UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2008/2009

June 2009

KFT 331 – Physical Chemistry III
[Kimia Fizik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **FOURTEEN** printed pages before you begin the examination.

Instruction

Answer any **FIVE** (5) questions, beginning the answer 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.

1. (a) Explain the meaning of 'acceptable functions'. Give examples of acceptable and unacceptable functions.

(6 marks)

(b) Given the operators $\hat{P} = \frac{d^2}{dx^2}$ and $\hat{Q} = x^2$, determine

(i) $\hat{P}\hat{Q}f(x)$ and $\hat{Q}\hat{P}f(x)$

(ii) commutator $(\hat{P}\hat{Q} - \hat{Q}\hat{P})$

(4 marks)

(c) If $\hat{A}$ and $\hat{B}$ are Hermitian operators, show that the operator $\hat{A}\hat{B}$ is also Hermitian provided that $\hat{A}$ and $\hat{B}$ commute.

Is $x\frac{d^2}{dx^2}$ a Hermitian operator?

(Given : Operator $\hat{R}$ is Hermitian if

$$\int \psi_m * \hat{R}\psi_n d\tau = \int \psi_n \left(\hat{R}\psi_m\right) * d\tau)$$

(10 marks)

2. Consider a particle with mass m moving in a one-dimensional box. The allowed wavefunction is given by $\psi = \sqrt{\frac{2}{\ell}} \sin\frac{n\pi x}{\ell}$ where ℓ is the dimension of the box.

(a) Calculate the probability of finding the particle in the region between $\frac{1}{4}\ell$ and $\frac{1}{2}\ell$ for the state n = 2.

(6 marks)

(b) Derive the energy expression for this system. What is the energy difference between the states $\psi_3 = \sqrt{\frac{2}{\ell}} \sin\frac{3\pi x}{\ell}$ and $\psi_4 = \sqrt{\frac{2}{\ell}} \sin\frac{4\pi x}{\ell}$?

(8 marks)

(c) Determine the expectation value of the momentum $<\hat{p}_x>$ for the ground state of this system.

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

(6 marks)

3. Show that the entropy for distinguishable particles is given by

$$S = NkT\left(\frac{\partial \ell n\, q}{\partial T}\right)_v + Nk\ell n\, q$$

Subsequently, show that the molar rotational entropy is given by

$$\bar{S}_r = R(\ell n\, q_r + 1)$$

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

Calculate $\bar{S}_r$ for O_2 (g) at 298.15 K. Given that $I = 1.9373 \times 10^{-46}$ kg m^2.

$$\left[\text{Hint}: E = NkT^2\left(\frac{\partial \ell n\, q}{\partial T}\right)_v\right]$$

(20 marks)

4. (a) A molecule has three states with the energies given by: $\epsilon_0 = 0$, $\epsilon_1 = 1 \times 10^{-20}\,J$ and $\epsilon_1 = 1 \times 10^{-20}\,J$. Calculate the partition function and the fraction of occupancy of each energy level at 298 and 1000 K. Comment on the effect of temperature.

(10 marks)

(b) For the following elementary reaction,

$$NO + O_3 \longrightarrow NO_2 + O_2$$

calculate the frequency factor, A, at 500 K by using the hard-sphere collision theory. The molecular radii for NO and O_3 are 1.4 x 10^{-10} m and 2.0 x 10^{-10}m, respectively. The experimental value of A at 500 K for this reaction is 8 x 10^{11} cm^3 mol^{-1} s^{-1}. Calculate the steric factor.

(10 marks)

5. Consider the following mechanism of the enzyme catalysis:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

where E is the free enzyme, S is the substrate, ES is the enzyme– substrate complex, and P is the product.

By applying the steady-state approximation to the intermediate, ES,

(a) Derive an expression for the reaction rate,

$$r = -\frac{d[S]}{dt}$$

(12 marks)

(b) Show that, when setting the product concentration, [P], equal to zero and [S] equal to $[S]_o$, the initial rate, r_o, is

$$r_o = \frac{k_2[E]_o[S]_o}{K_m + [S]_o}$$

where the Michaelis constant,

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

(6 marks)

(c) Write the Lineweaver–Burk equation.

