UNIVERSITI SAINS MALAYSIA

Final Examination
Academic Session 2007/2008

April 2008

JIK 220 – KINETIC AND ELECTROCHEMISTRY
[KINETIK DAN ELEKTROKIMIA]

Duration : 3 hours
[Masa : 3 jam]

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

Answer **FIVE** questions. You may answer **either** in Bahasa Malaysia or in English.

All answers must be written in the answer booklet provided.

Each questions is worth 20 marks and the marks for each sub question is given at the end of that question.

Sila pastikan bahawa kertas peperiksaan ini mengandungi SEPULUH muka surat yang bercetak sebelum anda memulakan peperiksaan ini.

*Jawab **LIMA** soalan. Anda dibenarkan menjawab soalan **sama ada** dalam Bahasa Malaysia atau Bahasa Inggeris.*

Setiap jawapan mesti dijawab di dalam buku jawapan yang disediakan.

Setiap soalan bernilai 20 markah dan markah subsoalan diperlihatkan di penghujung subsoalan itu.

1. (a) What is a rate law expression, and how is it determined?

Apakah pernyataan hukum kadar, dan bagaimana ia ditentukan?

(3 marks)

(b) Explain the differences between a first-order reaction and a second-order reaction.

Jelaskan perbezaan antara tindak balas tertib pertama dan tindak balas tertib kedua.

(5 marks)

(c) Hydrolysis of 17% sucrose in 0.099 mol L^{-1} aqueous HCl solution at 35 °C was given in table below :
What is the order of the reaction and the value of rate constant (k)?

t/min	9.82	59.60	93.18	142.9	294.8	589.4
Sucrose residue, %	96.5	80.3	71.0	59.1	32.8	11.1

Hidrolisis 17% sukrosa dalam 0.099 mol L^{-1} larutan HCl akues pada 35 °C diberikan seperti dalam jadual di bawah :
Apakah tertib tindak balas dan nilai pemalar kadarnya (k)?

t/min	*9.82*	*59.60*	*93.18*	*142.9*	*294.8*	*589.4*
Baki sukrosa, %	*96.5*	*80.3*	*71.0*	*59.1*	*32.8*	*11.1*

(12 marks)

2. (a) What is a reaction intermediate? Can an intermediate be present in the rate law expression for the overall reaction?

Apakah zat perantara? Bolehkah zat perantara hadir dalam penulisan hukum kadar bagi tindak balas keseluruhan?

(4 marks)

(b) What is the preequilibrium approximation, and under what condition is it considered valid?

Apakah penghampiran keadaan mantap, dan pada keadaan manakah ia dianggap sah?

(4 marks)

(c) The chlorination of vinyl chloride,

$$C_2H_3Cl + Cl_2 \longrightarrow C_2H_3Cl_3$$

is believed to proceed by the following mechanism :

$$Cl_2 \xrightarrow{k_1} 2Cl\bullet$$

$$Cl\bullet + C_2H_3Cl \xrightarrow{k_2} C_2H_3Cl_2\bullet$$

$$C_2H_3Cl_2\bullet + Cl_2 \xrightarrow{k_3} C_2H_3Cl_3 + Cl\bullet$$

$$C_2H_3Cl_2\bullet + C_2H_3Cl_2\bullet \xrightarrow{k_4} \text{stable species}$$

Derive the rate law expression for the chlorination of vinyl chloride based on this mechanism.

Pengklorinan vinil klorida,

$$C_2H_3Cl + Cl_2 \longrightarrow C_2H_3Cl_3$$

adalah berlaku seperti mekanisme yang diberikan :

$$Cl_2 \xrightarrow{k_1} 2Cl\bullet$$

$$Cl\bullet + C_2H_3Cl \xrightarrow{k_2} C_2H_3Cl_2\bullet$$

$$C_2H_3Cl_2\bullet + Cl_2 \xrightarrow{k_3} C_2H_3Cl_3 + Cl\bullet$$

$$C_2H_3Cl_2\bullet + C_2H_3Cl_2\bullet \xrightarrow{k_4} \textit{spesies stabil}$$

Terbitkan hukum kadar bagi pengklorinan vinil klorida berdasarkan mekanisme yang diberikan.

(12 marks)

3. (a) Calculate the most probable speed of Ne and Kr at 298 K. Compare the ratio between them.

(Relative atomic mass: Ne = 20, Kr = 83).

Kira laju paling mungkin bagi Ne dan Kr pada suhu 298 K. Bandingkan nisbah di antara mereka.

(Jisim atom relatif: Ne = 20, Kr = 83).

(6 marks)

(b) A gas mixture contains H_2 at 0.666 bar and O_2 at 0.333 bar at 25°C. The collision diameters (σ) of H_2 and O_2 are 0.272nm and 0.360 nm, respectively. Calculate :

(i) The collision frequency (z_{12}) of a hydrogen molecule with an oxygen molecule?
(ii) The collision frequency (z_{21}) of an oxygen molecule with a hydrogen molecule?
(iii) The collision density (Z_{12}) between hydrogen molecules and oxygen molecules in mol $L^{-1}s^{-1}$?

