UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2011/2012 Academic Session

June 2012

EKC 108 – Physical and Analytical Chemistry
[Kimia Fizik dan Kimia Analitis]

Duration : 3 hours
[Masa : 3 jam]

Please ensure that this examination paper contains SEVEN printed pages and THREE printed pages of Appendix before you begin the examination.

[Sila pastikan bahawa kertas peperiksaan ini mengandungi TUJUH muka surat yang bercetak dan TIGA muka surat Lampiran sebelum anda memulakan peperiksaan ini.]

Instruction: Answer **ALL** questions.

*[**Arahan:** Jawab **SEMUA** soalan.]*

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

[Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah digunapakai].

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Answer ALL questions.
Jawab SEMUA soalan.

1. [a] What is the molecular definition of an ideal solution?
Apakah definisi molekul bagi satu larutan unggul?

[2 marks/markah]

[b] Predict the sign of ΔS for the desalination of sea water without consulting entropy tables and justify your reason.
Ramalkan tanda ΔS untuk penyahgaraman air laut tanpa menggunakan jadual entropi dan berikan alasan yang wajar.

[3 marks/markah]

[c] Calculate the expansion work done on the system when 1 mol of solid ammonium chloride (NH_4Cl) decomposes completely to yield gaseous ammonia (NH_3) and hydrogen chloride (HCl) at a temperature of 1250 K. Assume the expansion is irreversible and the gases perform as perfect.

Kirakan pengembangan kerja yang dilakukan pada sistem apabila 1 mol pepejal ammonium klorida (NH_4Cl) terurai lengkap kepada hasil gas ammonia (NH_3) dan hidrogen klorida (HCl) pada suhu 1250 K. Anggapkan pengembangan adalah tidak berbalik dan gas yang dihasilkan adalah sempurna.

[4 marks/markah]

[d] Calculate the ΔS° (universe) for the process of dissolving sodium chloride (NaCl) in water at 298 K.

Kirakan ΔS° (semesta) untuk proses melarutkan sodium klorida (NaCl) ke dalam air pada 298 K.

[5 marks/markah]

[e] Hemocyanin (Hy) is a blood protein found in crabs. If 1.5 g of Hy dissolved in 0.250 L of water has an osmotic pressure of 0.00342 atm at 277 K, what is the molecular weight of Hy?

Hemosianin (Hy) adalah protein darah yang ditemui di dalam ketam. Jika 1.5 g Hy dilarutkan ke dalam 0.250 L air yang bertekanan osmosis 0.00342 atm pada 277 K, apakah berat molekul Hy?

[5 marks/markah]

[f] The equilibrium constant for the reaction below is given as $K_{eq} = 2.0 \times 10^{-27}$ at 25°C.

Pemalar keseimbangan untuk tindakbalas di bawah diberikan $K_{eq} = 2.0 \times 10^{-27}$ pada 25°C.

$$2Cu^{2+}(aq) + Hg_2^{2+}(aq) \rightleftharpoons 2Cu^{+}(aq) + 2Hg^{2+}(aq)$$

[i] Calculate $E°_{cell}$ for the reaction at 25 °C.
Kirakan $E°_{sel}$ untuk tindakbalas pada 25 °C.

[ii] Calculate ΔG for the reaction when the initial concentrations are as follows:

Kirakan ΔG untuk tindakbalas apabila kepekatan awal adalah seperti berikut:

(Cu^{2+}) = 0.0010 M, (Hg_2^{2+}) = 0.0020 M, (Cu^{+}) = 0.10 M, and (Hg^{2+}) = 0.20 M.

[iii] Which way the reaction will shift from the initial concentrations in order to reach equilibrium?

Cara manakah tindakbalas akan beranjak daripada kepekatan awal di dalam tertib untuk mencapai keseimbangan?

[6 marks/markah]

2. [a] Write short notes on the items numbered as shown in Figure Q.2.
Tuliskan nota-nota ringkas bagi butiran bernombor yang ditunjukkan di dalam Rajah S.2.

