UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KFT 331 – Physical Chemistry III
[Kimia Fizik III]

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, beginning the answers to 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.

...2/-

Answer any **FIVE** questions.

1. Consider the function $\psi(x) = A\left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right]$.

   (a) Determine whether $\psi(x)$ is an acceptable wave function for the particle in the box of dimension a.

   (4 marks)

   (b) Normalize $\psi(x)$.

   (8 marks)

   (c) Determine whether $\psi(x)$ is an eigenfunction of the Hamiltonian operator $\hat{\mathbf{H}}$ for the particle in the box of dimension a. Estimate the total energy.

   (8 marks)

   Given : $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

   $$\int \sin\theta \sin 2\theta \, d\theta = \frac{2}{3}\sin^3\theta + C$$

2. The normalized ground-state wave function for the harmonic oscillator is $\psi_o(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}}$ where $\alpha = \frac{\sqrt{km}}{\hbar}$. Given that the Hamiltonian operator for the system is $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$.

   (a) Determine the ground-state energy.

   (5 marks)

   (b) Show that the Hamiltonian operator is Hermitian. Given that $\hat{R}$ is Hermitian if $\int \psi_m^* \hat{R} \psi_n \, d\tau = \int \psi_n \left(\hat{R}\psi_m\right)^* d\tau$.

   (7 marks)

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(c) Determine the average value of the momentum for $\psi_o(x)$. Explain your results.

(8 marks)

Given : $\int xe^{-ax^2}dx = -\frac{1}{2a}e^{-ax^2} + C$

3. (a) By using the definition of the partition function, q, and $E = \sum_i n_i \epsilon_i$, derive the following:

$$E = NkT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

(5 marks)

(b) Derive the expressions for H and C_v using the results from (a).

(7 marks)

(c) For a system consisting of a mole of particles having two non-degenerate energy levels separated by 1.00×10^{-20} J, find the temperature at which the energy, E, of this system is equal to 1.00 kJ by using the result from (a). Assume that the energy for the ground energy level is zero.

(8 marks)

4. (a) Consider a collection of molecules where each molecule has two non-degenerate energy levels that are separated by 1000 cm^{-1}.

(i) What is the temperature (T) of the collection if there are 8 times more molecules in the ground energy level than in the upper energy level?

(ii) What is the population distribution if $T \rightarrow \infty$?

(10 marks)

(b) The following results show the variation of the second-order rate constant, k, with the hydrostatic pressure, P at 25 °C for a reaction between hydroxide ions and the quinoid form of the dye.

$P/10^4$ kPa	2.76	5.51	8.27	11.02
$k/10^{-4}$ mol^{-1} dm^3 s^{-1}	11.13	13.1	15.3	17.9

Calculate the volume of activation, $\Delta^{\neq}V°$.

(10 marks)

...4/-

5. (a) For an elementary bimolecular gas-phase reaction at 650 K,

$$H_2\,(g) + I_2\,(g) \longrightarrow 2HI\,(g)$$

calculate the second-order rate constant.

Given : Assume that the diameters of the molecules,
$d_{H_2} \approx d_{I_2} \approx 0.35$ nm;

The experimental activation energy,
$E_a^{exp} = 171\ kJ\ mol^{-1}$

(8 marks)

(b) The first-order rate constant, k, of a decomposition reaction at various temperatures are as follows:

T/°C	15	20	25	30	37
$k \times 10^5\ /s^{-1}$	0.418	0.762	1.37	2.41	5.15

Calculate the activation energy and at 25 °C, the enthalpy of activation, the Gibbs energy of activation, the pre-exponential factor and the entropy of activation.

(12 marks)

6. (a) The photochemical reaction between hydrogen and chlorine to yield hydrogen chloride proceeds by the following mechanism:

$$Cl_2 + h\nu \xrightarrow{I_a} 2Cl$$

$$Cl + H_2 \xrightarrow{k_1} HCl + H$$

$$H + Cl_2 \xrightarrow{k_2} HCl + Cl$$

$$Cl \xrightarrow{k_3} \tfrac{1}{2}Cl_2 \quad \text{(on vessel wall)}$$

Derive an expression for the rate of formation of hydrogen chloride.

(10 marks)

...5/-

(b) Consider a general reaction between A and B which proceeds via a transition state, $X^{\neq}$

$$A + B \rightleftharpoons X^{\neq} \longrightarrow \text{products}$$

calculate the frequency factor, A, for each of the following reactions from the transition state theory:

(i) a reaction between two atoms A and B, the transition state $X^{\neq}$ is diatomic.

