
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2011/2012 Academic Session

January 2012

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. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

You may answer the questions either in Bahasa Malaysia or in English.

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

Appendix: Fundamental constants in physical chemistry.

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

1. (a) Explain briefly the meaning of wave-particle duality. (5 marks)

- (b) An operator \hat{R} is Hermitian if

$$\int \Psi_m^* \hat{R} \Psi_n d\tau = \int \Psi_n (\hat{R} \Psi_m)^* d\tau$$

where Ψ_m and Ψ_n are acceptable functions. Show that if \hat{A} and \hat{B} are Hermitian operators,

$$\int \Psi_m^* \hat{A} \hat{B} \Psi_n d\tau = \left[\int \Psi_n^* \hat{B} \hat{A} \Psi_m d\tau \right]^*$$

(5 marks)

- (c) Evaluate the commutator $[(d/dx) - x, (d/dx) + x]$ by applying the operators to an arbitrary function $f(x)$. (5 marks)

- (d) Suppose that the wavefunction for a system can be written as

$$\Psi(x) = \frac{1}{2} \phi_1(x) + \frac{1}{4} \phi_2(x) + \left(\frac{3 + \sqrt{2}i}{4} \right) \phi_3(x)$$

where ϕ_1 , ϕ_2 and ϕ_3 are orthonormal functions. Verify that Ψ is normalized.

(5 marks)

2. (a) For a particle in a two-dimensional box, the wavefunction is given by

$$\Psi_{n_x, n_y}(x, y) = \left(\frac{4}{ab} \right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b}$$

- (i) Write the Hamiltonian operator for this system.
 (ii) Obtain an expression for the energy of this system.

(10 marks)

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- (b) The ground-state wavefunction for the quantum harmonic oscillator is given by

$$\Psi_0(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2)$$

where $\alpha = \frac{1}{2\hbar} \sqrt{km}$

- (i) Determine whether Ψ_0 is an eigenfunction of the position operator, \hat{x} , and the Hamiltonian operator.
- (ii) For the case in which Ψ_0 is not an eigenfunction, determine the mean value of the observable.

(10 marks)

3. Show that the expression for heat capacity at constant pressure for an ideal gas is given as

$$C_p = Nk \left[1 + 2T \left(\frac{\partial \ln q}{\partial T} \right)_v + T^2 \frac{\partial}{\partial T} \left(\frac{\partial \ln q}{\partial T} \right)_{v,p} \right]$$

Determine the contribution of rotational motion to molar heat capacity at constant pressure, \bar{C}_p , for $N_2(g)$ at 300 K.

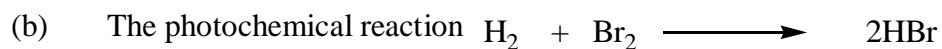
Given : $q_r = \frac{8\pi^2 I k T}{\sigma h^2}$

(20 marks)

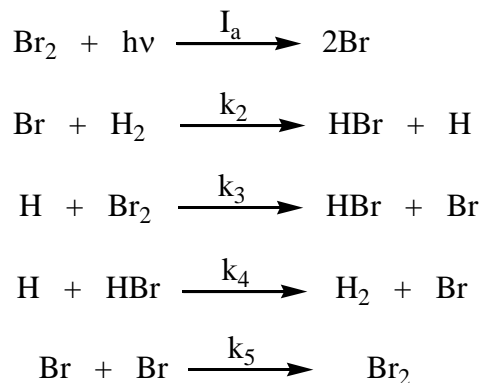
4. (a) A molecule has a nondegenerate ground energy level and two excited energy levels which are two- and three-fold degenerate. Given that $\epsilon_0 = 0$, $\epsilon_1 = 1 \times 10^{-22}$ J and $\epsilon_2 = 3 \times 10^{-22}$ J. Determine the fraction of molecule occupied in each level at 298 K and the distribution of the molecule if the temperature increases three times.

(10 marks)

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may be described by the following scheme:



Derive an expression for the rate of formation of hydrogen bromide and the quantum yield of the above photochemical reaction.

(10 marks)

5. (a) The Arrhenius plot of $\log k$ versus $1/T$, was linear with a negative slope of $4.5 \times 10^3 \text{ K}$ and intercept of 11.90 for a bimolecular reaction. Calculate E_a , $\Delta^\ddagger H^\circ$ (at 25°C) and $\Delta^\ddagger S^\circ$.

