NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY

FACULTY OF APPLIED SCIENCE

DEPARTMENT OF APPLIED CHEMISTRY

PHYSICAL CHEMISTRY II – SCH 2204

Second Semester Examination Paper

2024/2025 Academic Year

This examination paper consists of pages with questions + pages with tables and formulas.

TIME: (3) THREE HOURS

MATERIAL
Graph paper, ruler, calculator.
Tables and formulas are provided in the last pages of the paper.

INSTRUCTIONS TO STUDENT
Answer All questions.
Answer each question on a FRESH page.

$R = 8.314\ \mathrm{JK^{-1}mol^{-1}} = 0.08205\ \mathrm{dm^3\ atm^{-1}\ K^{-1}mol^{-1}}$
$F = eN_A = 96\ 485\ \mathrm{C\ mol^{-1}}$
$1\ \mathrm{V\ C} = 1\ \mathrm{J} = 1\ \mathrm{Nm}$
$1\ \mathrm{atm} = 760\ \mathrm{torr} = 760\mathrm{mmHg} = 101\ 325\ \mathrm{Pa}$
$\ln x = 2.3026 \log x$

SECTION A *Answer ALL questions. This section carries 40 marks.*

QUESTION 1

a) (i) 0.05M aqueous solution of acetic acid (CH_3COOH) has a molar conductivity(Λ_m) of 7.814×10^{-4} $Sm^2\ mol^{-1}$ at 298K. Calculate K_a. [4 marks]

(ii) Calculate the ionic mobilities of H^+ and Li^+ ions. [2 marks]

(iii) What are the ionic strengths of the following solutions, (1)0.5 $molkg^{-1}$ KNO_3, (2) 2.0 $molkg^{-1}$ $Al_2(SO_4)_3$. [4 marks]

b) (i) What is the role of a catalyst in a chemical reaction? Show its effect on a Boltzmann distribution profile. [3 marks]

(ii) What is the difference between rate order and molecularity? [2 marks]

(iii) Calculate the rate constants, *k*, for the two reactions in Table 1, at 298 K. Calculate the half-life for the first one. [5 marks]

Table 1 Arrhenius parameters

First-order reactions	Phase	A/s^{-1}	$E_a/(kJ\ mol^{-1})$
$CH_3NC \rightarrow CH_3CN$	gas	3.98×10^{13}	160
$2N_2O_5 \rightarrow 4NO_2 + O_2$	gas	4.94×10^{13}	103.4

c) (i)What four assumptions are made for the application of the Langmuir isotherm? [4 marks]

(ii) What types of bonds are expected in a system that follows the BET isotherm? Under what conditions does the BET isotherm reduce to the Langmuir isotherm form. [3 marks]

(iii) What is a surfactant? [1 mark]

(iv) An aqueous solution of an organic acid has a surface tension change with concentration at 293K:

$$\frac{d\gamma}{d\ln(c/c^0)} = -4.0 \times 10^{-5}\ Nm^{-1}$$

Calculate the surface excess, Γ_s, of the acid. [2 marks]

d) (i) Sketch a typical electrode concentration cell. [2 marks]

(ii) Name and sketch three models of the electric double layer at the electrode-electrolyte solution interface, showing how the potential changes from electrode to the bulk of the solution. [6 marks]

(iii) How do the overpotentials at the electrodes affect the working cell potential of a galvanic cells? [2 marks]

SECTION B *Answer All questions from this section. Each question 20 marks*

QUESTION 2

a) To show that standard electrode potentials can be calculated from other standard electrode potentials, calculate the standard electrode potentials of the redox couples Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+}, from E^0 (Fe^{3+}/Fe), E^0 (Fe^{2+}/Fe), E^0 (Cu^{2+}/Cu), and E^0 (Cu^{+}/Cu). [4 marks]

b) The exchange current density of the H^+/H_2 redox couple on a platinum electrode at 298K is 0.79 $mAcm^{-2}$. Estimate the current density when the overpotential, η, is +5.0 mV. [4 marks]

c) An inert platinum electrode of surface area 2.0 cm^2 in contact with an aqueous solution of a redox couple at 298 K, produced the tabulated currents with the change in overpotential. Determine the exchange-current density, j_0, and the transfer coefficient, α, for this electrode processes. [6 marks]