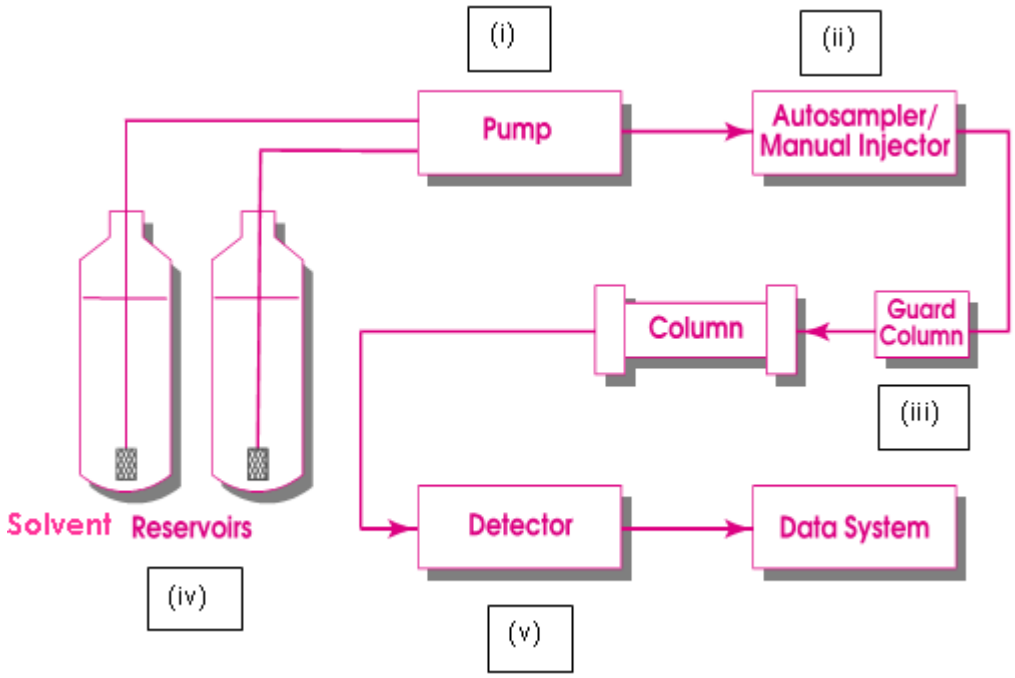

Figure Q.2. Schematic diagram of high performance liquid chromatography (HPLC) modules

Rajah S.2. Gambarajah skematik bagi modul kromatografi gas berprestasi tinggi.

[i] Pump
Pam

[ii] Auto-sampler
Pensampelan otomatik

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[iii] Guard column
Turus adang

[iv] Solvent reservoir
Takungan pelarut

[v] Detector
Pengesan

[10 marks/markah]

[b] List the variables that lead to band broadening and band separation in gas-liquid chromatography.
Senaraikan pembolehubah yang boleh menyebabkan perlebaran jalur dan pemisahan jalur di dalam kromatografi gas-cecair.

[5 marks/markah]

[c] The supplier gave the specification of the column to be used for sample analysis as shown in Table Q.2.[c].1.
Pembekal telah memberikan spesifikasi turus untuk digunakan bagi menganalisa sampel seperti yang ditunjukkan di dalam Jadual S.2.[c].1.

Table Q.2.[c].1
Jadual S.2.[c].1

Length of packing *Panjang penyendatan*	24.7 cm
Flow rate *Kadar aliran*	0.313 ml/min
V_M	1.37 ml
V_S	0.164 ml

A chromatogram of a mixture of species A, B, C and D is tabulated in the Table Q.2.[c].2.
Kromatogram bagi campuran spesis A, B, C dan D dijadualkan di dalam Jadual S.2.[c].2.

Table Q.2.[c].2
Jadual S.2.[c].2.

	Retention time, *Waktu penahanan* t_R(min.)	Width of peak base *Lebar puncak bawah* W, (min)
Non-retained *Tidak tersimpan*	3.1	-
A	5.4	0.41
B	13.3	1.07
C	14.1	1.16
D	21.6	1.72

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Calculate:
Kirakan:

[i] The number of plates for A, B, C and D.
Nombor plat bagi A, B, C dan D.

