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UNIVERSITI SAINS MALAYSIA

Second Semester Examination  
2010/2011 Academic Session

April/May 2011

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

Duration : 3 hours  
*[Masa : 3 jam]*

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Please ensure that this examination paper contains SEVEN printed pages before you begin the examination.

*[Sila pastikan bahawa kertas peperiksaan ini mengandungi TUJUH muka surat yang bercetak 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].*

...2/-

1. [a] Describe the stray radiation that cause deviation from Beer's Law.  
*Huraikan sinaran sesat yang menyebabkan sisihan Hukum Beer.*  
 [5 marks/markah]

[b] Outline a general method if a standard addition method is to be used in determining an analyte of concern. The answer should include:  
*Rangkakan suatu kaedah umum jika kaedah penambahan piawai diguna bagi menentukan analit yang terbabit. Jawapan anda harus merangkumi:*

[i] Brief description of the procedure  
 Huraian ringkas tatacara tersebut

[ii] Sketch of a diagram  
 Lakaran gambarajah [5 marks/markah]

[c] The stoichiometry for a metal-ligand (ML) complex was determined by the method of continuous variations. A series of solutions was prepared in which the combined concentrations of the metal (M) and ligand (L) were held constant at  $5.15 \times 10^{-4}M$ .

*Stoikiometri untuk suatu kompleks logam-ligan (ML) telah ditentukan dengan kaedah variasi selanjar. Suatu siri larutan telah disediakan di mana kepekatan tergabung logam (M) dan ligan (L) dikekalkan malar pada  $5.15 \times 10^{-4} M$ .*

The absorbances of these solutions were measured at a wavelength at which only the metal-ligand complex absorbs. Using data in Table Q.1.[c], determine the formula of the complex.

*Keserapan larutan-larutan tersebut telah diukur pada suatu panjang gelombang yang hanya diserap oleh kompleks logam-ligan tersebut. Tentukan formula kompleks tersebut dengan menggunakan data dalam Jadual S.1.[c].*

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

Mole fraction of M <i>Pecahan mol M</i>	Mole fraction of L <i>Pecahan mol L</i>	Absorbance <i>Keserapan</i>
1.0	0.0	0.001
0.9	0.1	0.126
0.8	0.2	0.260
0.7	0.3	0.389
0.6	0.4	0.515
0.5	0.5	0.642
0.4	0.6	0.775
0.3	0.7	0.771
0.2	0.8	0.513
0.1	0.9	0.253
0.0	1.0	0.000

[5 marks/markah]

...3/-

- [d] A mixture of  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  and standards of  $1.0 \times 10^{-4} \text{ M}$   $\text{KMnO}_4$  and  $1.0 \times 10^{-4} \text{ M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  gave the following results in Table Q.1. [d]:

*Suatu campuran  $\text{MnO}_4^-$  dan  $\text{Cr}_2\text{O}_7^{2-}$  serta larutan piawai  $1.0 \times 10^{-4} \text{ M}$   $\text{KMnO}_4$  dan  $1.0 \times 10^{-4} \text{ M}$   $\text{K}_2\text{Cr}_2\text{O}_7$  memberikan keputusan seperti di Jadual S.1.[d]:*

Table Q.1.[d].  
Jadual S.1.[d].

Wavelength Panjang gelombang (nm)	Absorbances Keserapan		
	$\text{MnO}_4^-$ Standard Piawai $\text{MnO}_4^-$	$\text{Cr}_2\text{O}_7^{2-}$ Standard Piawai $\text{Cr}_2\text{O}_7^{2-}$	Mixture Campuran
266	0.042	0.410	0.766
288	0.082	0.283	0.571
320	0.168	0.158	0.422
350	0.125	0.318	0.672
360	0.056	0.181	0.366

Determine the molar concentration of each analyte in the mixture.

*Tentukan kepekatan molar setiap analit dalam campuran tersebut.*

[10 marks/markah]

2. [a] Describe the principles of the following gas chromatography detectors:  
*Jelaskan prinsip-prinsip bagi pegasan kromatografi gas berikut:*

[i] thermal conductivity  
*keberkondukan haba*

[ii] flame ionization  
*pengionan nyala*

[iii] electron capture  
*penangkapan elektron*

[6 marks/markah]

- [b] What is a guard column and why is it used?  
*Apakah turus adang dan bagaimana ianya digunakan?*

[4 marks/markah]

- [c] List the variables that lead to zone broadening.  
*Senaraikan pembolehubah-pembolehubah yang menyebabkan perlebaran zon.*

[5 marks/markah]

- [d] The following chromatogram was obtained for 2  $\mu\text{l}$  injections of n-hexane using a gas-chromatograph of flame ionization detector (FID) with a 3 m capillary column (Figure Q.2.[d].).

