UNIVERSITI TEKNOLOGI PETRONAS

FINAL EXAMINATION
JANUARY 2025 SEMESTER

COURSE	**:**	**CFB1023 - PHYSICAL CHEMISTRY**
DATE	**:**	**19 APRIL 2025 (SATURDAY)**
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 papers will be provided.**

1. a. Fundamental engineering issues related to gas separation typically rely on the ideal gas equation. List **FOUR (4)** assumptions and define **THREE (3)** gas laws that govern the ideal gas equation.

[10 marks]

b. At 1 atm and 300 K, a 2 mol ideal gas system with $C_{V,m} = 3/2\ R$ expands adiabatically in a reversible manner from 1350 cm^3 to 1500 cm^3.

i. Calculate the final pressure and final temperature of the system.

[6 marks]

ii. Deduce the amount of heat (Q), change in internal energy (ΔU) and entropy (ΔS) of the system.

[4 marks]

2. a. Adiabatic bomb calorimeters are typically used to evaluate the enthalpy of combustion of materials. Describe the working principle of an adiabatic bomb calorimeter with pictorial aid and appropriate assumptions.

[5 marks]

b. Meor observes a shift in pressure and temperature of an ideal gas system which is confined to a rigid container due to heating while the mass of the system remains constant. Meor formulates the first inference on the work done by the ideal gas system. He then proceeds to add liquid water to the system and arrives at the second inference. The two inferences formulated are as follows:

Inference 1 : The work done by the ideal gas system has a negative value.

Inference 2 : The intensive properties of the ideal gas and liquid water are similar.

Validate Meor's inferences with proper reasoning. List **TWO (2)** intensive properties and **TWO (2)** extensive properties relevant to the system.

[5 marks]

c. A binary system consisting of crude oil and water observes liquid-liquid immiscibility at lower temperature conditions. However, upon continuous heating, the region of liquid-liquid immiscibility decreases. Sketch a phase diagram for the system correlating the relationship between temperature and compositions of crude oil and water. Label the axes, phase conditions, degree of freedom for each phase and critical points appropriately.

[5 marks]

d. Ethanol has a vapor pressure of 44.4 Torr at 25°C and 150.0 Torr at 45°C. Identify the normal boiling point of ethanol.

[5 marks]

3. Zul observed the dissolution of 1-bromo-1,1-dimethylethane, $(CH_3)_3CBr$ in water over a duration of one day. Zul deduced that the dissolution of $(CH_3)_3CBr$ in water follows a first-order reaction. The data collected on the concentration of $(CH_3)_3CBr$ over time is depicted in **TABLE Q3**:

TABLE Q3: Dissolution of $(CH_3)_3CBr$ over one day.

Time (hr)	0	3	6	9	18	24
Concentration of $(CH_3)_3CBr$ (mol/L)	1.08	0.90	0.75	0.63	0.37	0.26

a. Derive the first-order rate law equation.

[5 marks]

b. Analyze Zul's findings to affirm that the reaction follows a first-order rate law with respect to the derivation in **part (a)**.

[5 marks]

c. Based on **part (b)**, identify the rate constant, k and deduce the molar concentration of $(CH_3)_3CBr$ after 2 days.

[5 marks]

d. Zul intends to prolong the half-life of the reaction by increasing the initial concentration of $(CH_3)_3CBr$ to 2 mol/L. Evaluate Zul's proposal and justify your evaluation.

[5 marks]

4. a. Adsorption is the attachment of absorbate molecules or particles on the surface of an underlying material, also known as an adsorbent. Describe **FIVE (5)** key differences between physical and chemical adsorption.

[10 marks]

b. The adsorption of ammonia on barium fluoride adheres to the Brunauer-Emmett-Teller (BET) isotherm. The results for adsorption of ammonia on barium fluoride are shown in **TABLE Q4.**

TABLE Q4: Adsorption of ammonia on barium fluoride at 5 to 80 kPa.

Pressure (kPa)	5	15	30	60	75	80
Volume absorbed (cm^3)	9.2	10.3	11.3	12.9	13.1	13.4

i. At 20°C, the vapor pressure of adsorbate, P^* is 820 kPa. Examine that the reaction fits the BET isotherm by graphical method.

[5 marks]

ii. Based on **part b(i)**, identify the volume corresponding to a monolayer, V_{mon} and constant, c at 20°C.

[5 marks]

5. a. Electrochemical cells are heterogeneous systems observing a difference of electric potential between two or more phases. List the **TWO (2)** types of electrochemical cells, state their difference and **ONE (1)** application corresponding to each type of electrochemical cell.

[5 marks]

b. Consider an electrochemical cell that has the following notation:

$$Ni(s) \mid NiSO_4\ (0.5\ M) \mid Hg_2Cl_2(s) \mid Hg(l)$$

i. Define the half and overall cell reactions then, calculate the standard potential, $E°$ of the cell.

[5 marks]

ii. Assess the spontaneity of the electrochemical cell and calculate the equilibrium constant, K for the electrochemical system.

[5 marks]

iii. Should the concentration of $NiSO_4$ be raised to 1.0 M, evaluate the effect on the cell potential, E at 298 K. Provide adequate justification.

[5 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

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

$\Delta U = q + w$

$w = -\int PdV$

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

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

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

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

PV^{γ} = constant

$\gamma = \frac{C_p}{C_V}$

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

$T(K) = t(°C) + 273.15$

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

$\Delta G° = -nFE°$

$$\ln K = \frac{nFE°}{RT}$$

$$a_i = \left(\nu_{\pm} \gamma_{\pm} \frac{m_i}{m^o} \right)^{\nu}$$

$$(a_+)^{\nu_+}(a_-)^{\nu_-} = (\nu_+)^{\nu_+}(\nu_-)^{\nu_-}\left(\gamma_{\pm} \frac{m_i}{m^o} \right)^{\nu_+ + \nu_-}$$

$$\gamma_{\pm}^{\nu} = (\gamma_+^{\nu_+})(\gamma_-^{\nu_-})$$

$$\nu_{\pm}^{\nu} = (\nu_+^{\nu_+})(\nu_-^{\nu_-})$$

$$E^o = E_R - E_L$$

$$E = E° - \frac{RT}{nF} \ln Q$$

Chemical kinetics

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

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

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

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

Adsorption Isotherm Model

$$\theta = \frac{V}{V_{mon}} = \frac{KP}{1 + KP}$$

$$\frac{P}{V} = \frac{1}{KV_{mon}} + \frac{P}{V_{mon}}$$

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

$$slope = \frac{c-1}{V_{mon}c}$$

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

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

$$V = KP^a$$

Electrochemical Table

APPENDIX: C

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

Half-reaction	$\mathscr{E}^\circ$ (V)	Half-reaction	$\mathscr{E}^\circ$ (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		