[ii] The plate height for the column A, B, C and D.
Ketinggian plat turus bagi A, B, C dan D.

[iii] The capacity factor for A, B, C and D.
Faktor muatan bagi A, B, C dan D.

[iv] The partition coefficient for A, B, C and D.
Pekali sekatan bagi A, B, C dan D.

[v] The resolution factor for B and C only.
Faktor kebezajelasan bagi B dan C sahaja.

[10 marks/markah]

3. [a] An ideal gas expands reversible and isothermally from 10 bar to 1 bar at 298.15 K. What are the values of;

Satu gas unggul mengembang secara berbalik dan isoterma daripada 10 bar kepada 1 bar pada 298.15 K. Apakah nilai-nilai untuk:

[i] W per mole
W per mol

[ii] Q per mole
Q *per mol*

[iii] ΔU

[iv] ΔH

[v] The ideal gas expands isothermally against constant pressure of 1 bar. How much work is done on the gas.
Gas unggul mengembang secara isoterma melawan tekanan tetap pada 1 bar. Berapakah kerja yang dilakukan oleh gas.

[10 marks/markah]

[b] What is the concentration of oxygen (O_2) in a fresh water stream in equilibrium with air at 25 °C and 1.0 bar? Express the answer in grams of O_2 per kg of solvent.

Apakah kepekatan oksigen (O_2) di dalam aliran air tawar dalam keseimbangan dengan udara pada 25 °C dan 1.0 bar? Nyatakan jawapan dalam gram O_2 per kg pelarut.

[5 marks/markah]

[c] What is the mass of ethylene glycol ($HOCH_2CH_2OH$) must be added to 5.50 kg of water to lower the freezing point of the water from 0.0 °C to – 10.0°C?

Apakah jisim etilina glikol ($HOCH_2CH_2OH$) yang mesti ditambah kepada 5.50 kg air untuk menurunkan titik sejuk-beku air dari 0.0 °C kepada -10.0°C?

[5 marks/markah]

[d] A voltaic cell is set up at 25°C with the half-cells: [Al^{3+} (0.0010M) |Al and Ni^{2+} (0.50M) |Ni]. Write an equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

Satu sel voltik ditetapkan pada 25 °C dengan sel separuh: : [Al^{3+} (0.0010M) |Al dan Ni^{2+} (0.50M) |Ni]. Tuliskan satu persamaan bagi tindakbalas yang terlibat apabila sel dijana menjadi arus elektrik dan tentukan keupayaan sel.

[5 marks/markah]

4. [a] Why is an internal standard most appropriate for quantitative analysis when unavoidable sample losses are expected during sample preparation?

Mengapakah piawai dalaman adalah paling sesuai untuk analisis kuantitatif apabila kehilangan sampel yang tidak dapat dielakkan dijangka berlaku semasa penyediaan sampel?

[3 marks/markah]

[b] Outline the steps commonly employed in solving problem in an analytical approach. Briefly describe each step with the aid of a flow chart.

Jelaskan langkah-langkah umum yang diguna untuk menyelesaikan masalah di dalam satu pendekatan analitikal. Terangkan pernyataan setiap langkah dengan bantuan carta alir.

[7 marks/markah]

[c] Table Q.4.[c] lists the molar absorptivities for the Arseno complexes of copper and barium at selected wavelengths. Determine the optimum wavelengths for analysis of a mixture of copper and barium.

Jadual S.4.[c]. menyenaraikan keberserapan molar untuk komplek Arseno kuprum dan barium pada panjang gelombang yang dipilih. Tentukan panjang gelombang yang optimum untuk analisa campuran kuprum dan barium.

Table Q.4.[c].
Jadual S.4.[c].

