UNIVERSITI
TEKNOLOGI
PETRONAS

FINAL EXAMINATION
MAY 2024 SEMESTER

COURSE : **CFB1023 - PHYSICAL CHEMISTRY**

DATE : **1 AUGUST 2024 (THURSDAY)**

TIME : **9.00 AM - 12.00 NOON (3 HOURS)**

INSTRUCTIONS TO CANDIDATES

1. Answer **ALL** questions in the Answer Booklet.
2. Begin **EACH** answer on a new page in the Answer Booklet.
3. Indicate clearly answers that are cancelled, if any.
4. Where applicable, show clearly steps taken in arriving at the solutions and indicate **ALL** assumptions, if any.
5. **DO NOT** open this Question Booklet until instructed.

Note :

i. There are **NINE (9)** pages in this Question Booklet including the cover page and appendices.

ii. **DOUBLE-SIDED** Question Booklet.

iii. **Graph paper will be provided.**

1. a. Explain the construction and working principle of adiabatic bomb calorimeter.

[6 marks]

b. An ideal gas with 1.65 moles is subjected to two successive changes in as stated in following processes below:

PROCESS 1: From 39°C and 100×10^3 Pa, the gas is expanded isothermally against a constant pressure of 16.5×10^3 Pa to twice the initial volume.

PROCESS 2: At the end of the previous process, the gas is cooled at constant volume from 39°C to -25°C. The specific heat at constant volume is, $C_{v,m} = 3/2\ R$.

Calculate Q, W, ΔU and ΔH for each process and for the overall process.

[14 marks]

2. a. Ideal solutions assume no interactions between the solvent and solute molecules within the liquid as well as in the gas. Using vapor pressure diagram, explain **THREE (3)** laws that govern the behaviour of vapour pressure of ideal solution.

[9 marks]

b. Naphthalene ($C_{10}H_8$) melts at 353.35 K. If the vapour pressure of the liquid is 1.3 kPa and 5.3 kPa at 358.95 K and 392.45 K, respectively, calculate:

i. the enthalpy of vaporization.

[4 marks]

ii. the normal boiling point.

[4 marks]

iii. the entropy of vaporization at the boiling point.

[3 marks]

3. a. Consider reaction A→B is a second order of reaction, explain and prove that the rate constant is linearly correlated between inverse concentration of the reactant A with reaction time.

[8 marks]

b. The initial rate of reaction for the reaction, $2NO\ (g) + 2H_2\ (g) \rightarrow N_2\ (g) + 2H_2O\ (g)$ was measured for several different starting concentrations of NO and H_2 as given below in **TABLE Q3**.

TABLE Q3: Initial concentrations of NO and H_2

Experiment	[NO], M	[H_2], M	Initial rate, M/s
1	0.0050	0.0020	1.25×10^{-5}
2	0.0100	0.0020	5.00×10^{-5}
3	0.0100	0.0040	1.00×10^{-4}

i. Determine the rate law.

[4 marks]

ii. Find the overall order of reaction.

[4 marks]

iii. Calculate the rate constant, *k*.

[4 marks]

4. a. Nitrogen gas is adsorbed on TiO_2 at 75 K. N_2 adsorption at different pressure is given in **TABLE Q4**.

TABLE Q4

P(kPa)	1.60	1.87	6.11	11.67	17.02	21.92	27.29
V(mm^3)	235	559	649	719	790	860	950

The experimental conditions are:

Vapour pressure of N_2 at 75 K, P^* = 76 kPa.

Mass of TiO_2, m =1.0 g.

N_2 cross-sectional area = 0.16 nm^2.

i. Analyze and prove that the data follow BET isotherm.

[12 marks]

ii. Calculate the monolayer volume, (V_{mon}) of the adsorption process.

[4 marks]

iii. Calculate the specific surface area, (S_T) of TiO_2.

[4 marks]

5. a. Construct and explain the electrolytic cell used in industrial application.

[6 marks]

b. Consider the electrochemical cell

$$Zn(s) \mid ZnCl_2 \parallel Hg_2Cl_2(s) \mid Hg(l)$$

i. Write the relevant half-reactions at anode and cathode.

[4 marks]

ii. Calculate the standard potential of the cell, $E°$.

[4 marks]

iii. Assess the spontaneity of the electrochemical cell and calculate the equilibrium constant, k for the electrochemical system.

[6 marks]

-END OF PAPER-

APPENDIX: A

Ideal Gas

$PV = nRT$

Molar heat capacity at constant pressure, $C_{P,m}$: $\frac{5}{2}R$

Molar heat capacity at constant volume, $C_{V,m}$: $\frac{3}{2}R$

Constants

Gas constants, R:

- 83.145 cm^3 bar/K-mol
- 82.055 cm^3 atm/K-mol
- 0.0821 L atm/K-mol
- 8.314 J/K-mol
- 1.9872 cal/K-mol

Faraday's constant, F: 96,485 C/mol

Avogadro's constant, A: 6.022 x 10^{23} mol^{-1}

Gravitational acceleration, g: 980.7 cm/s^2

Thermodynamic formula

$PV=nRT$

$\Delta H = \Delta U + P\Delta V$ at constant P

$\Delta U = q + w$

$w = -\int PdV$

$\Delta H = q_P = \int C_P dT$

$\Delta U = q_V = \int C_V dT$

$\Delta S = \int \frac{dq_{rev}}{T}$

$ln\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$;

$\Delta S = \Delta H/T$

Properties of water

Specific heat capacity of liquid water, C_P: 4.184 J/g-K

Specific heat capacity of water vapour, C_P: 1.841 J/g-K

Molar heat capacity of liquid water, $C_{P,m}$: 75.312 J/mol-K

Molar heat capacity of water vapour, $C_{P,m}$: 33.138 J/mol-K

Conversion factors

$T(K) = t(^oC) + 273.15$

1 atm = 760 torr = 101325 Pa

1 bar =10^6 dyn/cm = 0.9869 atm-cm

1 bar = 750.062 torr = 10^5 Pa

1 Pa = 1 N/m^2

1 cal = 4.184 Joule

1 V = 1 J/C

1 dyn = 1 $g\text{-}cm/s^2$

1 dyn/cm = 1 erg/cm^2 = 10^{-3} J/m^2

1 erg = 10^{-7} J

1 inch = 2.54 cm

1 Å = 10^{-8} cm = 0.1 nm

1 liter = 1 dm^3 = 1000 cm^3

$$w_{rev} = -nRT\ln\left(\frac{V_2}{V_1}\right) = -nRT\ln\left(\frac{P_1}{P_2}\right)$$

APPENDIX: B

Electrochemical Formula

$\Delta G° = -nFE°$

$$\ln K = \frac{nFE^o}{RT}$$

$$E^o = E_R - E_L$$

Chemical kinetics

$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$[A] = [A]_0 - kt$$

$$[A] = [A]_0 e^{-kt}$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

$$K = Ae^{-Ea/RT}$$

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Adsorption Isotherm Model

$$\frac{P}{V(P^* - P)} = \frac{1}{V_{mon}c} + \frac{c-1}{V_{mon}c}\frac{P}{P^*}$$

$$V_{mon} = \frac{1}{Slope + Intercept}$$

$$S_T = \frac{(V_{mon})(N_A)(A_{CS})}{(V_{STP})(w)}$$

Electrochemical Table

APPENDIX: C

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		