(2 marks)

6. The kinetics of the gas–phase reaction,

$$H_2 + I_2 \longrightarrow 2HI$$

is second order. The rate constant and the activation energy for this reaction at 400 °C are 2.34 x 10^{-2} dm^3 mol^{-1} s^{-1} and 150 kJ mol^{-1}, respectively. Calculate $\Delta^{\#}H^{o}$, $\Delta^{\#}S^{\circ}$ and $\Delta^{\#}G^{\circ}$ at 400 °C.

(20 marks)

7. Predict the pre-exponential factor at 298 K for the reaction.

$$Br\,(g) + Cl_2\,(g) \underset{}{\overset{K^{\ddagger}}{\rightleftharpoons}} (Br - Cl - Cl)^{\ddagger}(g) \xrightarrow{k_1} BrCl\,(g) + Cl(g)$$

by using the transition state theory.

Assume that the activated complex is linear with the moment of inertia, $I = 1.14 \times 10^{-44}$ kg m^2 and the wavenumbers of the two bending vibrations, $\bar{\nu}_1 = 190$ cm^{-1} and $\bar{\nu}_2 = 110$ cm^{-1}.

For Cl_2 (g), the moment of inertia, $I = 1.15 \times 10^{-45}$ kg m^2 and the wavenumber is $\bar{\nu} = 550$ cm^{-1}

Given:

$$q_t = \left[\frac{2\pi mkT}{h^2}\right]^{3/2}$$

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

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

(20 marks)

TERJEMAHAN

<u>Arahan</u> :

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.

1. (a) Terangkan erti 'fungsi yang dapat diterima'. Berikan contoh bagi fungsi yang dapat diterima dan yang tidak dapat diterima.

(6 markah)

(b) Diberikan operator $\hat{P} = \frac{d^2}{dx^2}$ dan $\hat{Q} = x^2$, tentukan

(i) $\hat{P}\hat{Q}f(x)$ dan $\hat{Q}\hat{P}f(x)$

(ii) komutator $(\hat{P}\hat{Q} - \hat{Q}\hat{P})$

(4 markah)

(c) Jika $\hat{A}$ dan $\hat{B}$ adalah operator Hermitian, tunjukkan bahawa operator $\hat{A}\hat{B}$ juga adalah Hermitian asalkan $\hat{A}$ dan $\hat{B}$ berkomut.

Adakah $x\frac{d^2}{dx^2}$ suatu operator Hermitian?

(Diberikan: Operator $\hat{R}$ adalah Hermitian jika
$\int \psi_m{}^* \hat{R}\psi_n d\tau = \int \psi_n \left(\hat{R}\psi_m\right)^* d\tau$)

(10 markah)

2. Pertimbangkan satu zarah yang jisimnya m bergerak di dalam sebuah kotak satu dimensi. Fungsi gelombang yang dibenarkan adalah $\psi = \sqrt{\frac{2}{\ell}} \sin \frac{n\pi x}{\ell}$ dengan ℓ adalah dimensi kotak.

(a) Kirakan kebarangkalian untuk mendapati zarah itu di dalam kawasan antara $\frac{1}{4}\ell$ dengan $\frac{1}{2}\ell$ bagi keadaan n=2.

(6 markah)

(b) Terbitkan ungkapan tenaga bagi sistem ini. Berapakah bezanya tenaga di antara keadaan $\psi_3 = \sqrt{\frac{2}{\ell}} \sin \frac{3\pi x}{\ell}$ dengan keadaan $\psi_4 = \sqrt{\frac{2}{\ell}} \sin \frac{4\pi x}{\ell}$?

(8 markah)

(c) Tentukan nilai jangkaan bagi momentum $<\hat{p}_x>$ bagi keadaan asas sistem ini.