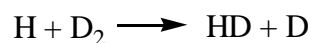
(10 marks)

- (b) For the decomposition of hydrogen iodide assuming its collision diameter is 350 pm and the activation energy is 184 kJ mol^{-1} , the experimental value of the rate constant obtained for this reaction is $1.57 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Calculate the rate of reaction, the rate constant and the steric factor at 700 K and 1 atm pressure.

(10 marks)

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6. Use the transition-state theory to calculate the partition functions for the reactants and the activated complex, the pre-exponential factor, A, and the rate constant, k, at 600 K for the reaction:



Given:

The classical barrier height or the maximum path of the reaction is 40.2 kJ mol^{-1} at 600 K. The transition-state structure is a linear arrangement of the three atoms with an internuclear distance of $0.930 \times 10^{-10} \text{ m}$. The HD_2 activated complex has vibrational wavenumbers 1762 cm^{-1} (symmetric stretching) and 694 cm^{-1} (doubly degenerate bending). D_2 has only one vibrational mode and its vibrational wavenumber is 3112 cm^{-1} . The D_2 internuclear distance is $0.741 \times 10^{-10} \text{ m}$. The electronic degeneracies are 2 for H and HD_2 and unity for D_2 .

The relative masses: $\text{H} = 1.008$ and $\text{D} = 2.014$.

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

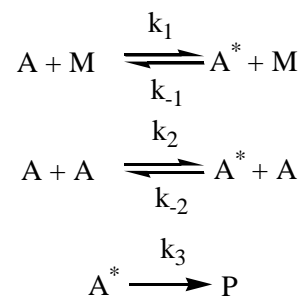
$$q_r = \frac{8\pi^2 IkT}{\sigma h^2}$$

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

(20 marks)

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7. (a) In the Lindemann mechanism, it was assumed that the rate of activation by collision with another reactant molecule, A, was the same as the collision with a non-reactant molecule, M. If the rates of activation for these two processes are different, the mechanism becomes:



- (i) Determine the rate law expression for the formation of the product, P.
- (ii) Does this rate law reduce to the expected form when $[\text{M}] = 0$?

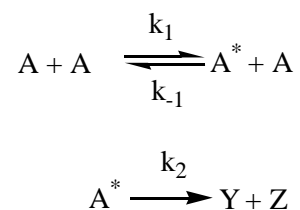
(10 marks)

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- (b) The experimental unimolecular first-order rate constant, k_{uni} , for the isomerization of cyclobutane to butylene at 350 K versus the initial pressure, P_0 , is as follows:

$k_{\text{uni}}/\text{s}^{-1}$	9.58	10.3	10.8	11.1
P_0/Torr	110	210	390	760

The following mechanism was proposed for the above unimolecular isomerization:



The species A^* is an energized molecule present in low concentration. From the data given, determine the first-order rate constant, k_{∞} , at high pressure and the Lindemann parameters k_1 and (k_{-1}/k_2) .

(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		$\text{J K}^{-1} \text{mol}^{-1}$
		8.31447	10^{-2}	$\text{L bar K}^{-1} \text{mol}^{-1}$
		8.20574	10^{-2}	$\text{L atm K}^{-1} \text{mol}^{-1}$
		6.23637	10	$\text{LTorr K}^{-1} \text{mol}^{-1}$
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	$1.60218 \times 10^{-19} \text{ J}$ $96.485 \text{ kJ mol}^{-1}$	2.303 RT/F = 0.0591 V at 25 °C	Energy	$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ = 1 A V s
	8065.5 cm^{-1}		Force	$1 \text{ N} = 1 \text{ kg m s}^{-2}$
1 cal	4.184 J		Pressure	$1 \text{ Pa} = 1 \text{ N m}^{-2}$ = $1 \text{ kg m}^{-1} \text{ s}^{-2}$ = 1 J m^{-3}
1 atm	101.325 kPa 760 Torr			
1 cm^{-1}	$1.9864 \times 10^{-23} \text{ J}$		Charge	$1 \text{ C} = 1 \text{ A s}$
1 Å	10^{-10} m		Potential difference	$1 \text{ V} = 1 \text{ J C}^{-1}$ = $1 \text{ kg m}^2 \text{ s}^{-3} \text{ A}^{-1}$
1 L atm	101.325 J			
1 Poise			Viscosity	$1 \text{ P} = 0.1 \text{ kg m}^{-1} \text{ s}^{-1}$

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. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

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

Jawab **LIMA** (5) soalan.

