UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2007/2008

June 2008

KFT 232 – Physical Chemistry II
[Kimia Fizik II]

Duration: 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **THIRTEEN** printed pages before you begin the examination.

Instructions:

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

Answer each question on a new page.

You may answer 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.

Appendix: Fundamental constants in Physical Chemistry.

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PART A
Answer not more than **FOUR** questions.

1. In the expansion of 1 mol of an ideal gas from initial volume of 0.010 m^3 to final volume of 0.100 m^3 at 25 °C.

   (a) Calculate the work done by the following processes:

   (i) Against a constant external pressure of 1 atm.

   (ii) Change from 0.010 m^3 to 0.025 m^3 against a constant external pressure of 0.330 atm, followed by a second expansion from 0.025 m^3 to 0.050 m^3 against a constant external pressure of 0.200 atm and a third expansion from 0.050 m^3 to 0.100 m^3 against a constant pressure of 0.100 atm.

   (iii) A reversible expansion.

   (17 marks)

   (b) Give comment on the work done by the above processes.

   (3 marks)

2. A reversible four-stroke engine uses 1 mol of an ideal gas as a working material. The four strokes are as follows:

   Stroke 1: Expansion from (P_1, V_1, T_1) to (P_1, V_2, T_2)

   Stroke 2: Cooling from (P_1, V_2, T_2) to (P_2, V_2, T_3)

   Stroke 3: Compression from (P_2, V_2, T_3) to (P_2, V_1, T_4)

   Stroke 4: Heating from (P_2, V_1, T_4) to (P_1, V_1, T_1)

   If C_V^m and C_P^m are 1.5 R and 2.5 R, respectively:

   (a) Sketch a complete diagramme of pressure – volume plot for the operational four- stroke engine.

   (5 marks)

   (b) Obtain an expression for the net work per cycle of the engine in terms of various temperatures.

   (8 marks)

(c) Obtain an expression for the total heat given to the engine in one cycle as a function of various temperatures.

(7 marks)

3. (a) From the relevant thermodynamic equation, obtain the criteria required for the equilibrium and spontaneity of a chemical reaction at constant entropy and pressure.

(8 marks)

(b) For a reversible heating of 1 mol ethane from 298 to 1000 K at constant pressure, the C_p value is given as

$$C_p = (5.350 + 186.532 \times 10^{-2} T - 584.12 \times 10^{-6} T^2 + 5.184 \times 10^{-8} T^3) \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate $\Delta S_{(system)}$ for the above system. If the above process is carried out irreversibly by placing the gas in the oven at 1000 K, calculate $\Delta S_{(surrounding)}$ and $\Delta S_{(universe)}$.

(12 marks)

4. (a) Show that by using the relevant thermodynamic equation, the internal energy for an ideal gas is independent of the constant volume and temperature,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

(10 marks)

(b) Consider the following chemical reaction

$$Cl_2 (g) + F_2 (g) \rightarrow 2 ClF (g) \qquad \Delta G°_{298} = -111.88 \text{ kJ}$$

If the pressures for $P_{(Cl2)} = 16.3$ bar, $P_{(F2)} = 5.2$ bar and $P_{(ClF)} = 0.063$ bar, determine the free energy change under this condition. Comment.

(10 marks)

5. (a) What is meant by the molar volume and partial molar volume of a substance?

Show that for a specific temperature and pressure, the volume of a solution, V, consisting of two components A and B, is given by the following equation

$$V = n_A \overline{V}_A + n_B \overline{V}_B$$

where n_A and n_B are the number of moles of A and B, respectively; $\overline{V}_A$ and $\overline{V}_B$ are the partial molar volumes of A and B, respectively.

(8 marks)

(b) At 75 °C, the vapour pressures for HNO_3 and H_2O are 4,670 and 11,500 Pa, respectively, in a nitric acid solution with a HNO_3 weight fraction of 0.650. Calculate the

(i) partial vapour pressure of ideal solution,

(ii) total vapour pressure of ideal and real solutions, and

(iii) mole fractions of the components for ideal and real solutions.

Given: Vapour pressures of pure HNO_3 and H_2O are 71,990 and 38,540 Pa, respectively.

(12 marks)

PART B
Answer at least **ONE** question

6. (a) Devise electrochemical cells in which the following overall cell reactions can occur:

(i) $Ce^{4+}(aq) + Fe^{2+}(aq) \rightarrow Ce^{3+}(aq) + Fe^{3+}(aq)$

(ii) $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$

(iii) $Zn(s) + Cl_2(g) \rightarrow ZnCl_2(aq)$

(8 marks)

(b) The emf, E, of the cell

$$Pt \mid H_2(g) \mid HCl(aq, m) \mid AgCl(s) \mid Ag$$

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

$m/10^{-3}$ mol kg^{-1}	123.8	25.63	9.138	5.619	3.215
$E/10^{-3}$ V	341.99	418.24	468.60	492.57	520.53

(i) Determine the standard emf, E°, of the cell.

