
UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2007/2008

Jun 2008

KFT 331 – Physical Chemistry III
[Kimia Fizik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **ELEVEN** 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.

Answer any **FIVE** questions

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

$$k_r = \left(\frac{kT}{h} \right) K_c^\ddagger$$

where k_r and K_c^\ddagger are the rate constant and equilibrium constant, respectively, for the process



in which activated complexes are formed from the reactants.
Starting from the equation:

$$\frac{d \ln K_c^\ddagger}{dT} = \frac{\Delta^\ddagger U^\circ}{RT^2}$$

where $\Delta^\ddagger U^\circ$ is the increase in internal energy in passing from the initial state to the activated state, derive the following equation:

$$E_a = \Delta^\ddagger H^\circ + nRT$$

where E_a is the experimental activation energy and n is the molecularity of the reaction.

(10 marks)

- (b) The rate constant and the activation energy for a second-order reaction in solution are $3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $120.0 \text{ kJ mol}^{-1}$, respectively, at 298.15 K . Calculate, at 298.15 K , the pre-exponential factor, A , the enthalpy of activation, $\Delta^\ddagger H^\circ$, the Gibbs energy of activation, $\Delta^\ddagger G^\circ$, and the entropy of activation, $\Delta^\ddagger S^\circ$.

(10 marks)

2. The following data have been obtained for an enzyme-catalysed reaction at various substrate concentrations:

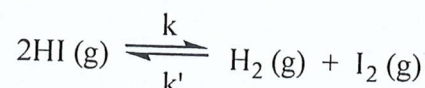
$10^3[S]/\text{mol dm}^{-3}$	2.0	4.0	8.0	12.0	16.0	20.0
$10^5 v/\text{mol dm}^{-3} \text{ s}^{-1}$	13	20	29	33	36	38

...3/-

The concentration of the enzyme is 2.0 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 .

(20 marks)

3. For the gas-phase reaction,



the measured rate constants as a function of temperatures are:

T/K	647	666	683	700	716	781
$k / 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.086	0.220	0.512	1.157	2.502	39.53
$k' / 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	5.227	14.15	24.6	64.2	140.0	1336.5

Demonstrate that these data are consistent with the collision theory of bimolecular gas-phase reaction. Given that the diameters of the molecules:

$$d_{\text{HI}} = d_{\text{H}_2} = d_{\text{I}_2} = 0.35 \text{ nm.}$$

(20 marks)

4. (a) For the case of two atoms giving a product,



show that the transition-state theory yields essentially the same expression for the rate constant as the collision theory.

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

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

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

(10 marks)

...4/-

- 4 -

- (b) Consider a molecule having two energy levels with the energy and degeneracy as follows:

$$\epsilon_1 = 0, g_1 = 1; \epsilon_2 = 1 \times 10^{-21} \text{ J}, g_2 = 2$$

- (i) Calculate the partition function at 300 K.
- (ii) Calculate the energy per molecule at 300 K.
- (iii) Calculate the temperature at which the ratio of the fractions of molecules in the excited and ground energy levels is 0.2.

(10 marks)

5. Given the translational partition function $q_t = (2\pi mkT/h^2)^{3/2} V$, derive the Sackur-Tetrode equation.

Calculate the molar entropy of O(g) at 298.15 K and 1 bar. Assume $q_e = 6.7335$.

(20 marks)

6. (a) 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 wave functions. Determine whether the following operators are Hermitian or not :

- (i) x
- (ii) $\frac{d}{dx}$
- (iii) $\frac{d^2}{dx^2}$

(10 marks)

...5/-

- (b) State the Uncertainty Principle.

An object of 10 kg in weight moves at a velocity of 1.5 m s^{-1} . If its momentum can be determined within $\pm 0.05 \%$ accuracy, what is the uncertainty in determining its position. What is the uncertainty if the value of the Planck constant, h , is 1 J s . Interpret the results.

(10 marks)

7. Consider a particle of mass m moving in a two-dimensional box of sides a and b . Assume the potential to be zero inside the box and infinite outside.

- (a) Write the basic Schrödinger equation that must be solved for the two-dimensional problem.

(5 marks)

- (b) If the wave function, ψ , can be expressed as $\psi = X(x)Y(y)$, separate the equation from (a) into two equations involving $X(x)$ and $Y(y)$, respectively.

