UNIVERSITI TEKNOLOGI PETRONAS

FINAL EXAMINATION
MAY 2022 SEMESTER

COURSE	**:**	**YAB2023 - PHYSICAL CHEMISTRY II**
DATE	**:**	**10 AUGUST 2022 (WEDNESDAY)**
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 **TEN (10)** pages in this Question Booklet including the cover page .

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

iii. Use graph paper for Question 4 and Question 5. d.

1. a. Discuss the Grotthus mechanism of proton conduction in liquid water.

[2 marks]

b. A sample of gaseous uranium hexafluoride, UF_6, (M_w: 352.0 g/mol) is held at a temperature of 300 K and a pressure of 0.1 mbar. The collision diameter of UF_6 is 0.40 nm. Under these conditions, calculate the:

i. Mean speed of the molecules, $\bar{c}$

[2 marks]

ii Collision frequency, z

[3 marks]

ii. Mean free path, λ

[3 marks]

c. Neon lighting is used in cold regions and aircraft because the light emitted from ionized neon can pass through water fog. Assuming neon gas, (M_w: 20.18 g/mol) is confined in a cubic vessel of length 15 cm, with different temperature at each wall, one wall at 305 K and the one opposite at 295 K. Given $C_{v,m}$: 12.4715 J/K.mol and σ: 0.24 nm, calculate the;

i. Thermal conductivity, k

[4 marks]

ii. Neon gas flux, J from one wall to the other

[4 marks]

iii. Rate of energy loss

[2 marks]

2. a. The rate of consumption of B in the reaction $A + 3B \rightarrow C + 2D$ is $7.20 \text{ mol dm}^{-3} \text{ s}^{-1}$.

i. State the rate of reaction, v.

[2 marks]

ii. Calculate the rates of formation or consumption of A, C and D.

[4 marks]

iii. If the experimental rate law was found to be $v = k_r [A] [B]^2$, suggest the unit for the rate constant.

[2 marks]

b. At 400 K, the rate of decomposition of acetaldehyde gaseous compound initially at a pressure of 12.6 kPa, dropped to 9.71 Pa/s when 10.0% had reacted and 7.67 Pa/s when 20.0% had reacted. Determine the order of the reaction.

[6 marks]

c. The rate constant of N_2O_5 decomposition is $1.70 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 24°C and $2.01 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 37°C.

i. Determine the activation energy, E_a of N_2O_5 decomposition.

[4 marks]

ii. Evaluate the Arrhenius parameters of the reaction.

[2 marks]

3. a. i. Distinguish between a diffusion-controlled reaction and an activation-controlled reaction.

[4 marks]

ii. Define the Cage effect.

[2 marks]

b. In a research laboratory, recombination of two atoms in benzene at 298 K will be conducted at 298 K with η = 0.601 cP. Assuming the reaction is elementary and initial concentration of the reactant is 1.8 mmol dm^{-3}.

i. Determine the diffusion-controlled rate constant, k_d.

[4 marks]

ii. Calculate the duration required for the reaction to be 50% complete.

[4 marks]

c. The reactive cross-section obtained from experimental value of the pre-exponential factor is 8.7×10^{-22} m^2 for the gaseous reaction A + B→P. The collision cross-sections of A and B estimated from the transport properties are 0.88 and 0.40 nm^2, respectively. Calculate the P factor for the reaction.

[6 marks]

4. The rates of thermolysis of a variety of *cis*- and *trans*-azoalkanes have been measured over a range of temperatures concerning the mechanism of the reaction. In ethanol solvent, an unstable *cis*-azoalkane decomposed at a rate that was followed by observing the N_2 progression, which led to the rate constants listed in **TABLE Q4**.

TABLE Q4: Rate constants of reaction at various temperatures.

T (°C)	−24.82	−20.73	−17.02	−13.00	−8.95
k (s^{-1})	1.22 x 10^{-4}	2.31 x 10^{-4}	4.39 x 10^{-4}	8.50 x 10^{-4}	14.3 x 10^{-4}

a. By using a graph paper, construct a suitable plot ($-ln\ k$ vs. $1/T$) and determine activation energy, E_a.

[8 marks]

c. Determine the pre-exponential factor, A with its correct unit.

[4 marks]

d. Evaluate the enthalpy of activation, ΔH at -40°C.

[3 marks]

e. Determine the entropy, ΔS at -40°C.

[3 marks]

f. Calculate the Gibbs free energy of activation, ΔG at -40°C.

[2 marks]

5. a. Propose **THREE (3)** examples of adsorption isotherms.

[6 marks]

b. A monolayer of carbon monoxide molecules with effective area 0.165 nm^2 is adsorbed on the surface of 1.00 g of an Fe/Al_2O_3 catalyst at 77 K. Immediately after warming, the carbon monoxide occupies 4.25 cm^3 at 0°C and 1.00 bar. Determine the surface area of the catalyst.

[4 marks]

c. The adsorption of hexacyanoferrate(III) ion, $[Fe(CN)_6]^{3-}$, on γ-Al_2O_3 from aqueous solution was examined in metal removal, part of a wastewater treatment research project. They modelled the adsorption with a modified Langmuir isotherm, which obtain the following values of K at pH = 6.5 in **Table Q5**. Given $\Delta_{ads}S^{\ominus}$ = +146 J mol^{-1} K^{-1} at 298 K under these conditions

TABLE Q5: Rate constants of reaction at various temperatures.

