UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2008/2009

June 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 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.

Appendix: Fundamental constants in Physical Chemistry.

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

1. Consider a system consisting of 3.0 mol $CO_2(g)$, initially at 35 °C and 9.0 atm and confined to a cylinder of cross-section 100.0 cm^2. The sample is allowed to expand adiabatically against an external pressure of 2.5 atm until the piston has moved outwards through 25 cm. Assume that carbon dioxide may be considered as a perfect gas with $C_{V,m}$ = 28.8 J K^{-1} mol^{-1}. Calculate q, w, ΔU, ΔT and ΔS.

(20 marks)

2. (a) The fugacity coefficient of gas X at 290 K and 3.1 MPa is 0.70.Calculate the difference of its molar Gibbs energy from that of an ideal gas in the same state.

(5 marks)

(b) Show that the change in internal energy of an ideal gas during an isothermal expansion is zero, i.e

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

(10 marks)

(c) The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression ΔG/J = -35.40 + 26.8(T/K). Calculate the value of ΔS for the process.

(5 marks)

3. (a) The apparent molar volume of NaCl, ϕ , in 1.000 kg water at 25 ^oC is expressed by the following equation

$$\phi = 27.45 + 2.51\sqrt{m}$$

where m is the molality of NaCl.

If the density of water at 25 ^oC is 0.997 g cm^{-3}, calculate the partial molar volume of NaCl for 1.5 m NaCl solution.

(10 marks)

(b) Calculate the change in entropy when 25 g of ethanol at 50 °C is poured into 70 g of ethanol at 10 °C in an insulated vessel. Given that $C_{p.m}$ = 111.5 J K^{-1} mol^{-1}.

(10 marks)

4. (a) Show that according to chemical potential, the transfer from phase A to phase B in a closed system occurred spontaneously at constant pressure and temperature.

(8 marks)

(b) If 1 mol $NO_2(g)$ at 298 K was filled into 1 L container, $NO_2(g)$ would dimerise to form $N_2O_4(g)$ according to the following reaction

$$2\ NO_2(g) \longrightarrow N_2O_4(g).$$

When the system reached an equilibrium, the number of mols $NO_2(g)$ and $N_2O_4(g)$ were 0.0530 and 0.4735, respectively. Calculate the Gibbs free energy change, ΔG, for the process and predict how the reaction occurs.

Given: $\mu^{o}_{NO_2(g)} = 5.131 \times 10^4$ J mol^{-1}; $\mu^{o}_{N_2O_4(g)} = 9.789 \times 10^4$ J mol^{-1}.

(12 marks)

5. (a) The activity of a solution consisting of two components α and β can be determined by the following Gibbs-Duhem equation:

$$X_\alpha\ d(\ln a_\alpha) + X_\beta\ d(\ln a_\beta) = 0$$

where X_α and X_β are mole fractions of α and β respectively; a_α and a_β the activities of α and β. Derive the above equation by stating the condition involved.

(10 marks)

(b) The vapour pressure of carvone, $C_{10}H_{14}O$, a ketone derived from the terpene limonene is as follows:

T / ^{o}C	57.4	100.4	133.0	157.3	203.5	237.5
P / mmHg	1.0	10.0	40.0	100	400	760

What is the (i) enthalpy of evaporation of carvone, and

(ii) normal boiling point?

(10 marks)

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

6. (a) An aqueous solution at 25 °C consists of 0.03 m $CuSO_4$ and 0.18 m NaCl.

Calculate:

(i) the ionic strength of the solution, and

(ii) the mean molality and the mean activity of Na_2SO_4 in the solution.

(Debye-Hückel constant, A = 0.5091 at 25 °C)

(8 marks)

(b) The solubilities, S, of $AgIO_3$ at 348.15 K in the presence of various concentrations of $MgSO_4$ are as follows:

C ($MgSO_4$) x 10^3 / mol kg^{-1}	0	0.5	1.0	5.0	10.0	20.0
S x 10^3 / mol kg^{-1}	0.8417	0.8698	0.8855	0.9629	1.0201	1.0928

(i) Calculate the solubility product for $AgIO_3$ at 348.15 K.

(ii) Determine the mean ionic activity coefficient of $AgIO_3$ in a solution saturated with $AgIO_3$ and 0.010 m in $MgSO_4$.

