UNIVERSITI SAINS MALAYSIA

Second Semester Examination
2012/2013 Academic Session

June 2013

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

Duration : 3 hours
[Masa : 3 jam]

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

[Sila pastikan bahawa kertas peperiksaan ini mengandungi ENAM muka surat yang bercetak dan DUA 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].

Answer ALL questions.
Jawab SEMUA soalan.

1. [a] State whether the following statement is True or False. If it is False explain why.

Nyatakan sama ada kenyataan berikut Betul atau Salah. Jika Salah, terangkan mengapa.

[i] A closed system cannot interact with its surroundings.
Sistem tertutup tidak boleh saling berhubung dengan sekelilingnya.

[ii] The USM engineering campus is an open system.
Kampus Kejuruteraan USM adalah satu sistem terbuka.

[iii] A homogeneous system must be a pure substance.
Sistem homegenus mestilah satu bahan tulen.

[iv] A system containing only one substance must be homogeneous.
Satu sistem mengandungi hanya satu bahan mestilah homogenus.

[8 marks/markah]

[b] For a constant-pressure process, $\Delta H = Q$. Consider a process in which *P* is not constant throughout the entire process, but the final and initial pressure are equal. Is ΔH equal to Q? Explain your answer.

Bagi suatu proses tekanan malar, $\Delta H = Q$. Anggapkan proses di mana P *tidak malar sepanjang keseluruhan proses, tetapi tekanan awal dan akhir adalah sama. Adakah ΔH sama dengan Q? Terangkan jawapan anda.*

[3 marks/markah]

[c] For each component of each of the following solutions state whether it will approximately obey Raoults's law, Henry's law, or neither.

Bagi setiap komponen untuk setiap larutan berikut, nyatakan sama ada ianya mematuhi undang-undang Raoult, undang-undang Henry, atau tidak kedua-duanya.

I. $X_{CCl4} = 0.5$; $X_{CH3OH} = 0.5$
II. $X_{CCl4} = 0.99$; $X_{CH3OH} = 0.01$

[4 marks/markah]

[d] Calculate Q, W, ΔU, and ΔH for the reversible isothermal expansion at 300K of 2 mol of a perfect gas from 500 cm^3 to 1500 cm^3.

Kirakan Q, W, ΔU, dan ΔH untuk pengembangan sesuhu berbalik pada 300 K bagi 2 mol gas sempurna daripada 500 sm^3 ke 1500 sm^3.

[8 marks/markah]

[e] Suppose 651 g of ethylene glycol, ($HOCH_2CH_2OH$), is dissolved in 1.50 kg of water. What is the vapor pressure of the water over the solution at 90 °C? Assume ideal behavior for the solution. By how many percent does the dissolved solute decrease its vapor pressure?

Andaikan 651 g ethylena glycol ($HOCH_2CH_2OH$), melarut di dalam 1.50 kg air. Apakah tekanan wap larutan pada 90 °C? Andaikan larutan itu bersifat unggul. Berapa peratuskah tekanan wap yang diturunkan oleh bahan larut terlarut?

[7 marks/markah]

2. [a] What is electromotive force?
Apakah daya elektromotif? *[2 marks/markah]*

[b] Decide whether hydrogen peroxide (H_2O_2) in acid solution is a stronger oxidizing agent than Cl_2 under standard condition.

Tentukan sama ada hidrogen peroksida (H_2O_2) di dalam larutan berasid adalah agen pengoksidaan kuat daripada Cl_2 di bawah keadaan piawai.

[3 marks/markah]

[c] Decide which of the halogens is capable of oxidizing gold metal to Au^{+3} (aq) under standard condition. Support your answer with E°_{cell} calculation.

Tentukan halogen yang mana berupaya mengoksidakan logam emas kepada Au^{+3} (ak) di bawah keadaan piawai. Sokong jawapan anda dengan pengiraan E°_{cell}.