1. (a) Terangkan dengan ringkas erti kedualan gelombang-zarah. (5 markah)

- (b) Suatu operator \hat{R} adalah Hermitian jika

$$\int \Psi_m^* \hat{R} \Psi_n d\tau = \int \Psi_n (\hat{R} \Psi_m)^* d\tau$$

dengan Ψ_m dan Ψ_n adalah fungsi yang dapat diterima. Tunjukkan bahawa jika \hat{A} dan \hat{B} adalah operator Hermitian,

$$\int \Psi_m^* \hat{A} \hat{B} \Psi_n d\tau = \left[\int \Psi_n^* \hat{B} \hat{A} \Psi_m d\tau \right]^* \quad (5 \text{ markah})$$

- (c) Tentukan komutator $[(d/dx) - x, (d/dx) + x]$ dengan mengaplikasikan operator itu kepada fungsi sebarang $f(x)$. (5 markah)

- (d) Andaikan bahawa fungsi gelombang bagi suatu sistem dapat ditulis sebagai

$$\Psi(x) = \frac{1}{2} \phi_1(x) + \frac{1}{4} \phi_2(x) + \left(\frac{3 + \sqrt{2}i}{4} \right) \phi_3(x)$$

dengan ϕ_1 , ϕ_2 dan ϕ_3 adalah fungsi ortonormal. Buktikan bahawa Ψ adalah ternormal.

(5 markah)

2. (a) Bagi suatu zarah di dalam sebuah kotak dua dimensi, fungsi gelombangnya diberikan dengan

$$\Psi_{n_x, n_y}(x, y) = \left(\frac{4}{ab} \right)^{1/2} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b}$$

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(i) Tuliskan operator Hamiltonian bagi sistem ini.

(ii) Dapatkan ungkapan bagi tenaga sistem ini.

(10 markah)

(b) Fungsi gelombang keadaan asas bagi pengayun harmonik kuantum diberikan dengan

$$\Psi_0(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} \exp(-\alpha x^2)$$

dengan $\alpha = \frac{1}{2\hbar} \sqrt{km}$

(i) Tentukan sama ada Ψ_0 adalah fungsi eigen bagi operator kedudukan, \hat{x} , dan operator Hamiltonian.

(ii) Bagi kes dengan Ψ_0 bukan fungsi eigen, tentukan nilai purata bagi observabel itu.

(10 markah)

3. Tunjukkan sebutan bagi muatan haba pada tekanan tetap bagi gas unggul sebagai berikut

$$C_p = Nk \left[1 + 2T \left(\frac{\partial \ln q}{\partial T} \right)_V + T^2 \frac{\partial}{\partial T} \left(\frac{\partial \ln q}{\partial T} \right)_{V,P} \right]$$

Tentukan sumbangan putaran kepada muatan haba pada tekanan tetap, \bar{C}_p , bagi $N_2(g)$ pada 300 K.

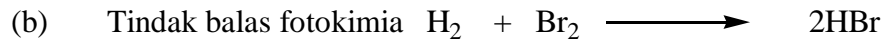
Diberi : $q_r = \frac{8\pi^2 I kT}{\sigma h^2}$

(20 markah)

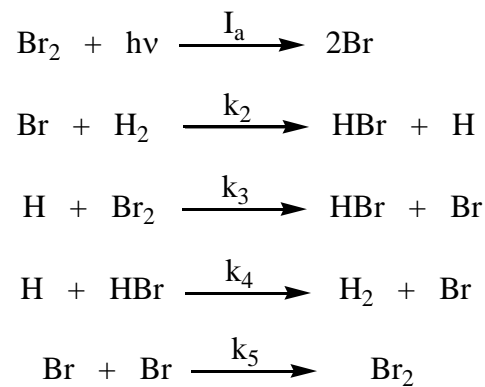
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- 4 (a) Suatu molekul mempunyai paras tenaga asas takdegenerat dan dua paras tenaga teruja yang mempunyai kedegeneratan dua dan tiga. Diberikan $\epsilon_0 = 0$, $\epsilon_1 = 1 \times 10^{-22}$ J dan $\epsilon_2 = 3 \times 10^{-22}$ J. Tentukan pecahan molekul yang mengisi setiap paras pada 298 K dan agihan molekul sekiranya suhu naik tiga kali ganda.

