UNIVERSITI SAINS MALAYSIA

First Semester Examination
2009/2010 Academic Session

November 2009

KFT 331 – Physical Chemistry III
[Kimia Fizik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of FIFTEEN 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.

Answer any **FIVE** questions.

1. On the basis of the transition-state theory, calculate the partition functions for the reactants and the activated complex, the pre-exponential factor, A and the rate constant, k_r. for the reaction:

$$D + H_2 \rightarrow DH + H$$

Use the following data:

Activation energy, E_o (from zero-point level) = 34.5 kJ mol^{-1}.

The bond distance and the vibrational wavenumber of H_2 are 0.0741 nm and 4400 cm^{-1}, respectively.

Assume the activated complex to be linear, with the following characteristics derivable from the quantum mechanics:

D – H bond distance = 0.093 nm

H – H bond distance = 0.093 nm

The vibrational wavenumbers of the activated complex are 1766 cm^{-1} (symmetric stretching) and 840 cm^{-1} (two degenerate bending).

The relative atomic masses are H = 1.008 and D = 2.014.

Given:

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

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

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

(20 marks)

2. (a) The Eyring equation is given by:

$$k_r = \frac{kT}{h} e^{-\Delta^{\neq}G^{o}/RT}$$

where k_r and $\Delta^{\neq}G^{o}$ are the rate constant and the Gibbs energy of activation, respectively, for the reaction

$$A + B \rightleftharpoons X^{\neq}$$

in which activated complex, $X^{\neq}$, is formed from the reactants, A and B. The equilibrium constant is given by,

$$\ell n\, K_c^{\neq} = -\frac{\Delta^{\neq}G^{o}}{RT}$$

Derive the following equation:

$$E_a = \Delta^{\neq}H^{o} + nRT$$

where E_a is the experimental activation energy, $\Delta^{\neq}H^{o}$, the enthalpy of activation and n is the molecularity of the reaction.

In a bimolecular reaction in which two molecules become one, write the relationship between E_a and $\Delta^{\neq}H^{o}$.

(10 marks)

(b) For the reaction,

$$H(g) + H_2(g) \underset{}{\overset{K_c}{\rightleftharpoons}} (H\text{-}H\text{-}H)^{\neq} \xrightarrow{k_1} H_2(g) + H(g)$$

The activation energy, E_a= 23 kJ mol^{-1} and the pre-exponential factor, A = 1.5 x 10^{13} cm^3 mol^{-1} s^{-1} at 25 °C. Calculate the enthalpy of activation, $\Delta^{\neq}H^{o}$, the entropy of activation, $\Delta^{\neq}S^{o}$, the Gibbs' energy of activation, $\Delta^{\neq}G^{o}$ and the equilibrium constant, $K_c^{\neq}$, for the formation of the activated complex from the reactants.

(10 marks)

3. (a) The following is the 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, the product and ES, the enzyme-substrate complex. Obtain an expression for the rate of the reaction by using the steady state approximation.

(10 marks)

(b) The following data have been obtained for an enzyme-catalyzed reaction:

[S] / mol dm^{-3}	2.5×10^{-4}	5.0×10^{-3}
Rate, v / mol dm^{-3} s^{-1}	2.3×10^{-4}	7.8×10^{-4}

The concentration of the enzyme is 2 g dm^{-3} and its molecular weight is 50,000. Calculate the Michaelis constant, K_m, the limiting rate, v_{max}, and the catalytic constant, k_c.

(10 marks)

4. (a) For the following photochemical reaction:

$$CHF_3 + F_2 \rightleftharpoons CF_4 + HF$$

The mechanism is:

$$F_2 + h\nu \xrightarrow{I_a} 2F$$

$$F + CHF_3 \xrightarrow{k_1} CF_3 + HF$$

$$CF_3 + F_2 \xrightarrow{k_2} CF_4 + F$$

$$2CF_3 + F_2 \xrightarrow{k_3} 2CF_4$$

If I_a is the intensity of light absorbed, derive the steady-state rate law for the formation of CF_4.

(10 marks)

(b) Consider a molecule that has two energy levels separated by $\in$, where the ground state has a degeneracy of 2 and the excited state has a degeneracy of 3. Calculate at 300 K

(i) the partition function of the molecule,
(ii) the fraction of molecules of the two levels, and
(iii) the internal energy per particle.

(10 marks)

5. Derive the Sackur-Tetrode equation for a monatomic gas confined in a region of space.

Calculate the **change** in molar entropy when the volume is doubled for Ne(g) at 298.15 K and 1 bar. Assume $q_e = 6.7335$.

