UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2008/2009

April/May 2009

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. Assume $C_{p,m}$ is constant at 3.5R for $N_2(g)$ in the temperature range of 100 to 400 K and at low pressure and behaves as ideal gas.

(a) Calculate q, w, ΔU and ΔH for the reversible adiabatic compression of 1.12 g $N_2(g)$ from 53.3 kPa and 1000 cm^3 to a final volume of 250 cm^3.

(10 marks)

(b) If a sample of $N_2(g)$ at room temperature and pressure (25 °C and 101 kPa) is cooled to 100 K in a reversible adiabatic expansion, what is the final pressure?

(10 marks)

2. (a) Consider 2.00 mol of argon undergoing a reversible isothermal expansion from 0.01 to 0.1 m^3 at 25 °C.

(i) Derive an equation for ΔS (system) for a van der Waals gas.

(ii) Compare the value with ΔS (system) for ideal gas.

Given: the van der Waals equation is

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

where a and b are 1.337 atm dm^6 mol^{-2} and 0.03219 dm^3 mol^{-1}, respectively.

(12 marks)

(b) (i) Derive the following Gibbs-Helmholtz equation:

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

(ii) Prove the Maxwell relation

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

(8 marks)

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3. (a) Prove the following equation:

$$\left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial U}{\partial S}\right)_V = T^2$$

(6 marks)

(b) (i) Derive the following Clausius-Clapeyron equation:

$$\frac{d\ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

(ii) The vapour pressure of propane at 200 K is 198 Torr and at 250 K is 2074 Torr. Calculate the heat of vaporization and the vapour pressure at 225 K.

(14 marks)

4. (a) Briefly explain the partial molar quantity of a system consisting of components 1 and 2.
According to the definition of apparent molar quantity, ϕ_1, for component 1,

$$\phi_1 = \frac{M - X_2 M_2}{X_1}$$

where X is the mole fraction, M the molar properties of mixture and M_2 the molar properties of pure components 2 at the solution temperature and pressure. Derive the equations to determine the partial molar properties of $\overline{M}_1$ and $\overline{M}_2$ with ϕ_1 as a function of X_1 at constant temperature T and pressure p. The equation must contain only quantities of X_1, M_2, ϕ_1 and $\frac{d\phi_1}{dX_1}$.

(12 marks)

(b) Consider a container of volume 250 mL that is divided into two compartments of equal size. The left compartment contains argon at 100 kPa and 0 °C whereas in the right compartment contains neon at the same temperature and pressure. Calculate the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are ideal.

(8 marks)

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

Show that for a specific temperature and pressure, the volume of 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 partial molar volume of A and B, respectively.

(10 marks)

(b) 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)

PART B
Answer at least **ONE** question.

6. (a) The activity, a_i, of species i is defined as

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

and $a_i = \gamma_i m_i$

where μ_i is the chemical potential of species i and μ_i°, the chemical potential of species i in its chosen standard state. For the strong electrolyte, $M_{v+} X_{v-}$, where v_+ and v_- are the number of cations and anions, respectively, show that the mean ionic activity, $a_\pm$, and the mean ionic activity coeffients, $\gamma_\pm$, are

$$(a_\pm)^v = (a_+)^{v+} (a_-)^{v-}$$

and $$(\gamma_\pm)^v = (\gamma_+)^{v+} (\gamma_-)^{v-}$$

(10 marks)

(b) The rate constant, k, for the reaction between persulphate ions and iodide ions varies with the ionic strength, I, as follows:

$I/10^{-3}$ mol dm^{-3}	2.45	3.65	4.45	6.45	8.45	12.45
k/dm^3 mol^{-1} s^{-1}	1.05	1.12	1.16	1.18	1.26	1.39

(i) Derive the Brϕnsted – Bjerrum relation.

(ii) Estimate the value of $Z_A Z_B$, the product of the charge number.

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

(10 marks)

7. (a) The emf of the cell

$$\mathrm{Pt} \mid \mathrm{H_2(g)} \mid \mathrm{HCl(aq,m)} \mid \mathrm{Hg_2Cl_2(s)} \mid \mathrm{Hg}(\ell)$$

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

Determine the standard emf of the cell and the mean activity coefficient of HCl at these molalities.

(10 marks)

(b) Compare the cell potentials at 25 °C for the cells without and with liquid junction:

$$\mathrm{Ag(s)} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl\ (0.1000\ m)} \parallel \mathrm{HCl\ (0.0100\ m)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)}$$

and

$$\mathrm{Ag(s)} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl\ (0.1000\ m)} \,\vdots\, \mathrm{HCl\ (0.0100\ m)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)}$$

Given: $\gamma_{\pm} = 0.798$ and $t(\mathrm{H^+}) = 0.8314$ for 0.1000 m HCl;
$\gamma_{\pm} = 0.906$ and $t(\mathrm{H^+}) = 0.8251$ for 0.0100 m HCl.

(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		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	
1 eV	1.60218 x 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	4.184 J		Pressure	1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2} = 1 J m^{-3}
1 atm	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 L atm	101.325 J			= 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		

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. Anggap $C_{p,m}$ adalah malar pada 3.5R bagi $N_2(g)$ pada julat suhu 100 hingga 400 K dan tekanan rendah dan berkelakuan unggul.

(a) Kiralah q, w, ΔU dan ΔH untuk proses pemampatan adiabatik berbalik bagi 1.12 g $N_2(g)$ dari 53.3 kPa dan 1000 cm^3 kepada isipadu akhir 250 cm^3.

(10 markah)

(b) Sekiranya sampel $N_2(g)$ disejukkan dari suhu dan tekanan bilik (25 °C dan 101 kPa) kepada 100 K menggunakan proses pengembangan adiabatik berbalik, berapakah tekanan akhir?