(ii) a complex reaction in which A and B are non-linear molecules which form non-linear transition state, $X^{\neq}$.

Given that the values of the partition functions per degree of freedom per molecule for translation (relative to a standard length of 1 cm), rotation and vibration are approximately 10^8, 10 and 1, respectively.

(10 marks)

7. The experimental unimolecular first-order rate constant, k_{uni}, for the isomerization of cyclopropane to propene at 743 K versus the initial pressures, P_o, are as follows:

$k_{uni} \times 10^5 / s^{-1}$	9.58	10.4	10.8	11.1
P_o / atm	0.1447	0.2776	0.5105	1.000

(a) The following mechanism was proposed for the above unimolecular isomerization of cyclopropane to propene:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} Y + Z$$

...6/-

The species A* is an energized molecule that is present in low concentrations. Show that the mechanism predicts first-order kinetics at high pressure limit and second-order kinetics at low-pressure limit.

(10 marks)

(b) From the data given, determine the first-order rate constant, k_{∞}, at high pressures and the Lindemann parameters k_1 and (k_{-1} / k_2).

(10 marks)

...7/-

TERJEMAHAN

Arahan :

Jawab **LIMA** soalan.

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.

...8/-

Jawab sebarang **LIMA** soalan.

1. Pertimbangkan fungsi $\psi(x) = A\left[\sin\left(\frac{\pi x}{a}\right) + \sin\left(\frac{2\pi x}{a}\right)\right]$.

   (a) Tentukan sama ada $\psi(x)$ adalah suatu fungsi gelombang yang dapat diterima bagi suatu zarah di dalam kotak yang berdimensi *a*.

   (4 markah)

   (b) Normalkan $\psi(x)$.

   (8 markah)

   (c) Tentukan sama ada $\psi(x)$ adalah suatu fungsi eigen bagi operator Hamiltonian $\hat{\mathbf{H}}$ bagi zarah di dalam kotak yang berdimensi *a*. Anggarkan tenaga total.

   (8 markah)

   Diberikan : $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

   $$\int \sin\theta \sin 2\theta \, d\theta = \frac{2}{3}\sin^3\theta + C$$

2. Fungsi gelombang keadaan asas yang dinormalkan bagi pengayun harmonik adalah $\psi_o(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\frac{\alpha x^2}{2}}$ dengan $\alpha = \frac{\sqrt{km}}{\hbar}$. Diberikan bahawa operator Hamiltonian bagi sistem itu adalah $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2$.

   (a) Tentukan tenaga bagi keadaan asas.

   (5 markah)

   (b) Tunjukkan bahawa operator Hamiltonian adalah Hermitian. Diberikan bahawa $\hat{R}$ adalah Hermitian jika $\int \psi_m^* \hat{R} \psi_n \, d\tau = \int \psi_n \left(\hat{R}\psi_m\right)^* d\tau$.

   (7 markah)

...9/-

(c) Tentukan nilai purata momentum bagi $\psi_o(x)$. Terangkan keputusan anda.

(8 markah)

Diberikan : $\int xe^{-ax^2}dx = -\frac{1}{2a}e^{-ax^2} + C$

3. (a) Dengan menggunakan takrifan bagi fungsi partisi, q, dan $E = \sum_i n_i \epsilon_i$, terbitkan persamaan yang berikut:

$$E = NkT^2 \left(\frac{\partial \ln q}{\partial T}\right)_V$$

(5 markah)

(b) Terbitkan ungkapan bagi H dan C_v dengan menggunakan keputusan daripada (a).

(7 markah)

(c) Bagi suatu sistem yang mengandungi satu mol zarah yang mempunyai dua paras tenaga takdegenerat dengan pemisahan tenaga sejumlah 1.00×10^{-20} J, carikan suhu yang mana tenaga bagi sistem ini, E, adalah 1.00 kJ dengan menggunakan keputusan daripada (a).

(8 markah)

4. (a) Pertimbangkan satu kutipan molekul dengan setiap molekul mempunyai dua paras tenaga takdegenerat yang terpisah sebanyak 1000 cm^{-1}.

(i) Berapakah suhu (T) bagi kutipan itu jika terdapat 8 kali ganda lebih banyak molekul dalam paras tenaga asas daripada paras tenaga atas?

(ii) Apakah taburan populasi jika $T \rightarrow \infty$?