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

(20 marks)

6. The wave function $\psi(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$, where α is a constant, is a complete state function for a particle free to move in either direction along the x axis and not influenced by any forces.

(a) Show that this wave function is a solution of the Schroedinger equation.

(5 marks)

(b) $\hat{R}$ and $\hat{S}$ are operators which commute. If ψ_R is an eigenfunction of $\hat{R}$, show that ψ_R is also an eigenfunction of $\hat{S}$ assuming that there is no degeneracy.

Can the momentum and energy of a free particle moving in one direction be known exactly and simultaneously?

(10 marks)

(c) What is the energy of this system? Is the energy quantized?

(5 marks)

7. The wave function for a particle in a three dimensional box of dimensions a, b and c is given by:

$$\psi = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

(a) Given that the Hamiltonian for this system is

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

Derive an expression for the energy of this system.

(8 marks)

(b) For a particle in a box with the dimensions a, a and 2a, prepare a table which shows the quantum numbers n_x, n_y and n_z, the energy levels and the degree of degeneracy for each energy level for the energy up to $\frac{9h^2}{8ma^2}$.

(8 marks)

(c) Determine the number of energy levels and states between the states (1, 1, 1) and (2, 2, 2) inclusive of the two.

(4 marks)

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 sebarang **LIMA** soalan.

1. Berdasarkan teori keadaan peralihan, kirakan fungsi partisi untuk bahan tindak balas dan kompleks yand diaktifkan, faktor pra-eksponen, A dan permalar kadar, k_r, bagi tindak balas

$$D + H_2 \rightarrow DH + H$$

Data berikut diberi:

Tenaga pengaktifan, E_o (daripada paras titik sifar) = 34.5 kJ mol^{-1}.

Jarak ikatan dan nombor gelombang getaran bagi H_2 masing-masing ialah 0.0741 nm dan 4400 cm^{-1}.

Anggapkan kompleks yang diaktifkan linear, dengan ciri berikut yang diterbitkan daripada mekanik kuantum.

Jarak ikatan D – H = 0.093 nm
Jarak ikatan H – H = 0.093 nm

Nombor gelombang getaran bagi kompleks yang diaktifkan ialah 1766 cm^{-1} (regangan simetri) dan 840 cm^{-1} (dua kedegeneratan pembengkokan)yang degenerat.

Jisim atom relatif ialah H = 1.008 dan D = 2.014.

Diberi:

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

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

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

(20 markah)

2. (a) Persamaan Eyring diberi sebagai:

$$k_r = \frac{kT}{h} e^{-\Delta^{\neq}G^{o}/RT}$$

dengan k_r dan $\Delta^{\neq}G^{o}$ masing-masing ialah pemalar kadar dan tenaga pengaktifan Gibbs bagi tindak balas

$$A + B \rightleftharpoons X^{\neq}$$

yang mana kompleks yang diaktifkan, $X^{\neq}$, dibentukkan daripada bahan tindak balas, A dan B. Pemalar keseimbangan diberi sebagai

$$\ell n\, K_c^{\neq} = -\frac{\Delta^{\neq}G^{o}}{RT}$$

Terbitkan persamaan yang berikut:

$$E_a = \Delta^{\neq}H^{o} + nRT$$

dengan E_a ialah tenaga pengaktifan eksperimen, $\Delta^{\neq}H^{o}$, entalpi pengaktifan dan n ialah kemolekulan tindak balas.

Di dalam satu tidak balas bimolekul yang mana dua molekul menjadi satu molekul, tuliskan hubungan di antara E_a dan $\Delta^{\neq}H^{o}$

(10 markah)

(b) Bagi tindak balas,

$$H(g) + H_2(g) \underset{}{\overset{K_c}{\rightleftharpoons}} (H\text{-}H\text{-}H)^{\neq} \xrightarrow{k_1} H_2(g) + H(g)$$

Tenaga perngaktifan, E_a= 23 kJ mol^{-1} dan faktor pra-eksponen, A = 1.5 x 10^{13} cm^3 mol^{-1} s^{-1} pada 25 °C. Kirakan entalpi pengaktifan, $\Delta^{\neq}H^{o}$, entropi pengaktifan, $\Delta^{\neq}S^{o}$, tenaga pengaktifan Gibbs, $\Delta^{\neq}G^{o}$, dan pemalar keseimbangan, $K_c^{\neq}$, untuk pembentukan kompleks yang diaktifkan daripada bahan tindak balas.

