UNIVERSITI SAINS MALAYSIA

First Semester Examination
2010/2011 Academic Session

November 2010

KFT 331 – Physical Chemistry III
[Kimia Fizik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of THIRTEEN pages of printed material before you begin the examination.

Instructions:

Answer any **FIVE (5)** questions.

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.

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

Appendix: Fundamental constants in physical chemistry.

Answer any **FIVE (5)** questions.

1. The wavefunction for a particle in a box is given by $\Psi_n = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi x}{\ell}$ where ℓ is the dimension of the box and n the quantum number.

   (a) Show that Ψ_n is an acceptable wavefunction.

   (6 marks)

   (b) Is Ψ_n an eigenfunction of the position operator?

   (4 marks)

   (c) Calculate the probability of finding the particle between 0.45ℓ and 0.55ℓ in the ground state.

   (6 marks)

   (d) What are the conditions which result in the quantization of energy?

   (4 marks)

2. The Schrödinger equation for the harmonic oscillator is $-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$. By selecting the function $\emptyset(x) = x \exp(-cx^2)$ where c is a constant,

   (a) determine c so that $\emptyset(x)$ is an eigenfunction of the Schrödinger equation, and

   (8 marks)

   (b) determine the eigenvalue E.

   (6 marks)

   (c) Normalize $\emptyset(x)$

$$\left(\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = 2 \, x \, \frac{1x3x5....(2n-1)}{2^{n+1}a^n} \sqrt{\frac{\pi}{a}} \right)$$

   (6 marks)

3. (a) Using the partition function, show that the energy, E, and heat capacity at constant volume, C_v, for a monatomic gas are

$$E = \frac{3}{2}NkT \quad \text{and} \quad C_V = \frac{3}{2}Nk \quad , \text{ respectively.}$$

Calculate the values of E and C_v for 1 mol of argon gas at 25 ^oC and 1 bar pressure.

(10 marks)

(b) (i) Derive the expression for vibrational contribution to the heat capacity, C_v.

(ii) Calculate the vibrational contribution to the C_v for N_2 given that its vibrational wavenumber is 2358 cm^{-1} at 25 ^oC.

Given: $q_v = \frac{1}{1-x}$ where $x = e^{-h\nu/kT}$; $E = NkT^2\left(\frac{\partial \ln q}{\partial T}\right)_V$

(10 marks)

4. (a) A system consists of 1 mol of identical and indistinguishable molecules. Each molecule has a nondegenerate ground level with $\epsilon_1 = 0$, a threefold degenerate electronically excited level with $\epsilon_2 = 50k$ and a twofold degenerate excited level with $\epsilon_3 = 150k$ (k is the Boltzmann constant). Calculate

(i) the partition function at 250 K, and

(ii) the fraction of molecules at each energy level.

(10 marks)

(b) The photochemical reaction $H_2 + Cl_2 \longrightarrow 2\,HCl$ may be described by the following reaction scheme when the oxygen is present in limited quantities:

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

$$Cl + H_2 \xrightarrow{k_2} HCl + H$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M$$

$$Cl + O_2 + M \xrightarrow{k_5} ClO_2 + M$$

Prove that the quantum yield of the above photochemical reaction is as follows:

$$\Phi(HCl) = \frac{k_A I_a^2 [H_2][Cl_2]}{([H_2] + k_B[Cl_2])[O_2][M]}$$

where: $k_A = \dfrac{4k_3}{k_4}$ and $k_B = \dfrac{k_3 k_5}{k_2 k_4}$.

Terms involving $[O_2]^2$ may be ignored because of the small oxygen concentration.

(10 marks)

5. (a) The following is a simplified form of the Michaelis-Menten mechanism that has been proposed for the enzyme-catalyzed reaction:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + Z$$

where E and S are the enzyme and substrate, respectively, Z is the product and ES is the enzyme-substrate complex. Obtain an expression for the rate of the reaction by using the steady state approximation and write the Lineweaver-Burk equation.

(10 marks)

(b) The enzyme catalase catalyzes the decomposition of hydrogen peroxide. The following data are obtained regarding the rate of reaction as a function of substrate concentration:

$[H_2O_2]_o$ / mol dm^{-3}	0.001	0.002	0.005
initial rate / mol dm^{-3} s^{-1}	1.38×10^{-3}	2.67×10^{-3}	6.00×10^{-3}

The concentration of catalase is 3.5×10^{-9} mol dm^{-3}. Use these data to determine the maximum rate, v_{max} , Michaelis-Menten constant, K_m, and the catalytic constant, k_{cat}, for this reaction.