[5 marks/markah]

[d] Describe how to set up a voltaic cell to generate an electric current using the reaction

Perihalkan bagaimana langkah bagi menyediakan sel voltik bagi menghasilkan arus elektrik menggunakan tindak balas

$$Fe(s) + Cd^{+2}(aq) \rightarrow Cd(s) + Fe^{+2}(aq)$$

Indicate the anode and cathode, direction of the electron flow, the directions of the ions flow, write equations for the half reactions that occur at each electrode, determine the E°_{sel} and calculate the equilibrium constant for the reaction.

Tunjukkan anod dan katod, arah aliran elektron, arah aliran ion, tuliskan persamaan bagi tindak balas separuh yang berlaku pada setiap elektrod, tentukan E°_{sel} dan kirakan keseimbangan tetap bagi tindak balas.

[10 marks/markah]

3. [a] Describe the differences between the following and list any particular advantages possessed by one over the other:

Perihalkan perbezaan di antara berikut dan senaraikan kelebihan-kelebihan khusus yang dimiliki oleh sesuatu berbanding yang lain:

[i] monochromators and polychromators
monokromator dan polikromator *[3 marks/markah]*

[ii] single beam and double beam spectrophotometer
spektrofotometer alur tunggal dan alur kembar *[4 marks/markah]*

[b] Why is a calibration curve likely to be linear over a wider range of concentrations at the wavelength of maximum absorption compared to a wavelength on a shoulder of the absorption curve?

Kenapakah lengkuk kalibrasi kelihatan lelurus pada julat kepekatan yang lebar pada panjang gelombang penyerapan maksimum berbanding dengan panjang gelombang pada bahu lengkuk penyerapan?

[3 marks/markah]

[c] The acidity constant for an organic weak acid was determined by measuring its absorbance as a function of pH while maintaining a constant total concentration of the acid. Using the data in Table Q.3.[c]., determine the acidity constant for the organic weak acid.

Keasidan malar bagi asid lemah organik ditentukan dengan mengukur penyerapannya sebagai satu fungsi pH dengan mengekalkan jumlah kepekatan malar bagi asid. Dengan menggunakan data di dalam Jadual S.3.[c]., tentukan keasidan malar bagi asid lemah organik.

Table Q.3.[c].
Jadual S.3.[c].

pH	Absorbance *Penyerapan*
1.53	0.010
2.20	0.010
3.66	0.035
4.11	0.072
4.35	0.103
4.75	0.169
4.88	0.193
5.09	0.227
5.69	0.288
7.20	0.317
7.78	0.317

[10 marks/markah]

[d] To determine the formula for the complex between Fe^{2+} and o-phenantroline, a series of solution was prepared in which the total concentration of metal and ligand was held constant at 3.15 x 10^{-4} M. The absorbance of each solution was measured at a wavelength of 510 nm. Using the data in Table Q.3.[d]., determine the formula for the complex.

Dalam penentuan formula bagi komplek di antara Fe^{2+} dan o-fenantrolin, satu siri larutan telah disediakan di mana jumlah kepekatan logam dan ligan berada pada keadaan malar 3.15 x *10^{-4} M. Penyerapan bagi setiap larutan diukur pada panjang gelombang 510 nm. Dengan menggunakan data di dalam Jadual S.3.[d]., tentukan formula komplek tersebut.*

Table Q.3.[d].
Jadual S.3.[d].

X_L	Absorbance *Penyerap*
0.0	0.000
0.1	0.116
0.2	0.231
0.3	0.347
0.4	0.462
0.5	0.578
0.6	0.693
0.7	0.809
0.8	0.693
0.9	0.347
1.0	0.000

[5 marks/markah]

4. [a] Define the following:
Berikan definisi bagi yang berikut:

[i] stationary phase
fasa pegun

[ii] elution
elutan

[iii] dead time
masa lenga

[iv] capacity factor
faktor kemuatan *[8 marks/markah]*

[b] Compare between high performance liquid chromatography (HPLC) and gas liquid chromatography (GLC).

