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.

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 Raoul's law and the causes using the appropriate phase diagram for solution A, B and C, respectively.

Solution	Deviation	Parameter
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, glyconeogenesis and glycogenolysis. A researcher experimentally determined that the work done from this metabolism process at 25 °C is -2315 kJ mol^{-1}. Infer if the work done is equivalent to the maximum reversible work.

Given that $\Delta U°$ and $\Delta S°$ are −2801.3 kJ mol^{-1} and 260.7 J K^{-1} mol^{-1} respectively.

(3 marks)

(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:

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

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 cm^3 mol^{-1}.

(8 marks)

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

Pt (s) │ H_2 (1 atm) │ HA (*m_1*), NaA (*m_2*), NaCl (*m_3*) │ AgCl (s) │ Ag (s)

(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)

(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	$\bar{V}_1$ / cm^3 mol^{-1}	$\bar{V}_2$ / cm^3 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 / mol dm^{-3}	0.001	0.005	0.010	0.020
Conductivity, κ / 10^{-4} S cm^{-1}	1.469	7.175	0.1412	0.2764

Calculate:

(i) molar conductivity, Λ_m, for each concentrations.

(ii) Kohlrausch coefficient, K, using the graphical method.

(9 marks)

SECTION B

4. (a) A container consists of He and N_2 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 cm^2 mol^{-1}, show that the dissociation constant value, K_α, 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 cm^2 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:

$$H_2O\ (\ell, -3\ °C, 1\ bar) \rightarrow H_2O\ (s, -3\ °C, 1\ bar)$$

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 $\overline{C_p}$ of water and ice at 0 °C are 75.3 and 38.0 J K^{-1} mol^{-1}, respectively.

(9 marks)

(b) The vapour pressure of a liquid sample in a temperature range of -175 °C and 25 °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.

Pt (s) | H_2 (g, P^0) | HCl (aq, m) | Hg_2Cl_2 (s) | Hg (l)

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)

APPENDIX

UNIVERSITI SAINS MALAYSIA
School of Chemical Sciences

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		J K^{-1} mol^{-1}
		8.31447	10^{-2}	L bar K^{-1} mol^{-1}
		8.20574	10^{-2}	L atm K^{-1} mol^{-1}
		6.23637	10	LTorr K^{-1} 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**

Conversion factors		Useful relation	Unit relations	
1 eV	1.60218×10^{-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}	1.9864×10^{-23} J		Charge	1 C = 1 A s
1 Å 1 L atm	10^{-10} m 101.325 J		Potential difference	1 V = 1 J C^{-1} = 1 kg m^2 s^{-3} A^{-1}

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		

-oooOooo-