T (K)	283	298	308	318
K	2.642 x 10^{-11}	2.078 x 10^{-11}	1.286 x 10^{-11}	1.085 x 10^{-11}

i. By using a graph paper, construct a suitable plot (*ln K vs. 1/T*) and determine the isosteric enthalpy of adsorption, $\Delta_{ads}H^{\ominus}$.

[6 marks]

ii. Determine $\Delta_{ads}G^{\ominus}$

[4 marks]

-END OF PAPER-

APPENDIX I

PHYSICAL CONSTANTS

Atomic mass unit	1 amu	= 1.661×10^{-24} g
	1 g	= 6.022×10^{23} amu
Avogadro's number	N_A	= 6.022×10^{23} / mol
Boltzmann's constant	k	= 1.381×10^{-23} J/K
Electron charge	e	= 1.602×10^{-19} C
Faraday's constant	$F = Ne$	= 9.649×10^{4} C/mol
Gas constant	R	= 8.314 J/mol-K
		= 0.08206 L-atm/mol-K
Mass of electron	m_e	= 9.110×10^{-31} kg
Mass of neutron	m_n	= 1.675×10^{-27} kg
Mass of proton	m_p	= 1.673×10^{-27} kg
Atomic mass constant	m_u	= 1.660×10^{-27} kg
Pi	π	= 3.142
Planck's constant	h	= 6.626×10^{-34} J-s
Speed of light	c	= 2.998×10^{8} m/s
Rydberg constant	R_H	= 1.097×10^{7} m^{-1}
	hcR_H	= 2.179×10^{-18} J

APPENDIX II

CONVERSION FACTORS AND FORMULAS

Length: SI unit: meter (m)		**Pressure: SI unit : Pascal (Pa)**	
1 km	= 0.62137 mi	1 Pa	= 1 N m^{-2}
1 mi	= 5280 ft		= 1 kg $m^{-1}s^{-2}$
	= 1.6093 km	1 atm	= 101325 Pa
1 m	= 1.0936 yd		= 760 torr
1 in.	= 2.54 cm		= 760 mmHg
1 cm	= 0.39370 in.		= 14.70 lb in^{-2} (or psi)
1 Å	= 10^{-10} m	1 bar	= 10^{5} Pa
			= 750 torr
			= 750 mmHg
Mass: SI unit: kilogram (kg)		**Volume: SI unit: cubic meter (m^3)**	
1 kg	= 2.2046 lb	1 L	= 10^{-3} m^3
1 lb	= 453.59 g		= 1 dm^3
	= 16 oz		= 10^3 cm^3
1 amu	= 1.66054 x 10^{-24} g		= 1.0567 qt
		1 gal	= 4 qt
			= 3.7854 L
		1 cm^3	= 1 mL
		1 in^3	= 16.39 cm^3

APPENDIX III

FORMULAS

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\bar{c}_{rel} = \sqrt{2}\,\bar{c}$$

$$\lambda = \frac{kT}{\sqrt{2}\sigma p}$$

$$z = \frac{\sigma \bar{c}_{rel}\, p}{kT}$$

$$z = \frac{\bar{c}_{rel}}{\lambda}$$

$$Z_W = \frac{N_A p}{(2\pi MRT)^{1/2}}$$

$$Rate = Z_W A = \frac{N_A p A}{(2\pi MRT)^{1/2}}$$

$$\Delta mass_{loss} = Z_W A m \Delta t$$

$$J(charge) = zuvcFE$$

$$J(ions) = \frac{s\Delta t A v c N_A}{A\Delta t} = svcN_A$$

$$D = \frac{1}{3}\lambda \bar{c}$$

$$\kappa = \frac{1}{3}\lambda \bar{c}\, C_{V,m}[A]$$

$$\eta = \frac{1}{3}\lambda \bar{c}\, m\mathrm{N}$$

Rate of reaction; $v = \left(\frac{1}{v_J}\right)\frac{d[J]}{dt}$

First order integrated law; $k_r t = \frac{\ln[A]_0}{[A]_0 - x}$

Second order integrated law; $k_r t = \frac{1}{[B]_0 - 2[A]_0} \ln[\frac{[A]_0([B]_0 - 2[P])}{([A]_0 - [P])[B]_0}]$

Third order integrated law; $2k_r t = \frac{1}{2}(\frac{1}{[A]^2} - \frac{1}{[A]_0^2})$

First order; $t_{½} = \frac{\ln 2}{k_r'}$

$$p = p_0 e^{-k_r t}$$

$$E_a = E_a(a) + E_a(b) - E_a'(a)$$

$$k_r = Ae^{-\frac{E_a}{RT}}$$

$$k_r = N_A \sigma c_{rel} e^{-E_a/RT}$$

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

$$k = Ae^{-E_a/RT}$$

$$\Delta^{‡}H = E_a - RT$$

$$\Delta^{‡} S = R\left[ln\left(\frac{hA}{kT}\right) - 1\right]$$

$$\Delta^{‡}G = \Delta^{‡}H - T\Delta^{‡}S$$

$$\theta = \frac{Kp}{1 + Kp}$$

$$\theta = \frac{V}{V_{mon}}$$

$$\frac{V_1/V_{mon}}{p_1(1 - V_1/V_{mon})} = \frac{V_2/V_{mon}}{p_2(1 - V_2/V_{mon})}$$

$$\ln(K) = \frac{-\Delta_{ad}H^{\ominus}}{RT} + \frac{\Delta S^{\ominus}}{R}$$

$$-\Delta_{ads}G^{\ominus} = -\Delta_{ads}H^{\ominus} - T\,\Delta_{ads}S^{\ominus}$$