(10 marks)

6. On the basis of the transition-state theory, calculate the ratio of the rate constants at 300 K for the following exchange reactions:

$$H + H_2 \longrightarrow H_2 + H$$

and

where deuterium, D, is ^2H. The transition-state structure for both reactions is a symmetric, linear arrangement of the three atoms with an internuclear distance of 0.90×10^{-10} m. The vibrational wavenumbers are 2184 cm^{-1} (symmetric stretching) and 979 cm^{-1}(doubly degenerate bending) for H_3 and 1764 cm^{-1} (symmetric stretching) and 870 cm^{-1} (doubly degenerate bending) for DH_2. The activation energy, E_o (from zero-point level), are the same for these reactions. The electronic degeneracies are unity for H_2 and two for H, D, H_3 and DH_2.

Given:

$$q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$q_v = \frac{1}{1 - e^{-h\nu/kT}}$$

(20 marks)

7. (a) The following data were obtained for the alkaline hydrolysis of methyl acetate at 25 ^{o}C:

$P/10^3$ kPa	0.1	27.6	55.2	82.7
k / dm^3 mol^{-1} s^{-1}	0.146	0.163	0.181	0.203

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

(10 marks)

(b) The unimolecular decomposition of urea in aqueous solution was measured at two different temperatures and the following rate constants were obtained:

T/ ^{o}C	60.0	71.5
$k/10^{-7}$ s^{-1}	1.2	4.4

Calculate the activation energy, E_a, and calculate at 60 ^{o}C, the pre-exponential factor, A, the enthalpy of activation, $\Delta^{\neq}H^{o}$, the Gibbs energy of activation, $\Delta^{\neq}G^{o}$, and the entropy of activation, $\Delta^{\neq}S^{o}$, for this reaction.

(10 marks)

APPENDIX **UNIVERSITI SAINS MALAYSIA**
School of Chemical Sciences

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	$F=N_Ae$	9.64853	10^{4}	C mol^{-1}
Boltzmann constant	k	1.38065	10^{-23}	J K^{-1}
Gas constant	$R=N_Ak$	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 x 10^{-19} J 96.485 kJ mol^{-1}	2.303 RT/F = 0.0591 V at 25 ^{o}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 x 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}
1 Poise			Viscosity	1 P = 0.1 kg m^{-1} s^{-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		

TERJEMAHAN

Arahan:

Jawab **LIMA (5)** 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.

Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Jawab **LIMA (5)** soalan.

1. Fungsi gelombang bagi suatu zarah dalam kotak diberikan sebagai $\Psi_n = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi x}{\ell}$ dengan ℓ adalah dimensi kotak dan n nombor kuantum.

   (a) Tunjukkan bahawa Ψ_n adalah fungsi gelombang yang dapat diterima.

   (6 markah)

   (b) Adakah Ψ_n suatu fungsi eigen bagi operator kedudukan?

   (4 markah)

   (c) Kirakan kebarangkalian untuk mendapati zarah itu di antara 0.45ℓ dan 0.55ℓ dalam keadaan asas.

   (6 markah)

   (d) Apakah syarat yang menyebabkan pengkuantuman tenaga?

   (4 markah)

2. Persamaan Schrödinger bagi pengayun harmonik adalah $-\frac{\hbar^2}{2m}\frac{d^2\Psi}{dx^2} + \frac{1}{2}kx^2\Psi = E\Psi$. Dengan memilih fungsi $\emptyset(x) = x \exp(-cx^2)$ dengan c adalah suatu pemalar,

   (a) tentukan c supaya $\emptyset(x)$ adalah fungsi eigen bagi persamaan Schrödinger itu, dan

   (8 markah)

   (b) tentukan nilai eigen E

   (6 markah)

(c) Normalkan ∅(x)

$$\left(\int_{-\infty}^{\infty} x^{2n} e^{-ax^2} dx = 2 \, x \, \frac{1x3x5....(2n-1)}{2^{n+1} a^n} \sqrt{\frac{\pi}{a}} \right)$$

(6 markah)

3. (a) Dengan menggunakan fungsi partisi, tunjukkan bahawa tenaga, E, dan muatan haba pada isipadu tetap, C_v, bagi gas monatom masing-masing adalah

$$E = \frac{3}{2} NkT \qquad \text{dan} \qquad C_V = \frac{3}{2} Nk$$

Kiralah nilai E dan C_v bagi satu mol gas argon pada suhu 25 ^oC dan tekanan 1 bar.

(10 markah)

(b) (i) Terbitkan sebutan bagi sumbangan getaran kepada C_v.

(ii) Kiralah sumbangan getaran kepada C_v bagi N_2, diberikan nombor gelombang getarannya adalah 2358 cm^{-1} pada 25 ^oC.