(Relative atomic mass; H = 1.0, O = 16.0)

Suatu campuran gas mengandungi H_2 pada 0.666 bar dan O_2 pada 0.333 bar pada suhu 25 °C. Diameter pelanggaran (σ) bagi H_2 dan O_2 masing-masing adalah 0.272nm dan 0.360 nm. Kira :

(i) Frekuensi pelanggaran (z_{12}) bagi satu molekul hidrogen dengan satu molekul oksigen?
(ii) Frekuensi pelanggaran (z_{21}) bagi satu molekul oksigen dengan satu molekul hidrogen?
(iii) Ketumpatan pelanggaran (Z_{12}) antara molekul-molekul hidrogen dan molekul-molekul oksigen dalam unit mol $L^{-1}s^{-1}$?

(Jisim atom; H = 1.0, O = 16.0)

(14 marks)

4. (a) Define q_{Total}, and how is it constructed using the partition functions for each energetic degree of freedom?

Takrifkan q_{Total}, dan bagaimanakah ia dibina daripada fungsi sekatan untuk setiap darjah kebebasan tenaga?

(4 marks)

(b) Evaluate the translational partition function for Ar confined to a volume of 1000 cm^3 at 298 K.

Nilaikan fungsi sekatan translasi untuk Ar pada suatu isipadu 1000 cm^3 pada suhu 298 K.

(8 marks)

(c) State the translational, vibrational and rotational degree of molecular freedom for the following molecules :

(i) CO_2
(ii) CCl_4
(iii) CH_3CH_2COOH
(iv) C_6H_6

Nyatakan darjah kebebasan translasi, getaran dan putaran molekul untuk molekul-molekul berikut :

(i) CO_2
(ii) CCl_4
(iii) CH_3CH_2COOH
(iv) C_6H_6

(8 marks)

5. (a) Calculate the ionic strength (I) in a solution containing 0.0050 *m* K_2SO_4, 0.0010 *m* Na_3PO_4, and 0.0025 *m* $MgCl_2$.
(Calculate each and total ionic strength. Given *m* is molality).

Kirakan kekuatan ionik (I) bagi suatu larutan mengandungi 0.0050 m K_2SO_4, *0.0010 m* Na_3PO_4, *dan 0.0025 m* $MgCl_2$.
(Kirakan kekuatan ionik bagi setiap satu dan keseluruhan. Diberi m ialah kemolalan).

(10 marks)

(b) Calculate K_{eq} value for overall reaction, given the following half-reaction :

$$Cu^{2+} + e^- \leftrightarrow Cu^+ \qquad (E^o = 0.158V)$$
$$I_3^- + 2e^- \leftrightarrow 3I^- \qquad (E^o = 0.536V)$$

Kirakan nilai K_{eq} *bagi tindak balas keseluruhan, diberi tindak balas setengah seperti berikut :*

$$Cu^{2+} + e^- \leftrightarrow Cu^+ \qquad (E^o = 0.158V)$$
$$I_3^- + 2e^- \leftrightarrow 3I^- \qquad (E^o = 0.536V)$$

(10 marks)

6. (a) Discuss how the Debye–Hückel screening length of an electrolyte solution changes as the following parameters increased :

(i) temperature
(ii) dielectric constant
(iii) ionic strength.

Bincangkan bagaimana panjang pengskrinan Debye–Hückel dalam suatu larutan elektrolit berubah dengan peningkatan parameter yang diberikan :

(i) suhu
(ii) pemalar dielektrik
(iii) kekuatan ionik.

(6 marks)

(b) Calculate $\Delta S^{o}_{reaction}$ for the reaction $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$.
S^{o} is given as below. (Hint : Please use the necessary data only).

$(AgCl, s) = 96.3\ J\ K^{-1}\ mol^{-1}$, $(Ag^{+}, aq) = 72.7\ J\ K^{-1}\ mol^{-1}$, $(Cl^{-}, aq) = 56.5\ J\ K^{-1}\ mol^{-1}$ $(K^{+}, aq) = 102.5\ J\ K^{-1}\ mol^{-1}$, $(NO_3^{-}, aq) = 146.4\ J\ K^{-1}\ mol^{-1}$.

Kirakan $\Delta S^{o}_{reaction}$ bagi tindak balas $AgNO_3(aq) + KCl(aq) \longrightarrow AgCl(s) + KNO_3(aq)$.
S^{o} diberikan seperti di bawah. (Petunjuk : Guna data yang sesuai sahaja).