(12 marks)

7. (a) The emf of the following concentration cell with transference was studied

$$Ag \mid AgCl \mid NaCl(aq, m_1) \vdots NaCl(aq, m_2) \mid AgCl \mid Ag$$

The temperature was kept at 25 °C, and for each of the cells studied the value of m_1 was 0.0498 mol kg^{-1}. The mean ionic activity coefficient, $\gamma_{\pm}$ of NaCl in this solution is 0.823.

The results obtained are as follows:

m_2, mol kg^{-1}	$\gamma_{\pm}$	E, mV
0.00996	0.904	30.39
0.01996	0.871	17.11
0.02998	0.852	9.44
0.07933	0.792	-8.59
0.09987	0.778	-12.81

Show that these emfs can be obtained by substituting the transference number, $t_+ = 0.39$ in this concentration ranges.

(10 marks)

(b) Consider the following cell,

$$Cd\ (Hg) \mid CdSO_4 . \frac{8}{3} H_2O(s) \mid Hg_2SO_4(s) \mid Hg$$

the emf of the cell is given as a function of temperature, T (°C), by the expression:

$$E(V) = 1.01845 - 4.05 \times 10^{-5}(T-20) - 9.5 \times 10^{-7}(T-20)^2$$

(i) Write the electrode reactions and the overall cell reaction.

(4 marks)

(ii) Calculate the changes in free energy, entropy, and enthalpy at 25 °C.

(6 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. Pertimbangkan suatu sistem yang mengandungi 3.0 mol $CO_2(g)$, pada 35 °C dan 9.0 atm pada mulanya dan diisikan ke dalam satu silinder dengan keratan rentas 100.0 cm^2. Sampel tersebut dibiarkan mengembang secara adiabatik melawan tekanan luar 2.5 atm sehingga omboh bergerak keluar sebanyak 25 cm. Anggap karbon dioksida suatu gas unggul dengan $C_{V,m}$ = 28.8 J K^{-1} mol^{-1}. Kiralah q, w, ΔU, ΔT dan ΔS.

(20 markah)

2. (a) Pekali fugasiti gas X pada 290 K dan 3.1 MPa adalah 0.70. Kiralah perbezaan tenaga Gibbs molar berbanding nilai tenaga bagi gas unggul pada keadaan yang sama.

(5 markah)

(b) Tunjukkan bahawa perubahan tenaga dalam bagi gas unggul semasa pengembangan isotermal adalah sifar, i.e

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

(10 markah)

(c) Perubahan tenaga Gibbs bagi satu proses tekanan tetap didapati mematuhi ungkapan $\Delta G/J = -35.40 + 26.8(T/K)$. Kiralah nilai ΔS bagi proses tersebut.

(5 markah)

3. (a) Isipadu molar ketara NaCl, ϕ, didalam 1.000 kg air pada 25 ^{o}C dinyatakan oleh persamaan

$$\phi = 27.45 + 2.51 \sqrt{m}$$

bagi m ialah kemolalan NaCl.

Jika ketumpatan air pada 25 ^{o}C ialah 0.997 g cm^{-3}, kiralah isipadu molar separa NaCl untuk larutan 1.5 m NaCl.

(10 markah)

(b) Hitunglah perubahan entropi apabila 25 g etanol pada 50 °C dituangkan ke dalam 70 g etanol pada 10 °C di dalam suatu bekas bertebat. Diberi $C_{p.m}$ = 111.5 J K^{-1} mol^{-1}

(10 markah)

4. (a) Tunjukkan berdasarkan keupayaan kimia, perpindahan dari fasa A ke fasa B di dalam suatu sistem tertutup berlaku secara spontan pada tekanan dan suhu tetap.

(8 markah)

(b) Sekiranya dimasukkan 1 mol $NO_2(g)$ pada 298 K ke dalam bekas 1 L. $NO_2(g)$ menjadi dimer membentuk $N_2O_4(g)$ melalui tindak balas

$$2\ NO_2(g) \longrightarrow N_2O_4(g).$$

Apabila sistem mencapai keseimbangan, bilangan mol $NO_2(g)$ dan $N_2O_4(g)$ masing-masing adalah 0.0530 dan 0.4735. Hitunglah perubahan tenaga bebas Gibbs, ΔG, bagi proses dan ramalkan bagaimanakah tindak balas tersebut berlaku.