Wavelength *Panjang Gelombang* (nm)	ε_{Cu}	ε_{Ba}
595	11900	7100
600	15500	7200
607	18300	7400
611	19300	6900
614	19300	7000
620	17800	7100
626	16300	8400
635	10900	9900
641	7500	10500
645	5300	10000
650	3500	8600
655	2200	6600
658	1900	6500
665	1500	3900
670	1500	2800
680	1800	1500

[5 marks/markah]

[d] A mixture of copper and zinc were determined by forming coloured complexes with 2-pyridyl-azo-resorcinol (PAR). The absorbances for PAR, a mixture of Cu^{2+} and Zn^{2+}, and standards of 1.0 ppm Cu^{2+} and 1.0 ppm Zn^{2+} are listed in Table Q.4.[d].

Campuran kuprum dan zink telah ditentukan dengan penghasilan komplek berwarna dengan 2-piridil-azo-resorsinol (PAR). Bahan penyerap bagi PAR, iaitu campuran Cu^{2+} dan Zn^{2+}, dan piawai 1.0 ppm Cu^{2+} dan 1.0 ppm Zn^{2+} disenaraikan dalam Jadual S.4.[d].

Table Q.4.[d].
Jadual S.4.[d].

Wavelength *Panjang Gelombang* (nm)	Absorbance *Serapan*			
	PAR	Cu^{2+} std	Zu^{2+} std	Mixture
480	0.211	0.698	0.971	0.656
496	0.137	0.732	1.018	0.668
510	0.100	0.732	0.891	0.627
526	0.072	0.602	0.672	0.498
540	0.056	0.387	0.306	0.290

Determine the molar concentration of each analyte in the mixture.
Tentukan kepekatan molar bagi setiap analit dalam campuran.

[10 marks/markah]

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Appendix

Values for R, the ideal gas law constant
R= 0.08205 L.atm/mol.K
0.08314L.bar/mol.K
1.987 cal/mol.K
8.314 J/mol.K
62.36 L.torr/mol.K

Table: Solubility of several gases in water at 25 °C

solute	formula	solubiliy, mol $L^{-1}atm^{-1}$
ammonia	NH_3	57
carbon dioxide	CO_2	0.0308
methane	CH_4	.00129
nitrogen	N_2	0.000661
oxygen	O_2	.00126
sulfur dioxide	SO_2	1.25

TABLE Some Boiling Point Elevation and Freezing Point Depression Constants

Solvent	Normal Boiling Point (°C) Pure Solvent	K_{bp} (°C/m)	Normal Freezing Point (°C) Pure Solvent	K_{fp} (°C/m)
Water	100.00	+0.5121	0.0	−1.86
Benzene	80.10	+2.53	5.50	−5.12
Camphor	207.4	+5.611	179.75	−39.7
Chloroform ($CHCl_3$)	61.70	+3.63	—	—

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TABLE Standard Reduction Potentials in Aqueous Solution at 25 °C*