(10 markah)

3. (a) Mekanisme Michaelis-Menten yang berbentuk sederhana telah dicadangkan untuk tindak balas pemangkinan 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 untuk kadar tindak balas dengan menggunakan penghampiran keadaan mantap.

(10 markah)

(b) Data yang berikut diperoleh untuk tindak balas pemangkingan enzim

[S] / mol dm^{-3}	2.5×10^{-4}	5.0×10^{-3}
Rate, v / mol dm^{-3} s^{-1}	2.3×10^{-4}	7.8×10^{-4}

Kepekatan enzim ialah 2 g dm^{-3} dan berat molekul ialah 50,000. Kiralah pemalar Michaelis, K_m, kadar penghadan, v_{max}, dan pemalar mangkinan, k_c.

(10 markah)

4. (a) Bagi tindak balas fotokimia yang berikut:

$$CHF_3 + F_2 \rightleftharpoons CF_4 + HF$$

mekanismenya ialah

$$F_2 + h\nu \xrightarrow{I_a} 2F$$

$$F + CHF_3 \xrightarrow{k_1} CF_3 + HF$$

$$CF_3 + F_2 \xrightarrow{k_2} CF_4 + F$$

$$2CF_3 + F_2 \xrightarrow{k_3} 2CF_4$$

Jika I_a adalah keamatan cahaya yang terserap, terbitkan hukum kadar keadaan mantap untuk pembentukan CF_4.

(10 markah)

(b) Pertimbangkan suatu molekul yang mempunyai dua paras tenaga yang dipisahkan dengan $\in$, di mana keadaan asas mempunyai kedegeneratan 2 dan keadaan teruja mempunyai kedegeneratan 3. Kiralah pada 300 K

(i) fungsi partisi molekul,
(ii) pecahan molekul bagi kedua paras, dan
(iii) tenaga dalam bagi setiap zarah.

(10 markah)

5. Terbitkan persamaan Sackur-Tetrode bagi gas monatomik yang terkandung di dalam suatu ruang.

Kirakan perubahan entropi molar apabila isipadu digandakan bagi Ne(g) pada 298.15 K dan 1 bar. Anggap $q_e = 6.7335$.

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

(20 markah)

6. Fungsi gelombang $\psi(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$, dengan α suatu pemalar, adalah suatu fungsi keadaan yang lengkap bagi suatu zarah yang bebas bergerak ke kedua-dua arah di sepanjang paksi x dan tidak dipengaruhi oleh sebarang daya.

(a) Tunjukkan bahawa fungsi gelombang ini adalah suatu penyelesaian bagi persamaan Schroedinger.

(5 markah)

(b) $\hat{R}$ dan $\hat{S}$ adalah operator yang berkomut. Jika ψ_R adalah fungsi eigen bagi $\hat{R}$ yang mempunyai nilai eigen R, tunjukkan bahawa ψ_R juga adalah fungsi eigen bagi $\hat{S}$ dengan menganggap bahawa tiada kedegeneratan.

Bolehkah momentum dan tenaga bagi suatu zarah bebas yang bergerak ke satu arah diketahui dengan tepat secara serentak?

(10 markah)

(c) Apakah tenaga bagi sistem ini? Adakah tenaga itu berkuantum?

(5 markah)

7. Fungsi gelombang bagi suatu zarah di dalam sebuah kotak tiga dimensi yang sisinya a, b dan c adalah:

$$\psi = \left(\frac{8}{abc}\right)^{1/2} \sin\frac{n_x \pi x}{a} \sin\frac{n_y \pi y}{b} \sin\frac{n_z \pi z}{c}$$

(a) Diberikan bahawa Hamiltonian bagi sistem ini adalah:

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)$$

Terbitkan satu ungkapan bagi tenaga sistem ini.

(8 markah)

(b) Bagi satu zarah di dalam sebuah kotak yang bersisi a, a dan 2a, sediakan satu jadual yang menunjukkan nombor kuantum n_x, n_y dan n_z, paras tenaga dan darjah kedegeneratan bagi setiap paras tenaga bagi tenaga hingga $\frac{9h^2}{8ma^2}$.

(8 markah)

(c) Tentukan bilangan paras tenaga dan keadaan di antara keadaan (1, 1, 1) dan 2, 2, 2) termasuk kedua-duanya.

(4 markah)

UNIVERSITI SAINS MALAYSIA
School of Chemical Sciences

APPENDIX

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	1.60218×10^{-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		

- oooOooo -