(ii) The emf was measured as 352.4 x 10^{-3} V when molality, m = 0.10 mol kg^{-1}. What are the pH and the mean ionic activity coefficient at this molality?

(12 marks)

7. (a) Suppose that the rates of ionic reactions in solution were proportional to the activities rather than the concentrations, of activated complexes. Derive an equation relating the logarithm of the rate constant to the ionic strength and the charge number of the ions.

(8 marks)

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 melebihi **EMPAT** soalan

1. Bagi pengembangan 1 mol suatu gas unggul daripada isipadu awal 0.010 m^3 kepada isipadu akhir 0.100 m^3 pada 25 °C.

   (a) Hitunglah kerja yang dilakukan oleh proses-prose berikut:

   (i) Melawan tekanan luar tetap pada 1 atm.

   (ii) Perubahan daripada 0.010 m^3 kepada 0.025 m^3 melawan tekanan luar tetap 0.330 atm, diikuti pengembangan kedua daripada 0.025 m^3 kepada 0.050 m^3 melawan tekanan tetap 0.200 atm, dan oleh pengembangan ketiga daripada 0.050 m^3 kepada 0.100 m^3 melawan tekanan tetap 0.100 atm.

   (iii) Suatu pengembangan berbalik.

   (17 markah)

   (b) Beri ulasan terhadap kerja berdasarkan proses di atas.

   (3 markah)

2. Suatu engin empat-lejang berbalik, menggunakan 1 mol gas unggul sebagai bahan kerjanya. Empat-lejang adalah seperti berikut:

   Lejang 1: Pengembangan daripada (P_1, V_1, T_1) kepada (P_1, V_2, T_2)

   Lejang 2: Pendinginan daripada (P_1, V_2, T_2) kepada (P_2, V_2, T_3)

   Lejang 3: Pemampatan daripada (P_2, V_2, T_3) kepada (P_2, V_1, T_4)

   Lejang 4: Pemanasan daripada (P_2, V_1, T_4) kepada (P_1, V_1, T_1)

   Jika C_V^m dan C_P^m masing-masing adalah 1.5 R dan 2.5 R:

   (a) Lakarkan suatu gambarajah plot tekanan-isipadu yang lengkap daripada operasi engin empat-lejang.

   (5 markah)

   (b) Dapatkan suatu ungkapan bagi kerja net per kitaran bagi engin dalam suatu sebutan berbagai suhu.

   (8 markah)

(c) Dapatkan suatu ungkapan bagi haba total diberikan kepada engin dalam satu kitaran sebagai fungsi berbagai suhu.

(7 markah)

3. (a) Daripada persamaan termodinamik yang bersesuaian, dapatkan kriteria yang diperlukan untuk keseimbangan dan kespontanan suatu tindak balas kimia pada entropi dan tekanan malar.

(8 markah)

(b) Bagi suatu pemanasan berbalik 1 mol etana daripada 298 kepada 1000 K pada tekanan malar, nilai C_p diberikan sebagai

$$C_p = (5.350 + 186.532 \times 10^{-2}\, T - 584.12 \times 10^{-6}\, T^2 + 5.184 \times 10^{-8}\, T^3)\ J\ K^{-1}\ mol^{-1}$$

Hitunglah $\Delta S_{(sistem)}$ bagi sistem diatas. Jika proses diatas dijalankan secara tak berbalik dengan menempatkan gas di dalam ketuhar pada 1000 K, hitunglah $\Delta S_{(sekitar)}$ and $\Delta S_{(alam\ semesta)}$.

(12 markah)

4. (a) Tunjukkan dengan menggunakan persamaan termodinamik bagi suatu gas unggul, bahawa tenaga dalam adalah tidak bersandar kepada isipadu dan suhu malar,

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

(10 markah)

(b) Pertimbangkan tindak balas kimia berikut

$$Cl_2\,(g) + F_2\,(g) \rightarrow 2\,ClF\,(g) \qquad \Delta G°_{298} = -111.88\ kJ$$

Jika tekanan bagi $P_{(Cl2)} = 16.3$ bar, $P_{(F2)} = 5.2$ bar dan $P_{(ClF)} = 0.063$ bar, tentukan perubahan tenaga bebas dibawah keadaan ini. Beri ulasan.