Diberi: $\mu^{o}_{NO_2(g)} = 5.131 \times 10^4$ J mol^{-1}; $\mu^{o}_{N_2O_4(g)} = 9.789 \times 10^4$ J mol^{-1}.

(12 markah)

5. (a) Keaktifan suatu larutan yang terdiri daripada dua komponen, α dan β dapat ditentukan dengan menggunakan persamaan Gibbs-Duhem berikut:

$$X_\alpha \, d(\ln a_\alpha) + X_\beta \, d(\ln a_\beta) = 0$$

bagi X_α dan X_β masing-masing ialah pecahan mol α dan β ; a_α dan a_β masing-masing ialah keaktifan α dan β. Terbitkan persamaan di atas dengan menyatakan syarat-syarat untuk menerbitkannya.

(10 markah)

(b) Tekanan wap karvon, $C_{10}H_{14}O$, suatu keton yang diterbitkan daripada terpena limonena adalah sebagai berikut:

T / ^oC	57.4	100.4	133.0	157.3	203.5	237.5
P / mmHg	1.0	10.0	40.0	100	400	760

Apakah (i) entalpi pengwapan karvon, dan

(ii) takat didih normalnya?

(10 markah)

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

6. (a) Suatu larutan akueus pada 25 °C mengandungi 0.03 m $CuSO_4$ dan 0.18 m NaCl.

Kirakan

(i) kekuatan ion bagi larutan itu, dan

(ii) kemolalan min dan keaktifan min bagi Na_2SO_4 di dalam larutan.

(Pemalar Debye-Hückel A = 0.5091 pada 25 °C)

(8 markah)

(b) Keterlarutan $AgIO_3$, S, pada 75 °C dalam kehadiran berbagai kepekatan $MgSO_4$ adalah seperti berikut:

C ($MgSO_4$) x 10^3 / mol kg^{-1}	0	0.5	1.0	5.0	10.0	20.0
S x 10^3 / mol kg^{-1}	0.8417	0.8698	0.8855	0.9629	1.0201	1.0928

(i) Kirakan hasildarab keterlarutan $AgIO_3$ pada 348.15 K.

(ii) Tentukan pekali keaktifan ion min $AgIO_3$ di dalam suatu larutan yang ditepukan dengan $AgIO_3$ dan 0.010 m $MgSO_4$.

(12 markah)

7. (a) Emf bagi sel kepekatan dengan transferens telah dikaji,

$$Ag \mid AgCl \mid NaCl(ak, m_1) \vdots NaCl(ak, m_2) \mid AgCl \mid Ag$$

Suhu ditetapkan pada 25 °C, dan bagi setiap sel yang dikaji, nilai m_1 ialah 0.0498 mol kg^{-1}. Pekali keaktifan ion min, $\gamma_{\pm}$ bagi NaCl di dalam larutan ini ialah 0.823.

Keputusan yang diperoleh adalah seperti berikut:

m_2, mol kg^{-1}	$\gamma_{\pm}$	E, mV
0.00996	0.904	30.39
0.01996	0.871	17.11
0.02998	0.852	9.44
0.07933	0.792	-8.59
0.09987	0.778	-12.81

Tunjukkan bahawa emf boleh diperoleh dengan menggantikan nombor transferens, $t_+ = 0.39$ di dalam julat kepekatan itu.

(10 markah)

(b) Pertimbangkan sel yang berikut,

$$Cd\ (Hg) \mid CdSO_4 . \frac{8}{3}\ H_2O(p) \mid Hg_2SO_4(p) \mid Hg$$

emf bagi sel diberi terhadap suatu fungsi suhu, T (°C), dengan ungkapan

$$E(V) = 1.01845 - 4.05 \times 10^{-5}(T-20) - 9.5 \times 10^{-7}(T-20)^2$$

(i) Tuliskan tindak balas elektrod dan tindak balas sel keseluruhan.

(4 markah)

(ii) Kirakan perubahan dalam tenaga bebas, entropi dan entalpi pada 25 °C.

(6 markah)

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 ^{o}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 x 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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