$(AgCl, s) = 96.3\ J\ K^{-1}\ mol^{-1}$, $(Ag^{+}, aq) = 72.7\ J\ K^{-1}\ mol^{-1}$, $(Cl^{-}, aq) = 56.5\ J\ K^{-1}\ mol^{-1}$ $(K^{+}, aq) = 102.5\ J\ K^{-1}\ mol^{-1}$, $(NO_3^{-}, aq) = 146.4\ J\ K^{-1}\ mol^{-1}$.

(4 marks)

(c) Calculate the value of mean ionic molality, $m_{\pm}$ in 5.0×10^{-4} molal solutions of

(i) KCl
(ii) $Ca(NO_3)_2$, and
(iii) $ZnSO_4$.

Assume complete dissociation.

Kirakan nilai kemolalan ionik purata, $m_{\pm}$ bagi larutan 5.0×10^{-4} molal.

(i) *KCl*
(ii) *$Ca(NO_3)_2$, dan*
(iii) *$ZnSO_4$.*

Anggap penceraian larutan adalah lengkap.

(6 marks)

(d) What is the difference between a strong and weak electrolyte?

Apakah perbezaan antara elektrolit kuat dan lemah?

(4 marks)

Jadual 1

Pemalar Asas Kimia

Simbol	Keterangan	Nilai
N_A	Nombor Avogadro	6.022×10^{23} mol^{-1}
F	Pemalar Faraday	96,500 C mol^{-1}, atau coulomb per mol, elektron
e	Cas elektron	4.80×10^{-10} esu 1.60×10^{-19} C atau coulomb
m_e	Jisim elektron	9.11×10^{-28} g 9.11×10^{-31} kg
m_p	Jisim proton	1.67×10^{-24} g 1.67×10^{-27} kg
R	Pemalar gas	8.314 kPa dm^3 mol^{-1} K^{-1} 8.314×10^7 erg K^{-1} mol^{-1} 8.314 J K^{-1} mol^{-1} 82.05 cm^3 atm K^{-1} mol^{-1} 0.0821 liter atm K^{-1} mol^{-1} 1.987 cal K^{-1} mol^{-1}
k	Pemalar Boltzmann	1.380×10^{-16} erg K^{-1} molekul^{-1} 1.380×10^{-23} J K^{-1} molekul^{-1}
g		981 cm s^{-2} 9.81 m s^{-2}
1 atm		760 mm Hg 101.325 kPa 76 cm Hg 1.013×10^6 dyn cm^{-2} 101,325 N m^{-2}
$2.303 \frac{RT}{F}$		0.0591 V, atau volt, pada 25°C

760 torr	=	101.325 kPa
1 Å	=	10^{-8} cm
pico	=	10^{-12}

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Jadual 2

PEMALAR DAN FAKTOR PERTUKARAN*

1 liter	1000.028 cm^3
1 atm	1.01325×10^6 dynes cm^{-2}
	760 mm raksa (Hg)
1 joule antarabangsa	1.00017 joule mutlak
1 cal (secara takrifan)	4.1833 joules antarabangsa
	4.1833 volt-coulombs antarabangsa
	4.1840 joules mutlak
	0.041292 liter-atm
	41.293 cc.-atm
1 liter-atm	1.0133×10^9 ergs
	1.0131×10^2 joules antarabangsa
	24.218 cal
1 cc.-atm	0.024212 cal.
Isipadu molar gas unggul 0°C dan 1 atm	22.4140 cal.
Takat ais	273.16 K
Pemalar gas molar	8.3144 joules mutlak K^{-1} mol^{-1}
	8.3130 joules antarabangsa K^{-1} mol^{-1}
	1.9872 cal. K^{-1} mol^{-1}
	0.082054 liter-atm K^{-1} mol^{-1}
	82.057 cc.-atm K^{-1} mol^{-1}
Nombor Avogadro (N_A)	6.0228×10^{23} mol^{-1}
Pemalar Boltzmann (k=R/N)	1.3805×10^{16} erg K^{-1}
Pemalar Planck (h)	6.6242×10^{-27} erg sec.
Laju cahaya (c)	2.99776×10^{10} cm $sec.^{-1}$
hc/k	1/4385 cm K
Faraday (F)	96,500 coulombs antarabangsa $g.equav^{-1}$

* Kebanyakan daripada terbitan National Bureau of Standards, c.f., J.Res. Nat. Bur. Stand., 34, 143 (1945)

Jadual 3 : Dalam teori gas kinetik persamaan kamilan bentuk ini sering ditemui.

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Kamilan	0	1	2	3	4	5
$\int_0^{\infty} x^n \exp(-ax^2)\,dx$	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{1/2}$	$\frac{1}{2a}$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{1/2}$	$\frac{1}{2a^2}$	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{1/2}$	$\frac{1}{a^3}$
$\int_{-\infty}^{+\infty} x^n \exp(-ax^2)\,dx$	$\left(\frac{\pi}{a}\right)^{1/2}$	0	$\frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2}$	0	$\frac{3}{4}\left(\frac{\pi}{a^5}\right)^{1/2}$	0

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