

SULIT



First Semester Examination
2020/2021 Academic Session

February 2021

KFT332 – Physical Chemistry II

Duration: 2 hours

Please check that this examination paper consists of **Seven (7)** pages of printed material before you begin the examination.

Instructions:

This paper has **FIVE (5)** questions in **SECTIONS A** and **B**. Answer all **THREE (3)** questions from **SECTION A** and at least **ONE (1)** question from **SECTION B**.

Answer each question on a new page.

If a candidate answers more than four questions, only the answers to the first four questions in the answer sheet will be graded.

Appendix: Fundamental constants in physical chemistry.

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SECTION A

1. (a) (i) Define the greenhouse effect.
- (ii) State the first and second laws of thermodynamics. Relate briefly these thermodynamic laws to the greenhouse effect.

(8 marks)

- (b) Describe the positive, negative and positive deviation from the Raoult's law and the causes using the appropriate phase diagram for solution A, B and C, respectively.

<u>Solution</u>	<u>Deviation</u>	<u>Parameter</u>
A	Positive	Pressure against a liquid-vapour composition
B	Negative	Temperature against a liquid-vapour composition
C	Positive	Vapour pressure against liquid composition

(9 marks)

- (c) Explain the asymmetric and electrophoretic effects with suitable illustrations.

(8 marks)

2. (a) Glucose metabolism involves multiple processes including glycolysis, gluconeogenesis and glycogenolysis. A researcher experimentally determined that the work done from this metabolism process at 25 °C is $-2315 \text{ kJ mol}^{-1}$. Infer if the work done is equivalent to the maximum reversible work.

Given that ΔU° and ΔS° are $-2801.3 \text{ kJ mol}^{-1}$ and $260.7 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively.

(3 marks)

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- (b) Starting from the first and second laws of thermodynamics, show that

$$\left(\frac{\partial H}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P + V$$

(6 marks)

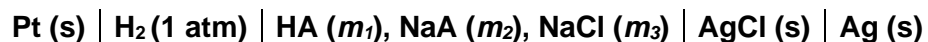
- (c) A partial molar volume of K_2SO_4 in 1 kg of aqueous solution at 25 °C is expressed as:

$$\bar{V}_{K_2SO_4} = (32.280 + 18.216m^{1/2} + 0.0222m) \text{ cm}^3 \text{ mol}^{-1}$$

where m is molality. Deduce the equation to state the partial molar volume of water, if the molar volume of water at 25 °C is $17.963 \text{ cm}^3 \text{ mol}^{-1}$.

(8 marks)

- (d) Derive the equation of dissociation constant, K_a , by applying cell e.m.f. principle and Nernst equation for the following cell notation.



(8 marks)

3. (a) Two reversible heat engines, A and B are arranged in series. Engine A receives 200 kJ of heat at a temperature of 421 °C from a boiler and rejects heat directly to engine B. Engine B is connected to a cold sink at a temperature of 5 °C. If the work produced from engine A is twice that of B, calculate

- (i) the intermediate temperature between A and B.
- (ii) the efficiency of each engine.
- (iii) the heat rejected to the cold sink.

(8 marks)

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- (b) The partial molar volume of ethanol, \bar{V}_1 , and water, \bar{V}_2 , at 20 °C to mole fraction of ethanol X_1 , in ethanol-water mixture solution is given by the following data:

X_1	$\bar{V}_1 / \text{cm}^3 \text{mol}^{-1}$	$\bar{V}_2 / \text{cm}^3 \text{mol}^{-1}$
0.10	53.10	18.11
0.20	55.40	17.67
0.40	57.10	17.01
0.60	57.87	16.21

Determine the volume of solution and its density for a solution containing 40.0 g of water and 60.0 g ethanol. Given the molecular weight of ethanol is 46 g mol⁻¹.

(8 marks)

- (c) The conductivity, κ , values for different concentrations of aqueous KCl is tabulated below:

Concentration, $C / \text{mol dm}^{-3}$	0.001	0.005	0.010	0.020
Conductivity, $\kappa / 10^{-4} \text{ S cm}^{-1}$	1.469	7.175	0.1412	0.2764

Calculate:

- molar conductivity, Λ_m , for each concentrations.
- Kohlrausch coefficient, K , using the graphical method.

(9 marks)

SECTION B

4. (a) A container consists of He and N₂ with a mole ratio of 1:2 at 298 K. Both gases are separated by a removable partition. Using the value of ΔS , compare ΔG and ΔA for the gases upon removing the partition in the container.

(8 marks)

- (b) A certain gas follows the following equation of state:

$$P\bar{V} = RT + \frac{4}{3}bP^3$$

where \bar{V} is the molar volume and b is a constant.