η (mV)	50	100	150	200	250	300
I(mA)	0.3	1.5	6.4	27.6	118.6	510

d) State the type of each electrode in each cell below, and write the cell reactions for the cells:

(i) $Pt(s)|H_2(g)|\ H^+(aq)\ ||\ MnCl_2(aq), HCl(aq)\ |\ MnO_2(s)\ |\ Pt(s)$

(ii) $Pt(s)|\ Fe^{3+}(aq), Fe^{2+}(aq)||\ Sn^{2+}(aq)\ |\ Sn(s)$. [6 marks]

QUESTION 3

a) Distinguish colloidal systems from solutions [2 marks]

b) Copy and complete the table with the type of colloidal system formed by each combination. [6 marks]

		Disperse phase		
		Gas	liquid	solid
Dispersion medium	Gas			
	liquid			
	solid			

c) Sketch the DVLO potential energy curve for the stability of colloidal particles. Indicate regions where flocculation, coagulation, and separation, and give brief descriptions. [6 marks]

d) The adsorption of CO on charcoal at 273K produced the following set of data. Show that the adsorption process obeys the Langmuir isotherm, and evaluate the parameters α and V_∞. [6 mark]

p (Pa)	13 300	26 700	40 000	53 300	66 700	80 000	93 300
V (cm^3)	10.2	18.6	25.5	31.5	36.9	41.6	46.1

QUESTION 4

a) A certain industrial process has a reaction that has two paths to two different products, one product being favoured by kinetics and the other being favoured by thermodynamics. How can one manipulate the reaction to favour either of the products? [4 marks]

b) Use the steady state approximation to derive the rate law for the decomposition of N_2O_5. [6 marks]

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

This is the suggested mechanism:

$N_2O_5 \rightarrow NO_2 + NO_3$ $\quad k_{a1}$
$NO_2 + NO_3 \rightarrow N_2O_5$ $\quad k_{a2}$
$NO_2 + NO_3 \rightarrow NO_2 + NO + O_2$ $\quad k_b$
$N_2O_5 + NO \rightarrow NO_2 + NO_2 + NO_2$ $\quad k_c$

c) The rate constants of the forward and the reverse reactions for a dimerization reaction were found to be 8.0×10^8 dm^3 $mol^{-1}s^{-1}$ (2nd order) and 2.0×10^6 s^{-1} (1st order). Calculate the equilibrium constant for this reaction. [4 marks]

d) A decomposing organic compound's concentration with time followed and 327 °C produced data in the table below. Confirm that the reaction is first order and find the rate constant and half-life for this reaction. [6 marks]

t(s)	0	1000	2000	3000	4000
$[A]/[A_0]$	1	0.700	0.488	0.340	0.0238

Table 6D.1 Standard potentials at 298 K. (b) In alphabetical order

Reduction half-reaction	E°/V	Reduction half-reaction	E°/V
$Ag^+ + e^- \rightarrow Ag$	+0.80	$Cu^+ + e^- \rightarrow Cu$	+0.52
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713	$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$F_2 + 2e^- \rightarrow 2F^-$	+2.87
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$AgF + e^- \rightarrow Ag + F^-$	+0.78	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04
$AgI + e^- \rightarrow Ag + I^-$	−0.15	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$Al^{3+} + 3e^- \rightarrow Al$	−1.66	$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36
$Au^+ + e^- \rightarrow Au$	+1.69	$2H^+ + 2e^- \rightarrow H_2$	0, by definition
$Au^{3+} + 3e^- \rightarrow Au$	+1.40	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.91	$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60
$Be^{2+} + 2e^- \rightarrow Be$	−1.85	$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63
$Bi^{3+} + 3e^- \rightarrow Bi$	+0.20	$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76	$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.81	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40	$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.48	$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	$I_3^- + 2e^- \rightarrow 3I^-$	+0.53
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89	$In^+ + e^- \rightarrow In$	−0.14
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23	$In^{2+} + e^- \rightarrow In^+$	−0.40
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36	$In^{3+} + 2e^- \rightarrow In^+$	−0.44
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	$In^{3+} + 3e^- \rightarrow In$	−0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$In^{3+} + e^- \rightarrow In^{2+}$	−0.49
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91	$K^+ + e^- \rightarrow K$	−2.93
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33	$La^{3+} + 3e^- \rightarrow La$	−2.52
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74	$Li^+ + e^- \rightarrow Li$	−3.05
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$Cs^+ + e^- \rightarrow Cs$	−2.92	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51	$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56	$Ra^{2+} + 2e^- \rightarrow Ra$	−2.92
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60	$Rb^+ + e^- \rightarrow Rb$	−2.93
$Na^+ + e^- \rightarrow Na$	−2.71	$S + 2e^- \rightarrow S^{2-}$	−0.48
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05
$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49	$Sc^{3+} + 3e^- \rightarrow Sc$	−2.09
$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	+0.80	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.10	$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40	$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.37
$O_2 + e^- \rightarrow O_2^-$	−0.56	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08	$Tl^+ + e^- \rightarrow Tl$	−0.34
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07	$U^{3+} + 3e^- \rightarrow U$	−1.79
$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24	$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13	$V^{2+} + 2e^- \rightarrow V$	−1.19
$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67	$V^{3+} + e^- \rightarrow V^{2+}$	−0.26
		$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76