*Kromatogram berikut telah diperolehi bagi suntikan 2  $\mu\text{l}$  n-heksana dengan menggunakan kromatografi gas bagi pengesanan pengionan nyala (FID) dengan turus kapilari. (Gambarajah S.2.[d].).*

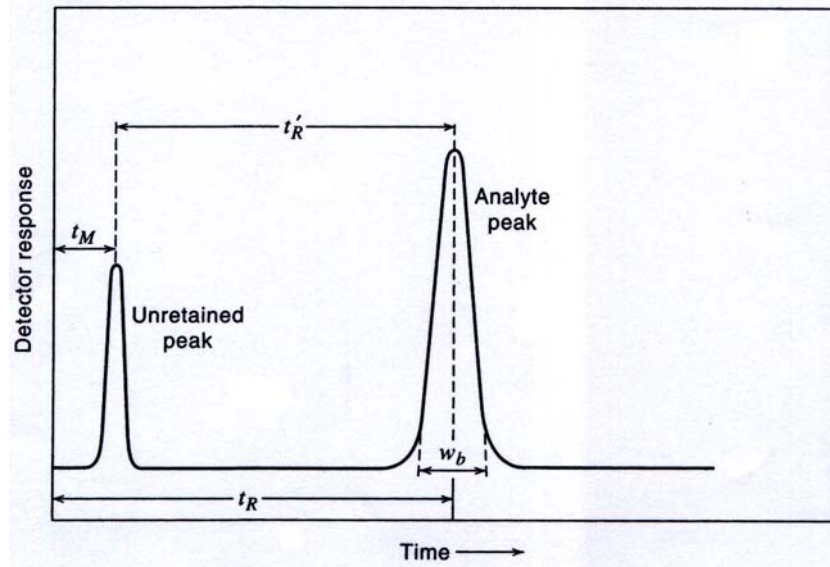


Figure Q.2.[d].  
Gambarajah S.2.[d].

Given:

Diberikan:

$$t_R = 52.3 \text{ mm}$$

$$t_M = 8.0 \text{ mm}$$

$$W_b = 9.0 \text{ mm}$$

- [i] Calculate the number of plates in the column.  
*Kirakan bilangan plat di dalam turus.*
- [ii] Calculate the retention factor of the chromatographic peak. Explain your answer.  
*Kirakan faktor penahanan bagi puncak kromatografi itu. Terangkan jawapan anda.*
- [iii] Ethanol and methanol were also separated in the column with retention times of 370 and 385 s, and  $W_b$  of 16.0 and 17.0 s respectively. An unretained air peak occurs at 10.0 s. Calculate the separation factor and the resolution.

*Etanol dan metanol telah juga dipisahkan di dalam turus dengan waktu penahanannya masing-masing 370 dan 386 saat, dan lebar bawah  $W_b$  ialah 16.0 dan 17.0 saat. Puncak udara kekal ialah 10 saat. Kirakan faktor pemisah dan resolusinya.*

[10 marks/markah]

...5/-

3. State whether the following statements are true or false. Justify your answer if it is false.

*Nyatakan sama ada yang berikut adalah benar atau palsu. Justifikasikan jawapan anda sekiranya ia palsu.*

- [a]  $\Delta U = q + w$  for every thermodynamic system in the absence of external fields.  
 *$\Delta U = q + w$  bagi setiap sistem termodinamik yang tiada medan luaran.*
- [b] The infinitesimal P-V work in a mechanically reversible process in a closed system is not always equal to  $-PdV$ .  
*Kerja P-V yang tak terhingga dalam suatu proses berbalik mekanik, dalam suatu sistem tertutup, adalah tidak sentiasa sama dengan  $-PdV$ .*
- [c] A process in which the final temperature equals the initial temperature must be an isothermal process.  
*Suatu proses di mana suhu akhir ialah sama dengan suhu awal adalah semestinya suatu proses sesuhu.*
- [d] The volume of a solution at  $T$  and  $P$  equals the sum of the volumes of its pure components at  $T$  and  $P$ .  
*Isipadu suatu larutan pada  $T$  dan  $P$  ialah sama dengan jumlah isipadu komponen-komponen tulennya pada  $T$  dan  $P$ .*
- [e] A liquid mixture of the two optical isomers of  $\text{CH}_3\text{ClBr}$  is not an ideal solution.  
*Suatu campuran cecair dua isomer optik  $\text{CH}_3\text{ClBr}$  bukan suatu larutan unggul.*
- [f] Adding a pinch of  $\text{NaCl}$  to the  $\text{CuSO}_4$  solution of cell  $[\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) \mid \text{Cu}(\text{s})]$  thermostated at  $25^\circ\text{C}$ , the  $E^\circ$  does not change.  
*Apabila secubit  $\text{NaCl}$  ditambahkan pada larutan  $\text{CuSO}_4$  sel  $[\text{Zn}(\text{s}) \mid \text{Zn}^{2+}(\text{ak}) \parallel \text{Cu}^{2+}(\text{ak}) \mid \text{Cu}(\text{p})]$  dan dilarasuhkan ialah pada  $25^\circ\text{C}$ ,  $E^\circ$  tidak akan berubah.*
- [g] If the electrochemical reaction cell is multiplied by 2, the  $n$  in the Nernst equation remains unchanged.  
*Jika sel tindakbalas elektrokimia didarab dengan 2,  $n$  dalam persamaan Nernst kekal tidak berubah.*
- [h] When a perfect gas undergoes an expansion process at constant pressure, its internal energy decreases.  
*Apabila suatu gas sempurna melalui proses pengembangan pada tekanan malar, tenaga dalamnya akan menurun.*
- [i] The osmotic pressure is the pressure exerted on the semipermeable membrane by the solute molecules.  
*Tekanan osmosis ialah tekanan yang dikenakan pada membran separa telap oleh molekul-molekul bahan larut.*