Bandingkan di antara kromatografi cecair prestasi tinggi (HPLC) dengan kromatografi cecair gas (GLC). *[8 marks/markah]*

[c] A mixture of alkyl iodides is separated by gas chromatography. The column was heated so that its temperature rose linearly during the separation. Data of the peaks obtained in the separation are shown in Table Q.4.

Campuran alkil iodida dipisah menggunakan kromatografi gas. Turusnya dipanaskan supaya suhunya meningkat secara linear semasa pemisahan. Data untuk puncak yang di dapati dalam pemisahan ditunjukkan di dalam Jadual S.4.

Table Q.4.
Jadual S.4.

Peak *Puncak*	Identity *Identiti*	Molecular weight *Berat molekul*	t_R (min)	t_W (min)	Temperature *Suhu* (^oC)	Peak area *Kawasan puncak* (cm^2)
1	Air peak *Puncak udara*	-	$t_M = 0.50$	Small *Kecil*	55	Small *Kecil*
2	CH_3I	141.9	6.60	0.55	100	13.0
3	C_2H_5I	156.0	9.82	1.00	127	12.0
4	Iso-C_3H_7I	170.0	11.90	1.04	139	10.0
5	n-C_3H_7I	170.0	13.04	1.08	148	7.2
6	CH_2I_2	267.8	19.10	1.60	193	2.0

[i] What is the resolution, R, of peaks 4 and 5?
Apakah resolusi R bagi puncak 4 dan 5?

[ii] The length of column used in the separation was 365 cm. What length of column would be needed so that the resolution of peaks 4 and 5 were $R' = 1.50$?

Panjang turus yang digunakan di dalam pemisahan ialah 365 sm. Berapakah panjang turus yang diperlukan supaya resolusi puncak 4 dan 5 adalah R' = 1.50?

[iii] The flame ionization used in the chromatographic analysis had a response that was directly proportional to the number of molecules of alkyl iodide. If 20.0 μg of CH_3I was present in the sample, how much C_2H_5I was formed?

Pengesan pengionan bernyala yang digunakan di dalam analisis kromatografi mempunyai tindak balas yang sejajar dengan nombor molekul bagi alkil iodida. Sekiranya 20.0 μg CH_3I wujud di dalam sampel, berapa banyakkah C_2H_5I yang terbentuk?

[9 marks/markah]

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Appendix

Ideal gas constant
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

pooled standard deviation

$$s_p = \sqrt{\frac{\sum(x_{i1} - \overline{x}_1)^2 + \sum(x_{i2} - \overline{x}_2)^2}{N - k}}$$

slope of regression line

$$m = \frac{\Sigma(x_i - \bar{x})(y_i - \bar{y})}{\Sigma(x_i - \bar{x})^2}$$

$$b = \bar{y} - m\bar{x}$$

Easier Form of Least Squares Equations

$$m = \frac{\Sigma x_i y_i - [(\Sigma x_i \Sigma y_i)/n]}{\Sigma x_i^2 - [(\Sigma x_i)^2/n]}$$

- n is the number of data points

Standard Deviation of Deviations

$$s_y = \sqrt{\frac{\Sigma[y_i - (mx_i + b)]^2}{N - 2}} = \sqrt{\frac{[\Sigma y_i^2 - (\Sigma y_i)^2/N] - m^2[\Sigma x_i^2 - (\Sigma x_i)^2/N]}{N - 2}}$$

Uncertainty in the slope

$$s_m = \sqrt{\frac{s_y^2}{\Sigma(\bar{x} - x_i)^2}} = \sqrt{\frac{s_y^2}{\Sigma x_i^2 - (\Sigma x_i)^2/N}}$$

Uncertainty in the intercept

$$s_b = s_y \sqrt{\frac{\Sigma x_i^2}{N\Sigma x_i^2 - (\Sigma x_i)^2}} = s_y \sqrt{\frac{1}{N - (\Sigma x_i)^2/\Sigma x_i^2}}$$

TABLE 1 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.