Table 21.5 Limiting ionic conductivities in water at 298 K, $\lambda/(\mathrm{mS\ m^2\ mol^{-1}})$

Cations		Anions	
Ba^{2+}	12.72	Br^-	7.81
Ca^{2+}	11.90	$CH_3CO_2^-$	4.09
Cs^+	7.72	Cl^-	7.635
Cu^{2+}	10.72	ClO_4^-	6.73
H^+	34.96	CO_3^{2-}	13.86
K^+	7.350	$(CO_2)_2^{2-}$	14.82
Li^+	3.87	F^-	5.54
Mg^{2+}	10.60	$[Fe(CN)_6]^{3-}$	30.27
Na^+	5.010	$[Fe(CN)_6]^{4-}$	44.20
$[N(C_2H_5)_4]^+$	3.26	HCO_2^-	5.46
$[N(CH_3)_4]^+$	4.49	I^-	7.68
NH_4^+	7.35	NO_3^-	7.146
Rb^+	7.78	OH^-	19.91
Sr^{2+}	11.89	SO_4^{2-}	16.00
Zn^{2+}	10.56		

Ions in solution

$$\Lambda_m^\circ = \nu_+\lambda_+ + \nu_-\lambda_-$$

$$\Lambda_m = \alpha\Lambda_m^\circ$$

$$\lambda = zuF$$

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

$$\log \gamma_\pm = -|z_+z_-|AI^{1/2}$$

$$I = \tfrac{1}{2}\sum_i z_i^2(b_i/b^\ominus)$$

$$I = \tfrac{1}{2}(b_+z_+^2 + b_-z_-^2)/b^\ominus$$

Electrode process

$$E^{\ominus}_{\text{cell}} = -\frac{\Delta_r G^{\ominus}}{\nu F}$$

$$E^{\ominus}_{\text{cell}} = \frac{RT}{\nu F}\ln K$$

$$j \approx j_0 f\eta \qquad \text{for } |\eta| < 0.1 \;;\; F/RT = f$$

$$\ln j = \ln j_0 + (1-\alpha) f\eta \qquad \eta > 0.1\text{ V}$$

$$\ln j = \ln j_0 - \alpha f\eta \qquad \eta < -0.1\text{ V}$$

Kinetics

$$[\mathrm{A}] = [\mathrm{A}]_0 - k_r t$$

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -k_r t, \qquad [\mathrm{A}] = [\mathrm{A}]_0 \mathrm{e}^{-k_r t}$$

$$\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0} = k_r t, \quad [\mathrm{A}] = \frac{[\mathrm{A}]_0}{1 + k_r t[\mathrm{A}]_0}$$

$$K = \frac{[\mathrm{B}]_{\text{eq}}}{[\mathrm{A}]_{\text{eq}}} = \frac{k_r}{k_r'}$$

$$\ln k_r = \ln A - \frac{E_a}{RT}$$

$$\ln\frac{k_{r,2}}{k_{r,1}} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Adsorption

$$\frac{p}{V} = \frac{1}{\alpha V_\infty} + \frac{1}{V_\infty}p$$

$$\left(\frac{\partial \ln(\alpha p^{\ominus})}{\partial(1/T)}\right)_\theta = -\frac{\Delta_{\text{ad}} H^{\ominus}}{R}$$

$$\Gamma_s = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln(c/c^{\ominus})}\right)_T$$