(10 markah)

5. (a) Apakah yang dimaksudkan dengan isipadu molar dan isipadu molar separa suatu zat?
Tunjukkan bahawa pada nilai suhu dan tekanan tertentu, isipadu suatu larutan, V, yang mengandungi dua komponen A dan B diberikan oleh persamaan

$$V = n_A \overline{V}_A + n_B \overline{V}_B$$

bagi n_A dan n_B, masing-masing adalah bilangan mol A dan B; $\overline{V}_A$ dan $\overline{V}_B$, masing-masing adalah isipadu molar separa A dan B.

(8 markah)

(b) Pada 75 °C, tekanan wap bagi HNO_3 dan H_2O masing-masing adalah 4,670 dan 11,500 Pa didalam suatu larutan asid nitrik dengan pecahan berat HNO_3 ialah 0.650. Hitunglah

(i) tekanan wap separa bagi larutan unggul,

(ii) tekanan wap total larutan-larutan unggul dan sahih, dan

(iii) pecahan mol komponen-komponen bagi larutan-larutan unggul dan sahih.

Diberi: Tekanan wap tulen HNO_3 dan H_2O masing-masing 71,990 dan 38,540 Pa.

(12 markah)

BAHAGIAN B
Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Ciptakan sel eletrokimia yang mana tindak balas sel keseluruhan yang berikut dapat berlaku:

(i) Ce^{4+} (ak) + Fe^{2+} (ak) → Ce^{3+} (ak) + Fe^{3+} (ak)

(ii) Zn (p) + Cu^{2+} (ak) → Cu (p) + Zn^{2+} (ak)

(iii) Zn (p) + Cl_2 (g) → $ZnCl_2$ (ak)

(8 markah)

(b) Emf, E, bagi sel

$$Pt \mid H_2 \text{ (g)} \mid HCl \text{ (ak, m)} \mid AgCl \text{ (p)} \mid Ag$$

telah disukat dengan keputusan yang berikut pada 25 °C.

$m/10^{-3}$ mol kg^{-1}	123.8	25.63	9.138	5.619	3.215
$E/10^{-3}$ V	341.99	418.24	468.60	492.57	520.53

(i) Tentukan emf piawai, E°, bagi sel ini.

(ii) Emf disukat ialah 352.4 x 10^{-3} V apabila kemolalan, m = 0.10 mol kg^{-1}. Apakah nilai pH dan pekali keaktifan ion min pada kemolalan ini?

(12 markah)

7. (a) Andaikan bahawa kadar tindak balas ion di dalam larutan berkadar dengan keaktifan lebih tepat daripada kepekatan kompleks yang diaktifkan. Terbitkan satu ekspresi yang berhubung logaritma pemalar kadar kepada kekuatan ion dan bilangan cas ion.

(8 markah)

(b) Data keterlarutan, S, berikut untuk garam $[Co(NH_3)_6]^{3+}[Fe(CN)_6]^{3-}$ yang berlarut dengan sedikit di dalam kehadiran KNO_3 diperoleh pada 25 °C.

$m(KNO_3)$ / mol kg^{-1}	0.0000	0.0005	0.0010	0.0020
S x 10^5 / mol kg^{-1}	2.900	3.308	3.586	4.080

Tunjukkan bahawa data yang diperoleh adalah selaras dengan teori Debye-Hückel. Kiralah pekali keaktifan min bagi ion $[Co(NH_3)_6]^{3+}$ dan $[Fe(CN)_6]^{3-}$ pada setiap kepekatan.

Pemalar Debye-Hückel, $A = 0.5091\ kg^{\frac{1}{2}}\ mol^{-\frac{1}{2}}$

(12 markah)

APPENDIX

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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	$F=N_A e$	9.64853	10^{4}	$C\ mol^{-1}$
Boltzmann constant	k	1.38065	10^{-23}	$J\ K^{-1}$
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	$L Torr\ K^{-1}\ mol^{-1}$
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	
1 eV	1.60218×10^{-19} J 96.485 kJ mol^{-1}	2.303 RT/F = 0.0591 V at 25 °C	Energy	$1\ J = 1\ kg\ m^2\ s^{-2}$ $= 1\ A\ V\ s$
	8065.5 cm^{-1}		Force	$1\ N = 1\ kg\ m\ s^{-2}$
1 cal 1 atm	4.184 J 101.325 kPa 760 Torr		Pressure	$1\ Pa = 1\ N\ m^{-2}$ $= 1\ kg\ m^{-1}\ s^{-2}$ $= 1\ J\ m^{-3}$
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		

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