If b is zero, show:

- (i) the value of fugacity is equal to the value of the pressure.
 (ii) the value of fugacity coefficient is one.

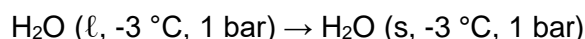
(8 marks)

- (c) The table below depicts molar conductivity, Λ_m , of chloroacetic acid for different concentrations at 25 °C. If the limiting molar conductivity, Λ^0 , value is 390.7 S cm² mol⁻¹, show that the dissociation constant value, K_a , for each concentration obeys Ostwald's dilution law.

Concentration, C / mol dm⁻³	0.005	0.01	0.02	0.05	0.10
Molar conductivity, Λ_m / S cm² mol⁻¹	22.80	16.20	11.57	7.36	5.20

(9 marks)

5. (a) Water is supercooled according to the following irreversible process:



Calculate ΔH , ΔS and ΔG for the above process.

Given that the molar enthalpy of fusion of ice is 6000 J mol⁻¹ at 0 °C and the \bar{C}_p of water and ice at 0 °C are 75.3 and 38.0 J K⁻¹ mol⁻¹, respectively.

(9 marks)

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- (b) The vapour pressure of a liquid sample in a temperature range of $-175\text{ }^{\circ}\text{C}$ and $25\text{ }^{\circ}\text{C}$ is expressed by the following equation:

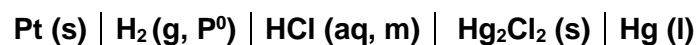
$$\ln P = T - 25000T^{-1} - 150$$

where P is in atm and T is in Kelvin.

Calculate the normal boiling point and the vaporisation enthalpy of the liquid.

(8 marks)

- (c) In an experiment, a researcher measured the cell e.m.f. values at ambient condition. The cell notation and the data obtained from the experiment is given below.



C / mmol kg⁻¹	3.2154	6.1538	10.0806	15.3876	21.8948
E / V	0.5708	0.5399	0.5165	0.4966	0.4800

Determine the standard cell potential, E° , graphically.

(8 marks)

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APPENDIX

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General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.99792458	10^8	m s^{-1}
Elementary charge	e	1.60218	10^{-19}	C
Faraday constant	$F = N_A e$	9.64853	10^4	C mol^{-1}
Boltzmann constant	k	1.38065	10^{-23}	J K^{-1}
Mass of electron	m_e	9.10938356	10^{-31}	kg
Gas constant	$R = N_A k$	8.31447		$\text{J K}^{-1} \text{mol}^{-1}$
		8.31447	10^{-2}	$\text{L bar K}^{-1} \text{mol}^{-1}$
		8.20574	10^{-2}	$\text{L atm K}^{-1} \text{mol}^{-1}$
		6.23637	10	$\text{LTorr K}^{-1} \text{mol}^{-1}$
Planck constant	h	6.62608	10^{-34}	J s
	$\hbar = h/2\pi$	1.05457	10^{-34}	J s
Avogadro constant	N_A	6.02214	10^{23}	mol^{-1}
Standard acceleration of free fall	g	9.80665		m s^{-2}

Conversion factors

Useful relation

Unit relations

1 eV	1.60218 x 10^{-19} J 96.485 kJ mol $^{-1}$ 8065.5 cm $^{-1}$	2.303 RT/F = 0.0591 V at 25 °C	Energy	1 J = 1 kg m 2 s $^{-2}$ = 1 A V s
			Force	1 N = 1 kg m s $^{-2}$
1 cal	4.184 J		Pressure	1 Pa = 1 N m $^{-2}$ = 1 kg m $^{-1}$ s $^{-2}$ = 1 J m $^{-3}$
1 atm	1.013 bar 101.325 kPa 760 Torr			
1 cm $^{-1}$	1.9864 x 10^{-23} J		Charge	1 C = 1 A s
1 Å	10^{-10} m		Potential difference	1 V = 1 J C $^{-1}$ = 1 kg m 2 s $^{-3}$ A $^{-1}$
1 L atm	101.325 J			

Atomic Weights

Al	26.98	C	12.01	Fe	55.85	P	30.97
Sb	121.76	Cs	132.92	Kr	83.80	K	39.098
Ar	39.95	Cl	35.45	Pb	207.2	Ag	107.87
As	74.92	Cr	51.996	Li	6.941	Na	22.99
Ba	137.33	Co	58.93	Mg	24.31	S	32.066
Be	9.012	Cu	63.55	Mn	54.94	Sn	118.71
Bi	208.98	F	18.998	Hg	200.59	W	183.84
B	10.81	Au	196.97	Ne	20.18	Xe	131.29
Br	79.90	He	4.002	Ni	58.69	Zn	65.39
Cd	112.41	H	1.008	N	14.01		
Ca	40.078	I	126.90	O	15.999		