(10 markah)

(b) Data berikut menunjukkan perubahan pemalar kadar tertib kedua, k, dengan tekanan hidrostatik, P, pada 25 °C untuk tindak balas di antara ion hidroksida dan bentuk kuinoid pewarna.

$P/10^4$ kPa	2.76	5.51	8.27	11.02
$k/10^{-4}$ mol^{-1} dm^3 s^{-1}	11.13	13.1	15.3	17.9

Kiralah isipadu pengaktifan, $\Delta^{\neq}V°$.

(10 markah)

...10/-

5. (a) Untuk tindak balas fasa-gas bimolekul pada 650 K,

$$H_2\,(g) + I_2\,(g) \longrightarrow 2HI\,(g)$$

kiralah pemalar kadar tertib kedua.

Diberikan : Anggapkan bahawa diameter molekul,
$d_{H_2} \approx d_{I_2} \approx 0.35$ nm;

Tenaga pengaktifan eksperimen,
$E_a^{eksp} = 171\ kJ\ mol^{-1}$

(8 markah)

(b) Pemalar kadar bertertib pertama, k, untuk sesuatu tindak balas penguraian pada beberapa suhu ialah:

T/°C	15	20	25	30	37
$k \times 10^5 / s^{-1}$	0.418	0.762	1.37	2.41	5.15

Kiralah tenaga pengaktifan dan pada 25 °C, entalpi pengaktifan, tenaga pengaktifan Gibbs, faktor pra-eksponen dan entropi pengaktifan.

(12 markah)

6. (a) Tindak balas fotokimia di antara hidrogen dan klorin untuk menghasilkan hidrogen klorida berlaku melalui mekanisme yang berikut :

$$Cl_2 + h\nu \xrightarrow{I_a} 2Cl$$

$$Cl + H_2 \xrightarrow{k_1} HCl + H$$

$$H + Cl_2 \xrightarrow{k_2} HCl + Cl$$

$$Cl \xrightarrow{k_3} \tfrac{1}{2}Cl_2 \text{ (pada dinding bekas)}$$

Terbitkan satu ungkapan untuk kadar pembentukan hidrogen klorida.

(10 markah)

...11/-

(b) Pertimbangkan suatu tindak balas am di antara A dan B yang berlaku melalui satu keadaan peralihan, $X^{\neq}$

$$A + B \rightleftharpoons X^{\neq} \longrightarrow \text{hasil}$$

Kiralah faktor frekuensi, A, untuk setiap tindak balas yang berikut daripada teori keadaan peralihan:

(i) Satu tindak balas di antara dua atom A dan B, keadaan peralihan $X^{\neq}$ ialah diatom.

(ii) Satu tindak balas kompleks yang mana A dan B ialah molekul taklinear yang membentuk suatu keadaan peralihan, $X^{\neq}$ yang taklinear.

Diberikan bahawa nilai fungsi partisi per darjah pembebasan per molekul untuk translasi (relatif kepada satu jarak piawai 1 cm), putaran dan getaran masing-masing ialah 10^8, 10 dan 1 secara penghampiran.

(10 markah)

7. Pemalar kadar tertib pertama unimolekul eksperimen, k_{uni}, untuk pengisomeran siklopropana kepada propena pada 743 K melawan dengan tekanan awal, P_o, adalah berikut:

$k_{uni} \times 10^5 / s^{-1}$	9.58	10.4	10.8	11.1
P_o / atm	0.1447	0.2776	0.5105	1.000

(a) Mekanisme yang berikut dicadangkan untuk pengisomeran unimolekul bagi siklopropana kepada propena:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^* + A$$

$$A^* \xrightarrow{k_2} Y + Z$$

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Spesies A* ialah molekul bertenaga yang hadir dalam kepekatan rendah. Tunjukkan bahawa mekanisme ini meramalkan kinetik tertib pertama pada had tekanan tinggi dan kinetik tertib kedua pada tekanan rendah.

(10 markah)

(b) Daripada data yang diberikan, tentukan pemalar kadar tertib pertama, k_∞ pada tekanan tinggi dan parameter Lindemann k_1 dan (k_{-1} / k_2).

(10 markah)

...13/-

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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	$F=N_A e$	9.64853	10^{4}	$C\ mol^{-1}$
Boltzmann constant	k	1.38065	10^{-23}	$J\ K^{-1}$
Gas constant	$R=N_A k$	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	1.60218×10^{-19} J 96.485 kJ mol^{-1}	2.303 RT/F = 0.0591 V at 25 °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}	1.9864×10^{-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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