(10 markah)

2. (a) Pertimbangkan 2.00 mol argon melalui prosses pengembangan isotermal berbalik daripada 0.01 kepada 0.1 m^3 pada 25 °C.

(i) Terbitkan persamaan ΔS (sistem) bagi gas van der Waals.

(ii) Bandingkan nilai tersebut dengan nilai ΔS (sistem) bagi gas unggul.

Diberikan: persamaan van der Waals adalah

$$p = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

dengan a dan b adalah 1.337 atm dm^6 mol^{-2} and 0.03219 dm^3 mol^{-1}, masing-masing.

(12 markah)

(b) (i) Terbitkan persamaan Gibbs-Helmholtz berikut:

$$\left[\frac{\partial(G/T)}{\partial T}\right]_p = -\frac{H}{T^2}$$

(ii) Buktikan kaitan Maxwell

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

(8 markah)

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3. (a) Buktikan persamaan berikut:

$$\left(\frac{\partial H}{\partial S}\right)_p \left(\frac{\partial U}{\partial S}\right)_V = T^2$$

(6 markah)

(b) (i) Terbitkan persamaan Clausius-Clapeyron berikut:

$$\frac{d \ln p}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

(ii) Tekanan wap propana pada 200 K adalah 198 Torr dan pada 250 K adalah 2074 Torr. Hitunglah haba pengwapan dan tekanan wap pada 225 K.

(14 markah)

4. (a) Terangkan dengan ringkas maksud kuantiti molar separa untuk suatu sistem yang terdiri daripada komponen 1 dan 2.

Sifat molar ketara, ϕ_1, bagi komponen 1 ditakrifkan sebagai,

$$\phi_1 = \frac{M - X_2M_2}{X_1}$$

bagi X ialah pecahan mol, M ialah sifat molar campuran, dan M_2 ialah sifat molar komponen tulen 2 pada suhu dan tekanan larutan tersebut. Terbitkan persamaan untuk menentukan sifat molar separa $\overline{M}_1$ dan $\overline{M}_2$ dengan ϕ_1 ialah suatu fungsi X_1 pada suhu T dan tekanan p tetap. Persamaan tersebut mestilah hanya mengandungi kuantiti X_1, M_2, ϕ_1 dan $\frac{d\phi_1}{dX_1}$.

(12 markah)

(b) Pertimbangkan suatu bekas berisipadu 250 mL dibahagikan kepada dua ruang bersaiz sama. Ruang kiri mengandungi argon pada 100 kPa dan 0 °C manakala ruang kanan mengandungi neon pada suhu dan tekanan yang sama. Hitunglah entropi dan tenaga Gibbs campuran apabila pemisahnya disingkirkan. Anggapkan gas adalah unggul.

(8 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.

(10 markah)

(b) Tekanan wap cecair tulen A pada 293 K adalah 68.8 kPa dan bagi cecair tulen B adalah 82.1 kPa. Kedua-dua sebatian ini membentuk campuran cecair dan gas unggul. Pertimbangkan komposisi keseimbangan suatu campuran di mana pecahan mol A dalam wap adalah 0.612, hitunglah tekanan total wap dan komposisi campuran cecair.

(10 markah)

BAHAGIAN B

Jawab sekurang-kurangnya **SATU** soalan.

6. (a) Keaktifan, a_i, bagi spesies i diaktifkan sebagai

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

dan $$a_i = \gamma_i m_i$$

dengan μ_i ialah keupayaan kimi bagi spesies i dan μ_i°, keupayaan kimia bagi spesies i dalam keadaan piawai terpilihnya. Bagi elektrolit kuat, $M_{v+} X_{v-}$, dengan v_+ dan v_- masing-masing ialah bilangan kation dan anion, tunjukkan bahawa keaktifan ion min, $a_\pm$, dan pekali keaktifan ion min, $\gamma_\pm$, ialah

$$(a_\pm)^v = (a_+)^{v+} (a_-)^{v-}$$

dan $$(\gamma_\pm)^v = (\gamma_+)^{v+} (\gamma_-)^{v-}$$

(10 markah)

(b) Pemalar kadar, k, untuk tindak balas di antara ion persulfat dan ion iodida berubah dengan kekuatan ion, I, seperti berikut:

$I/10^{-3}$ mol dm^{-3}	2.45	3.65	4.45	6.45	8.45	12.45
k/dm^3 mol^{-1} s^{-1}	1.05	1.12	1.16	1.18	1.26	1.39

(i) Terbitkan hubungan Brϕnsted – Bjerrum.

(ii) Anggarkan nilai Z_AZ_B, iaitu hasil darab nombor cas

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

(10 markah)

7. (a) Emf bagi sel,

$$\mathrm{Pt} \mid \mathrm{H_2(g)} \mid \mathrm{HCl(ak,m)} \mid \mathrm{Hg_2Cl_2(p)} \mid \mathrm{Hg}(\ell)$$

disukat pada 25 °C dengan keputusan yang berikut:

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

Tentukan emf piawai sel itu dan pekali keaktifan min HCl pada kemolalan itu.

(10 markah)

(b) Bandingkan keupayaan sel pada 25 °C untuk sel tanpa dan dengan simpangan cecair:

$$\mathrm{Ag(s)} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl\ (0.1000\ m)} \parallel \mathrm{HCl\ (0.0100\ m)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)}$$

dan

$$\mathrm{Ag(s)} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl\ (0.1000\ m)} \vdots \mathrm{HCl\ (0.0100\ m)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)}$$

Diberi: $\gamma_{\pm} = 0.798$ and t (H^+) = 0.8314 untuk 0.1000 m HCl;
$\gamma_{\pm} = 0.906$ and t (H^+) = 0.8251 untuk 0.0100 m HCl.

(10 markah)

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