where a is the activity*) (30 marks)

(d) The proton (mobility of $H^+ = 36.23 \times 10^{-8}$ m^2 s^{-1} V^{-1}) has very high mobility compared to a sodium ion (mobility of $Na^+ = 5.19 \times 10^{-8}$ m^2 s^{-1} V^{-1}) in water. Briefly explain this observation. (20 marks)

(3).Answer all parts

A sample of Hydrogen gas is initially at 3.0×10^5 N m^{-2} pressure and at 25 °C temperature and has a volume of 1.5 dm^3. It is subjected to a reversible, adiabatic expansion until the volume is 5.0 dm^3. The molar heat capacity at constant pressure, $C_{p,m}$ of H_2 is 28.80 J K^{-1} mol^{-1}. Assuming H_2 behaves as an ideal gas and C_p is independent of temperature, calculate,

(a) the final pressure and temperature of the gas sample after the expansion. Derive equations used for this calculation. (60 marks)

(b) the change in internal energy (ΔU) and the change in enthalpy (ΔH) for the process. (40 marks)

(4) Answer ***any two parts*** from PART (A), (B) and (C)

PART A

(i) At steady state plot how the concentration of each of the species vary with time for the reaction A → I → B where I is an intermediate.

(ii) The proposed mechanism for the reaction of NO with H_2 is given below.

$2NO (g) \rightarrow N_2O_2 (g)$ (rate constant k_1)
$N_2O_2 (g) \rightarrow 2NO (g)$ (rate constant k_{-1})
$N_2O_2 (g) + H_2(g) \rightarrow N_2O(g) + H_2O (l)$ (rate constant k_2)

(a) Write the overall reaction for the above mechanism

(b) Show that the overall rate of the reaction is given by the following expression at the steady state. State any assumptions made.

$$-\frac{d[H_2]}{dt} = \frac{k_2[H_2]\,.\,k_1[NO]^2}{(k_{-1} + k_2[H_2])}$$

(c) If large excess of H_2 gas is present, show how is equation in (ii) for the overall rate of the reaction can be revised. Clearly state any assumptions made. (50 marks)

PART B

(i) (a) Consider the cell Al(s)|Al^{3+}(0.030 mol/L)||Cu^{2+}(0.010 mol/L),Cu^{+}(0.010 mol/L)|Pt(s). The standard reduction potentials (E°) for Al/Al^{3+} and Cu^{+}/Cu^{2+} redox couples are -1.61 V and 0.15 V respectively. Calculate the cell potential (E_{cell}) and the Gibbs free energy change (ΔG) for the cell reaction (30 marks)

$\Delta G = -\nu FE$

(b) State the main difference between a Galvanic cell and electrolytic cell.

(ii) Considering the standard reduction potentials given write the cell reaction in the direction of energy production to identify whether pyruvate or the lactate is a waste product. Show your work clearly.

Pyruvate(aq) + $2H^{+}$(aq) + 2e → lactate (aq) E° = -0.16 V
NAD^{+} (aq) + $2H^{+}$ (aq) + 2e → NADH(aq) + H^{+}(aq) E° = -0.28 V

(20 marks)

PART C

(i) One mole of an ideal gas at 25 °C is allowed to expand reversibly and isothermally from 1 dm^3 to 10 dm^3. (Molar heat capacity at constant volume, $C_{v,m} = 3R/2$)

Calculate,

(a) the change in entropy for the gas. Derive any equation that you used in the calculation.
(b) the change in entropy for the surrounding.

(35 marks)

(ii) The same gas in above part(a) is expanded adiabatically and irreversibly from 1 dm^3 to 10 dm^3 with no work done. Calculate,

(a) the final temperature of the gas
(b) the change in entropy ΔS for the gas. (15 marks)