
UNIVERSITI SAINS MALAYSIA

Supplementary Semester Examination
Academic Session 2010/2011

June 2011

KFT 232 – Physical Chemistry II
[Kimia Fizik II]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of ELEVEN pages of printed material before you begin the examination.

Instructions:

Answer any **FIVE** (5) questions with at least **ONE** (1) question from Part B.

Answer each question on a new page.

You may answer the questions either in Bahasa Malaysia or in English.

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

In the event of any discrepancies, the English version shall be used.

Appendix: Fundamental constants in Physical Chemistry.

PART A

Answer not more than **FOUR** questions.

1. (a) A 64.0 g of O₂ is present at 25 °C and 1 atm pressure. Molar heat capacity of oxygen is equal to 29.33 J K⁻¹ mol⁻¹. Find the values of q, w and ΔU,
- (i) when the volume of the gas double under reversible isothermal process and,
- (ii) when the pressure of the gas double under isobaric process.

(10 marks)

- (b) A 25 g of ethanol at 50 °C is poured into 70 g of ethanol at 20 °C in an isolated vessel. Calculate the change in entropy for this process. Given that C_p = 111.5 J K⁻¹ mol⁻¹.

(10 marks)

2. (a) Use the following data for lead to calculate the standard entropy at 1000 K.

$$C_p(\text{Pb}_{(s)}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 23.6 + 9.6 \times 10^{-3} T$$

$$C_p(\text{Pb}_{(l)}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 32.2 - 2.75 \times 10^{-3} T$$

$$T_{\text{fus}} = 601 \text{ K}, \Delta_{\text{fus}}H = 4.77 \text{ kJ mol}^{-1}$$

(10 marks)

- (b) Derive the following equations;

$$(i) \quad \left(\frac{\partial H}{\partial T}\right)_S = C_P \left(\frac{\partial \ln T}{\partial \ln V}\right)_P$$

$$(ii) \quad \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$$

(10 marks)

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3. (a) A 20-L vessel is divided into two compartments with the help of a partition. The first compartment contains 12 L of hydrogen and the second compartment contains 10 L of nitrogen. The partition is withdrawn and the gases are allowed to mix isothermally at 1 atm and 298 K. Estimate ΔG_{mixing} , ΔH_{mixing} and ΔS_{mixing} .

(10 marks)

- (b) The vapour pressure of a chemical compound in the solid and liquid states are given by

$$\ln(P_{\text{solid}}) = 29.28 - \frac{4308}{T}$$

$$\ln(P_{\text{liquid}}) = 24.05 - \frac{3284}{T}$$

where P is in Pa and T in K. Calculate the temperature and pressure of the triple point of the compound, and $\Delta_{\text{fus}}H$ and $\Delta_{\text{fus}}S$ at the triple point.

(10 marks)

4. (a) The vapour pressure of propene at 200 K is 198 Torr and at 250 K is 2074 Torr. Calculate the heat and entropy of vaporization and the vapour pressure of propene at 225 K.

(10 marks)

- (b) Derive the Gibbs-Duhem equation shown below and state three of its applications

$$n_A d\mu_A + n_B d\mu_B = 0$$

(10 marks)

5. (a) The vapour pressure of a pure liquid A at 293 K is 68.8 kPa and that of a pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixture. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612, calculate the total pressure of the vapour and the composition of the liquid mixture.

(10 marks)

- (b) The density of a ethanol-water solution (25% w/w) at 20 °C is 961.7 kg m⁻³. Given the partial molar volume of ethanol in the solution is 53.4 cm³ mol⁻¹. Calculate the partial molar volume of the water.

(10 marks)

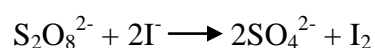
PART B

Answer at least **ONE** question.

6. (a) The rate of ionic reaction in solution is proportional to the concentration of activated complex. Derive an equation relating the logarithm of the rate constant to the ionic strength and the charge numbers, Z_A and Z_B , of the ions, A and B, respectively.

(8 marks)

- (b) The following rate constants, k , at various initial concentrations of sodium chloride, C_{NaCl} , were obtained for the second-order reaction between persulfate and iodide ions,



The initial concentrations of potassium persulfate and potassium iodide were 0.00015 and $0.00050 \text{ mol dm}^{-3}$, respectively.

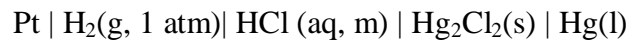
$k \times 10^5 / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	1.733	1.862	2.000	2.147	2.300	2.417
$C_{\text{NaCl}} / \text{mol dm}^{-3}$	0.0018	0.0036	0.0060	0.0090	0.0120	0.0144

Calculate the rate constant at zero ionic strength.