- [j] Addition of non volatile solute to a pure solvent at a constant always lowers the vapor pressure.

*Penambahan bahan larut tak meruap kepada suatu larutan tulen pada suatu T malar akan sentiasa merendahkan tekanan wap.*

[20 marks/markah]

4. [a] For a certain perfect gas,  $C_{V,m} = 2.5R$  at all temperatures. Calculate  $q$ ,  $w$ ,  $\Delta U$ , and  $\Delta H$  when 2 mol of this gas undergoes a reversible isobaric (1 atm) expansion process from  $20 \text{ dm}^3$  to  $40 \text{ dm}^3$ .

*$C_{Vm} = 2.5R$  untuk suatu gas sempurna tertentu pada semua suhu. Kirakan  $q$ ,  $w$ ,  $\Delta U$  dan  $\Delta H$  apabila 2 mol gas ini melalui proses pengembangan setekanan (1 atm) berbalik dari  $20 \text{ dm}^3$  ke  $40 \text{ dm}^3$ .*

$$R = 8.314 \text{ J/mol.K}$$

[10 marks/markah]

- [b] Benzene ( $C_6H_6$ ) and toluene ( $C_6H_5CH_3$ ) form nearly ideal solutions. At  $20^\circ\text{C}$  the vapor pressure of benzene is 74.7 torr, and that of toluene is 22.3 torr. Find the equilibrium partial vapor pressures at  $20^\circ\text{C}$  solution of 100 g of benzene plus 100 g of toluene.

*Benzena ( $C_6H_6$ ) dan toluena ( $C_6H_5CH_3$ ) membentuk larutan hampir unggul. Pada  $20^\circ\text{C}$ , tekanan wap benzena ialah 74.7 torr dan tekanan wap toluena ialah 22.3 torr. Carikan tekanan wap separa keseimbangan pada  $20^\circ\text{C}$  untuk larutan 100 g benzena dan 100 g toluena.*

[5 marks/markah]

- [c] 6 g of a mixture of naphthalene ( $C_{10}H_8$ ) and anthracene ( $C_{14}H_{10}$ ) is dissolved in 300 g of benzene. When the solution is cooled, it begins to freeze at a temperature  $0.7^\circ\text{C}$  below freezing point ( $5.5^\circ\text{C}$ ) of pure benzene. Find the composition of the mixture, given that  $k_f$  for benzene is  $5.1^\circ\text{C kg mol}^{-1}$ .

*6 g suatu campuran naftalena ( $C_{10}H_8$ ) dan antrasena ( $C_{14}H_{10}$ ) dilarutkan dalam 300 g benzena. Apabila larutan tersebut disejukkan, ia mula membeku pada suatu suhu  $0.7^\circ\text{C}$  di bawah takat beku benzena tulen ( $5.5^\circ\text{C}$ ). Carikan komposisi campuran tersebut apabila  $k_f$  untuk benzena ialah  $5.1^\circ\text{C kg mol}^{-1}$ .*

[5 marks/markah]

- [d] How many Faradays are required to produce 21.58 g of silver from a silver nitrate solution?

*Berapa banyak Faradaykah yang perlu untuk menghasilkan 21.58 g perak daripada suatu larutan perak nitrat?*

$$\text{Ag} = 107.9 \text{ g/mol}$$

[4 marks/markah]

- [e] A voltaic cell consists of a copper electrode in a solution of copper (II) ions and a palladium electrode in a solution of palladium (II) ions. The palladium is the cathode and its reduction potential is 0.951 V.

*Suatu sel voltan mengandungi satu elektrod kuprum dalam satu larutan ion kuprum (II) dan satu elektrod paladium dalam satu larutan ion paladium (II). Paladium tersebut ialah katod dan keupayaan penurunannya ialah 0.951V.*

- [i] Write the half-reaction that occurs at the anode.  
*Tuliskan tindak balas separa yang berlaku di anod.*
- [ii] If  $E^\circ$  is 0.609 V, what is the potential for the oxidation half-reaction?  
*Jika  $E^\circ$  ialah 0.609 V, apakah keupayaan untuk tindak balas separa pengoksidaan?*
- [iii] What is  $K_{eq}$  for this reaction?  
*Apakah  $K_{eq}$  untuk tindak balas ini?*

*[6 marks/markah]*