(Diberikan : $\cos 2\theta = 1 - 2\sin^2 \theta$; $\cos 2\theta = 2\sin \theta \cos \theta$)

(6 markah)

3. Tunjukkan bahawa entropi bagi zarah terkenalbezakan diberi dengan persamaan

$$S = NkT\left(\frac{\partial \ell n\, q}{\partial T}\right)_v + Nk\ell n\, q$$

Seterusnya, tunjukkan bahawa entropi putaran molar diberi dengan persamaan

$$\bar{S}_r = R(\ell n\, q_r + 1)$$

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

Kirakan $\bar{S}_r$ bagi $O_2(g)$ pada 298.15 K. Diberikan I = 1.9373 x 10^{-46} kg m^2.

$$\left[\text{Petunjuk} : E = NkT^2\left(\frac{\partial \ell n\, q}{\partial T}\right)_v\right]$$

(20 markah)

4. (a) Suatu molekul mempunyai tiga keadaan dengan tenaganya diberikan dengan:
$\in_0 = 0$, $\in_1 = 1 \times 10^{-20}$ J dan $\in_2 = 1 \times 10^{-20}$ J. Kirakan fungsi partisi dan pecahan pengisian setiap paras tenaga pada 298 dan 1000 K.
Ulaskan kesan suhu.

(10 markah)

(b) Bagi tindak balas asas yang berikut:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

kirakan faktor frekuensi, A, pada 500 K dengan menggunakan teori pelanggaran sfera tegas. Jejari molekul bagi NO dan O_3 masing-masing ialah 1.4×10^{-10} m dan 2.0×10^{-10} m. Nilai eksperimen bagi A pada 500 K untuk tindak balas itu ialah 8×10^{11} $cm^3\ mol^{-1}\ s^{-1}$. Kirakan faktor sterik.

(10 markah)

5. Pertimbangkan mekanisme bagi pemangkinan enzim:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

dengan E ialah enzim bebas, S, substrat, ES, kompleks enzim–substrat, dan P ialah hasil.

Dengan menggunakan penghampiran keadaan mantap terhadap bahan pengantaraan, ES,

(a) Terbitkan satu ungkapan bagi kadar tindak balas,

$$r = -\frac{d[S]}{dt}$$

(12 markah)

(b) Tunjukkan bahawa, apabila kepekatan hasil, [P], sama dengan sifar dan [S] sama dengan $[S]_o$ kadar awal, r_o, ialah

$$r_o = \frac{k_2[E]_o[S]_o}{K_m + [S]_o}$$

yang mana pemalar Michaelis,

$$K_m = \frac{k_{-1} + k_2}{k_1}$$

(6markah)

(c) Tuliskan persamaan Lineweaver-Burk

(2 markah)

6. Kinetik bagi tindak balas fasa gas

$$H_2 + I_2 \longrightarrow 2HI$$

bertertib kedua. Pemalar kadar dan tenaga pengaktifan untuk tindak balas ini pada 400 °C masing-masing ialah 2.34 x 10^{-2} $dm^3\ mol^{-1}\ s^{-1}$ dan 150 kJ mol^{-1}. Kirakan $\Delta^{\neq}H°$, $\Delta^{\neq}S°$ dan $\Delta^{\neq}G°$ pada 400 °C.

(20 markah)

7. Ramalkan faktor pra-eksponen pada 298 K bagi tindak balas

$$Br\,(g) + Cl_2\,(g) \overset{K^{\ddagger}}{\rightleftharpoons} (Br - Cl - Cl)^{\ddagger}(g) \xrightarrow{k_1} BrCl\,(g) + Cl(g)$$

dengan menggunakan teori keadaan peralihan.

Anggapkan bahawa kompleks yang diaktifkan ialah linear dengan momen inersia, I = 1.14 x 10^{-44} kg m^2 dan nombor gelombang bagi dua getaran pembengkokan, $\bar{\nu}_1$ = 190 cm^{-1} dan $\bar{\nu}_2$=110 cm^{-1}.

Bagi Cl_2 (g), momen inersia, I = 1.15 x 10^{-45} kg m^2 dan nombor gelombang, $\bar{\nu}$ = 550 cm^{-1}

Diberikan:

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

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

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

(20 markah)

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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 °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}

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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