Given: Debye-Hückel constant, $A = 0.5091 \text{ kg}^{1/2} \text{ mol}^{1/2}$

(12 marks)

7. (a) The potential of the cell



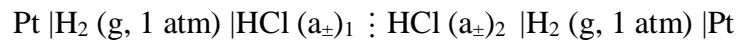
has been measured with the following results at 25 °C:

m/ mmol kg ⁻¹	1.6077	3.0769	5.0403	7.6938	10.9474
E/V	0.60080	0.56825	0.54366	0.52267	0.50532

Calculate the standard cell potential and the mean activity coefficient of HCl at these molalities.

(10 marks)

- (b) At 25 °C, the potential of the following cell with transference is 0.02802 V when the mean ionic activities of HCl, $(a_{\pm})_1 = 0.009048$ and $(a_{\pm})_2 = 0.01751$. The corresponding cell without transference has a potential of 0.01696 V.



- (i) Derive an expression for the potential of this cell with transference.
- (ii) Calculate the transference number of H⁺ ion and the value of the liquid junction potential.

(10 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	1.602176	10^{-19}	C
Faraday constant	$F=N_Ae$	9.64853	10^4	C mol^{-1}
Boltzmann constant	k	1.38065	10^{-23}	J K^{-1}
Gas constant	$R=N_Ak$	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	$1.60218 \times 10^{-19} \text{ J}$ $96.485 \text{ kJ mol}^{-1}$	2.303 RT/F = 0.0591 V at 25 °C	Energy	$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ = 1 A V s
	8065.5 cm^{-1}		Force	$1 \text{ N} = 1 \text{ kg m s}^{-2}$
1 cal	4.184 J		Pressure	$1 \text{ Pa} = 1 \text{ N m}^{-2}$ = $1 \text{ kg m}^{-1} \text{ s}^{-2}$ = 1 J m^{-3}
1 atm	101.325 kPa 760 Torr			
1 cm^{-1}	$1.9864 \times 10^{-23} \text{ J}$		Charge	$1 \text{ C} = 1 \text{ A s}$
1 Å	10^{-10} m		Potential difference	$1 \text{ V} = 1 \text{ J C}^{-1}$ = $1 \text{ kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$
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		

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan sahaja dengan sekurang-kurangnya **SATU** soalan daripada Bahagian B.

Jawab setiap soalan pada muka surat yang baru.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Lampiran: Pemalar asas dalam kimia fizik.

BAHAGIAN A

Jawab tidak lebih daripada **EMPAT** soalan.

1. (a) Gas O₂ berjisim 64.0 g berada pada 25 °C dan tekanan 1 atm. Muatan haba molar bagi O₂ ialah 29.33 J K⁻¹ mol⁻¹. Carilah nilai q, w dan ΔU

(i) apabila isipadu gas digandakan dibawah proses isothermal berbalik, dan

(ii) apabila tekanan gas digandakan dibawah proses isobarik.

(10 markah)

- (b) Etanol berjisim 25 g pada 50 °C dituangkan ke dalam 70 g etanol pada 20 °C di dalam bekas bertebat. Kirakan perubahan entropi bagi proses ini

Diberi C_p = 111.5 J K⁻¹ mol⁻¹.

(10 markah)

2. (a) Gunakan data berikut bagi plumbum untuk mengira entropi piawai pada 1000 K.

$$C_p(\text{Pb}_{(p)}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 23.6 + 9.6 \times 10^{-3} T$$

$$C_p(\text{Pb}_{(c)}) / (\text{J K}^{-1} \text{ mol}^{-1}) = 32.2 - 2.75 \times 10^{-3} T$$

$$T_{\text{lakur}} = 601 \text{ K}, \Delta_{\text{lakur}}H = 4.77 \text{ kJ mol}^{-1}$$

(10 markah)

- (b) Terbitkan persamaan berikut:

$$(i) \quad \left(\frac{\partial H}{\partial T}\right)_S = C_P \left(\frac{\partial \ln T}{\partial \ln V}\right)_P$$

$$(iii) \quad \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P$$

(10 markah)

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3. (a) Suatu bekas 20 L dibahagikan kepada dua petak dengan menggunakan sekatan. Petak pertama mengandungi 12 L hidrogen dan petak kedua mengandungi 10 L nitrogen. Sekatan dikeluarkan dan kedua-dua gas dibenarkan mencampur secara isothermal pada 1 atm dan 298 K. Anggarkan $\Delta G_{\text{percampuran}}$, $\Delta H_{\text{percampuran}}$ dan $\Delta S_{\text{percampuran}}$.