Diberi: $q_v = \frac{1}{1-x}$ dengan $x = e^{-h\nu/kT}$; $E = NkT^2 \left(\frac{\partial \ln q}{\partial T} \right)_V$

(10 markah)

4. (a) Suatu sistem mengandungi 1 mol molekul serba sama dan tidak terkenalbezakan. Setiap molekul mempunyai keadaan asas takdegenerat dengan tenaga $\in_1$ = 0, dan keadaan teruja yang mempunyai kedegeneratan tiga dengan tenaga $\in_2$ = 50k dan keadaan teruja yang mempunyai kedegeneratan dua dengan tenaga $\in_3$ = 150k (k adalah pemalar Boltzmann). Kirakan

(i) fungsi partisi pada 250 K, dan
(ii) pecahan molekul pada setiap paras tenaga.

(10 markah)

(b) Tindak balas fotokimia $H_2 + Cl_2 \longrightarrow 2HCl$ mungkin boleh dihuraikan dengan skema tindak balas yang berikut apabila oksigen hadir dalam kuantiti terhad:

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

$$Cl + H_2 \xrightarrow{k_2} HCl + H$$

$$H + Cl_2 \xrightarrow{k_3} HCl + Cl$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M$$

$$Cl + O_2 + M \xrightarrow{k_5} ClO_2 + M$$

Buktikan bahawa hasil kuantum bagi tindak balas fotokimia ini ialah:

$$\Phi(HCl) = \frac{k_A I_a^2 [H_2][Cl_2]}{([H_2] + k_B[Cl_2])[O_2][M]}$$

dengan: $k_A = \frac{4k_3}{k_4}$ dan $k_B = \frac{k_3 k_5}{k_2 k_4}$.

Sebutan $[O_2]^2$ boleh diabaikan sebab kepekatan oksigen adalah kecil.

(10 markah)

5. (a) Suatu mekanisme Michaelis-Menten yang sederhana telah dicadangkan bagi tindak balas yang dimangkinkan oleh enzim:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + Z$$

dengan E dan S masing-masing ialah enzim dan substrat, Z ialah hasil dan ES ialah kompleks enzim-substrat. Dapatkan satu ungkapan bagi kadar tindak balas dengan menggunakan penghampiran keadaan mantap dan tuliskan persamaan Lineweaver-Burk.

(10 markah)

(b) Enzim katalasa bermangkinkan penguraian hidrogen peroksida. Data yang berikut diperoleh bagi kadar tindak balas sebagai fungsi kepekatan substrat:

$[H_2O_2]_o$ / mol dm^{-3}	0.001	0.002	0.005
Kadar awal / mol dm^{-3} s^{-1}	1.38×10^{-3}	2.67×10^{-3}	6.00×10^{-3}

Kepekatan katalasa ialah 3.5×10^{-9} mol dm^{-3}. Tentukan kadar maksimum, v_{max}, pemalar Michaelis-Menten, K_m dan pemalar mangkinan, k_{cat}, bagi tindak balas ini.

(10 markah)

6. Berdasarkan teori keadaan peralihan, kirakan nisbah pemalar kadar pada 300 K bagi tindak balas pertukaran yang berikut:

$$H + H_2 \longrightarrow H_2 + H$$

dan

dengan deuterium, D, ialah ^2H. Struktur keadaan peralihan bagi kedua-dua tindak balas ialah susunan simetri dan linear bagi tiga atom dengan jarak antara nukleus bernilai 0.90×10^{-10} m. Nombor gelombang getaran ialah 2184 cm^{-1} (regangan simetri) dan 979 cm^{-1} (dua kedegeneratan pembengkokan) bagi H_3 dan 1764 cm^{-1} (regangan simetri) dan 870 cm^{-1} (dua kedegeneratan pembengkokan) bagi DH_2. Tenaga pengaktifan, E_o, (daripada paras titik sifar) adalah sama bagi kedua-dua tindak balas. Kedegeneratan elektronik ialah uniti bagi H_2 dan dua bagi H, D, H_3 and DH_2.

Diberi:

$$q_t = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

$$q_v = \frac{1}{1 - e^{-h\nu/kT}}$$

(20 markah)

7. (a) Data yang berikut diperoleh bagi hidrolisis beralkali metil asetat pada 25 ^oC:

$P/10^3$ kPa	0.1	27.6	55.2	82.7
k / $dm^3\ mol^{-1}\ s^{-1}$	0.146	0.163	0.181	0.203

Kirakan isipadu pengaktifan, $\Delta^{\neq}V^o$.

(10 markah)

(b) Penguraian unimolekul urea dalam larutan akueus telah disukat pada dua suhu berbeza dan pemalar kadar yang berikut diperoleh:

T/^oC	60.0	71.5
k/ $10^{-7}\ s^{-1}$	1.2	4.4

Kirakan tenaga pengaktifan, E_a, dan kirakan pada 60 ^oC, faktor pra-eksponen, A, entalpi pengaktifan, $\Delta^{\neq}H^o$, tenaga pengaktifan Gibbs, $\Delta^{\neq}G^o$, dan entropi pengaktifan, $\Delta^{\neq}S^o$, bagi tindak balas ini.

(10 markah)

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