Reduction Half-Reaction		$E°$ (V)
$F_2(g) + 2\ e^-$	$\rightarrow 2\ F^-(aq)$	+2.87
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^-$	$\rightarrow 2\ H_2O(\ell)$	+1.77
$PbO_2(s) + SO_4^{2-}(aq) + 4\ H^+(aq) + 2\ e^-$	$\rightarrow PbSO_4(s) + 2\ H_2O(\ell)$	+1.685
$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^-$	$\rightarrow Mn^{2+}(aq) + 4\ H_2O(\ell)$	+1.51
$Au^{3+}(aq) + 3\ e^-$	$\rightarrow Au(s)$	+1.50
$Cl_2(g) + 2\ e^-$	$\rightarrow 2\ Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^-$	$\rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(\ell)$	+1.33
$O_2(g) + 4\ H^+(aq) + 4\ e^-$	$\rightarrow 2\ H_2O(\ell)$	+1.229
$Br_2(\ell) + 2\ e^-$	$\rightarrow 2\ Br^-(aq)$	+1.08
$NO_3^-(aq) + 4\ H^+(aq) + 3\ e^-$	$\rightarrow NO(g) + 2\ H_2O(\ell)$	+0.96
$OCl^-(aq) + H_2O(\ell) + 2\ e^-$	$\rightarrow Cl^-(aq) + 2\ OH^-(aq)$	+0.89
$Hg^{2+}(aq) + 2\ e^-$	$\rightarrow Hg(\ell)$	+0.855
$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	+0.799
$Hg_2^{2+}(aq) + 2\ e^-$	$\rightarrow 2\ Hg(\ell)$	+0.789
$Fe^{3+}(aq) + e^-$	$\rightarrow Fe^{2+}(aq)$	+0.771
$I_2(s) + 2\ e^-$	$\rightarrow 2\ I^-(aq)$	+0.535
$O_2(g) + 2\ H_2O(\ell) + 4\ e^-$	$\rightarrow 4\ OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2\ e^-$	$\rightarrow Cu(s)$	+0.337
$Sn^{4+}(aq) + 2\ e^-$	$\rightarrow Sn^{2+}(aq)$	+0.15
$2\ H^+(aq) + 2\ e^-$	$\rightarrow H_2(g)$	0.00
$Sn^{2+}(aq) + 2\ e^-$	$\rightarrow Sn(s)$	−0.14
$Ni^{2+}(aq) + 2\ e^-$	$\rightarrow Ni(s)$	−0.25
$V^{3+}(aq) + e^-$	$\rightarrow V^{2+}(aq)$	−0.255
$PbSO_4(s) + 2\ e^-$	$\rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.356
$Cd^{2+}(aq) + 2\ e^-$	$\rightarrow Cd(s)$	−0.40
$Fe^{2+}(aq) + 2\ e^-$	$\rightarrow Fe(s)$	−0.44
$Zn^{2+}(aq) + 2\ e^-$	$\rightarrow Zn(s)$	−0.763
$2\ H_2O(\ell) + 2\ e^-$	$\rightarrow H_2(g) + 2\ OH^-(aq)$	−0.8277
$Al^{3+}(aq) + 3\ e^-$	$\rightarrow Al(s)$	−1.66
$Mg^{2+}(aq) + 2\ e^-$	$\rightarrow Mg(s)$	−2.37
$Na^+(aq) + e^-$	$\rightarrow Na(s)$	−2.714
$K^+(aq) + e^-$	$\rightarrow K(s)$	−2.925
$Li^+(aq) + e^-$	$\rightarrow Li(s)$	−3.045

* In volts (V) versus the standard hydrogen electrode.

TABLE Selected Thermodynamic Values* *(continued)*

Species	ΔH_f° (298.15 K) (kJ/mol)	S° (298.15 K) (J/K · mol)	ΔG_f° (298.15 K) (kJ/mol)
Cesium			
Cs(s)	0	85.23	0
$Cs^+(g)$	457.964	—	—
CsCl(s)	−443.04	101.17	−414.53
Chlorine			
Cl(g)	121.3	165.19	105.3
$Cl^-(g)$	−233.13	—	—
$Cl_2(g)$	0	223.08	0
HCl(g)	−92.31	186.2	−95.09
HCl(aq)	−167.159	56.5	−131.26
Chromium			
Cr(s)	0	23.62	0
$Cr_2O_3(s)$	−1134.7	80.65	−1052.95
$CrCl_3(s)$	−556.5	123.0	−486.1
Copper			
Cu(s)	0	33.17	0
CuO(s)	−156.06	42.59	−128.3
$CuCl_2(s)$	−220.1	108.07	−175.7
$CuSO_4(s)$	−769.98	109.05	−660.75
Fluorine			
$F_2(g)$	0	202.8	0
F(g)	78.99	158.754	61.91
$F^-(g)$	−255.39	—	—
$F^-(aq)$	−332.63		−278.79
HF(g)	−273.3	173.779	−273.2
HF(aq)	−332.63	88.7	−278.79
Hydrogen			
$H_2(g)$	0	130.7	0
H(g)	217.965	114.713	203.247
$H^+(g)$	1536.202	—	—
$H_2O(\ell)$	−285.83	69.95	−237.15
$H_2O(g)$	−241.83	188.84	−228.59
$H_2O_2(\ell)$	−187.78	109.6	−120.35
Iodine			
$I_2(s)$	0	116.135	0
$I_2(g)$	62.438	260.69	19.327
I(g)	106.838	180.791	70.250

(continued)