(10 markah)

- (b) Tekanan wap bagi sebatian kimia dalam keadaan pepejal dan cecair diberi dengan:

$$\ln(P_{\text{pepejal}}) = 29.28 - \frac{4308}{T}$$

$$\ln(P_{\text{cecair}}) = 24.05 - \frac{3284}{T}$$

dengan P dalam Pa dan T dalam K . Kirakan suhu dan tekanan bagi titik tripel sebatian dan $\Delta_{\text{lakur}}H$ dan $\Delta_{\text{lakur}}S$ pada titik tripel.

(10 markah)

4. (a) Tekanan wap bagi propena pada 200 K ialah 198 Torr dan pada 250 K ialah 2074 Torr. Kirakan haba dan entropi pengwapan dan tekanan wap bagi propena pada 225 K.

(10 markah)

- (b) Terbitkan persamaan Gibbs-Duhem yang berikut dan nyatakan tiga penggunaannya.

$$n_A d\mu_A + n_B d\mu_B = 0$$

(10 markah)

5. (a) Tekanan wap cecair tulen A pada 293 K ialah 68.8 kPa dan yang bagi cecair tulen B ialah 82.1 kPa. Kedua-dua sebatian ini membentuk campuran cecair dan gas unggul. Pertimbangkan komposisi keseimbangan bagi satu campuran yang mana pecahan mol A dalam wap ialah 0.612, kirakan tekanan total wap dan komposisi bagi campuran cecair.

(10 markah)

- (b) Pada 20 °C ketumpatan bagi larutan air-etanol (25% w/w) ialah 961.7 kg m⁻³. Diberi isipadu molar separa etanol dalam larutan ialah 53.4 cm³ mol⁻¹. Kirakan isipadu molar separa bagi air.

(10 markah)

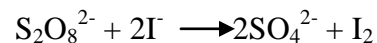
BAHAGIAN B

Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Kadar tindak balas ion di dalam larutan berkadar dengan kepekatan Kompleks yang diaktifkan. Terbitkan satu persamaan yang berhubungan logaritma pemalar kadar kepada kekuatan ion dan bilangan cas, Z_A dan Z_B , masing-masing bagi ion A dan B.

(8 markah)

- (b) Pemalar kadar, k , yang berikut pada pelbagai kepekatan awal natrium klorida, C_{NaCl} , diperoleh bagi tindak balas tertib kedua di antara ion persulfat dan iodida,



Kepekatan awal kalium persulfat dan kalium iodida masing-masing ialah 0.00015 and 0.00050 mol dm⁻³.

$k \times 10^5 /$ $dm^3 mol^{-1} s^{-1}$	1.733	1.862	2.000	2.147	2.300	2.417
$C_{NaCl} /$ $mol dm^{-3}$	0.0018	0.0036	0.0060	0.0090	0.0120	0.0144

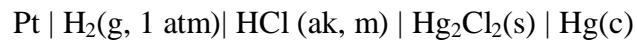
Kirakan pemalar kadar pada kekuatan ion sifar.

Diberi: Pemalar Debye-Hückel, $A = 0.5091 \text{ kg}^{1/2} \text{ mol}^{1/2}$

(12 markah)

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7. (a) Keupayaan sel



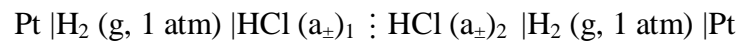
telah disukat dengan keputusan yang berikut pada 25 °C:

m/ mmol kg ⁻¹	1.6077	3.0769	5.0403	7.6938	10.9474
E/V	0.60080	0.56825	0.54366	0.52267	0.50532

Kirakan keupayaan sel piawai dan pekali keaktifan min bagi HCl pada kemolalan ini.

(10 markah)

- (b) Pada 25 °C, keupayaan sel dengan pindahan yang berikut ialah 0.02802 V apabila keaktifan ion min bagi HCl, $(a_{\pm})_1 = 0.009048$ dan $(a_{\pm})_2 = 0.01751$. Sel yang sepadan tanpa pindahan mempunyai keupayaan bernilai 0.01696 V.



- (i) Terbitkan satu ungkapan bagi keupayaan sel ini dengan pindahan.
- (ii) Kirakan nombor pindahan ion H⁺ dan nilai keupayaan sempadan cecair.

(10 markah)

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