(10 markah)



mungkin dapat dihuraikan oleh skema yang berikut:-



Terbitkan satu ungkapan bagi kadar pembentukan hidrogen bromida dan hasil kuantum bagi tindak balas fotokimia itu.

(10 markah)

5. (a) Plot Arrhenius $\log k$ melawan $1/T$ ialah linear dengan kecerunan negatif 4.5×10^3 K dan pintasan sama dengan 11.90 bagi tindak balas dwimolekul. Kirakan E_a , $\Delta^\ddagger H^\circ$ (pada 25 °C) dan $\Delta^\ddagger S^\circ$.

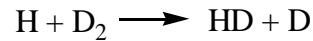
(10 markah)

- (b) Bagi penguraian hidrogen iodida dengan menganggapkan diameter pelanggaran ialah 350 pm dan tenaga pengaktifan ialah 184 kJ mol^{-1} , nilai eksperimen pemalar kadar yang diperoleh bagi tindak balas ini ialah $1.57 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Kirakan kadar tindak balas, pemalar kadar dan faktor sterik pada 700 K dan tekanan 1 atm.

(10 markah)

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6. Gunakan teori keadaan peralihan untuk mengira fungsi partisi bagi bahan tindak balas dan kompleks yang diaktifkan, faktor pra-eksponen, A, dan pemalar kadar, k, pada 600 K bagi tindak balas:



Diberi:

Ketinggian halangan klasik atau lintasan maksimum bagi tindak balas ialah 40.2 kJ mol^{-1} pada 600 K. Struktur keadaan peralihan ialah susunan linear bagi tiga atom dengan jarak antara nuklear sama dengan $0.930 \times 10^{-10} \text{ m}$. Kompleks yang diaktifkan, HD_2 , mempunyai nombor gelombang getaran 1762 cm^{-1} (regangan simetri) dan 694 cm^{-1} (dua pembengkokan yang degenerat). D_2 mempunyai hanya satu mod getaran dan nombor gelombang getarannya ialah 3112 cm^{-1} . Jarak antara nuklear bagi D_2 ialah $0.741 \times 10^{-10} \text{ m}$. Kedegeneratan elektronik ialah 2 bagi H dan HD_2 dan satu bagi D_2 .

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

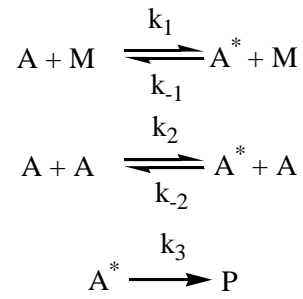
$$q_t = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

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

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

(20 markah)

7. (a) Bagi mekanisme Lindemann, dianggap bahawa kadar pengaktifan oleh pelanggaran dengan molekul bahan tindak balas yang lain, A, ialah sama dengan pelanggaran dengan molekul bukan bahan tindak balas, M. Jika kadar pengaktifan bagi kedua-dua proses adalah berbeza, mekanisme menjadi:



- (i) Tentukan ungkapan hukum kadar bagi pembentukan hasil tindak balas, P.
- (ii) Adakah hukum kadar ini diturunkan kepada bentuk jangkaan apabila $[M] = 0$?

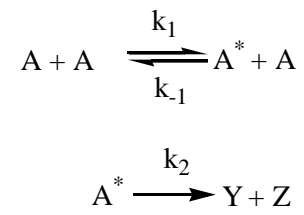
(10 markah)

- (b) Pemalar kadar tertib pertama unimolekul eksperimen, k_{uni} , bagi pengisomeran siklobutana kepada butilena pada 350 K melawan tekanan awal, P_o , adalah berikut:

$k_{\text{uni}}/\text{s}^{-1}$	9.58	10.3	10.8	11.1
P_o/Torr	110	210	390	760

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Mekanisme yang berikut dicadangkan bagi pengisomeraan unimolekul tersebut:



Spesies A^* ialah molekul teruja yang wujud dalam kepekatan rendah. Daripada data yang diberi, tentukan pemalar kadar tertib pertama, k_{∞} , pada tekanan tinggi dan parameter Lindemann k_1 dan (k_{-1}/k_2) .

(10 markah)

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