(7 marks)

- (c) Determine the expressions for $X(x)$ and $Y(y)$.

(4 marks)

- (d) Obtain the expression for the total energy.

(4 marks)

(Given: The wave function for a particle in a one-dimensional box of side a is

given by $\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$)

Jawab LIMA soalan.

1. (a) Persamaan Eyring diberi sebagai:

$$k_r = \left(\frac{kT}{h} \right) K_c^\ddagger$$

dengan k_r dan K_c^\ddagger masing-masing ialah pemalar kadar dan pemalar keseimbangan bagi proses



yang mana kompleks yang diaktifkan dibentukkan daripada bahan tindak balas.

Bermula daripada persamaan:

$$\frac{d \ln K_c^\ddagger}{dT} = \frac{\Delta^\ddagger U^\circ}{RT^2}$$

dengan $\Delta^\ddagger U^\circ$ ialah penambahan tenaga dalam keadaan awal kepada keadaan yang diaktifkan, terbitkan persamaan:

$$E_a = \Delta^\ddagger H^\circ + nRT$$

E_a ialah tenaga pengaktifan eksperimen dan n ialah kemolekulan tindak balas.

(10 markah)

- (b) Pemalar kadar dan tenaga pengaktifan untuk tindak balas bertertib kedua dalam larutan masing-masing ialah $3.95 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ dan $120.0 \text{ kJ mol}^{-1}$, pada 298.15 K . Pada 298.15 K , kiralah faktor pra-eksponen, A , entalpi pengaktifan, $\Delta^\ddagger H^\circ$, tenaga pengaktifan Gibbs, $\Delta^\ddagger G^\circ$, dan entropi pengaktifan, $\Delta^\ddagger S^\circ$.

(10 markah)

2. Data berikut diperoleh untuk tindak balas bermangkin enzim pada beberapa kepekatan substrat:

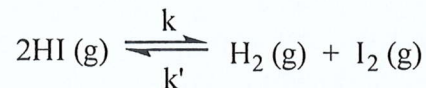
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$10^5 v/\text{mol dm}^{-3} \text{ s}^{-1}$	13	20	29	33	36	38

...8/-

Kepekatan enzim ialah 2.0 g dm^{-3} , dan berat molekul ialah 50,000. Kiralah pemalar Michaelis, K_m , kadar penghadam, v_{\max} dan pemalar mankinan, k_c .

(20 markah)

3. Untuk tindak balas fasa gas,



pemalar kadar tersebut diberi sebagai satu fungsi terhadap suhu:

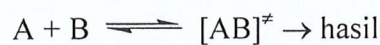
T/K	647	666	683	700	716	781
$k / 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	0.086	0.220	0.512	1.157	2.502	39.53
$k' / 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	5.227	14.15	24.6	64.2	140.0	1336.5

tunjukkan bahawa data itu selaras dengan teori pelanggaran bagi tindak balas fasa gas. Diberi diameter molekul:

$$d_{\text{HI}} = d_{\text{H}_2} = d_{\text{I}_2} = 0.35 \text{ nm.}$$

(20 markah)

4. (a) Bagi tindak balas di antara dua atom,



Tunjukkan bahawa teori keadaan peralihan menghasilkan persamaan yang sama bagi pemalar kadar yang didapati daripada teori pelanggaran.

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

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

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

(10 markah)

- (b) Pertimbangan suatu molekul yang mempunyai dua paras tenaga dengan tenaga dan kedegeneratan seperti berikut:

$$\epsilon_1 = 0, g_1 = 1; \epsilon_2 = 1 \times 10^{-21} \text{ J}, g_2 = 2$$

- (i) Kirakan fungsi partiti pada 300 K.
- (ii) Kirakan tenaga per molekul pada 300 K.
- (iii) Kirakan suhu yang mana nisbah pecahan molekul dalam paras tenaga teruja dan asas adalah 0.2.

(10 markah)

5. Diberi fungsi partiti translasi $q_t = (2\pi mkT/h^2)^{3/2} V$, terbitkan persamaan Sackur-Tetrode

Kirakan entropi molar bagi $O(g)$ pada 298.15 K dan 1 bar. Andaikan $q_e = 6.7335$.

(20 markah)

6. (a) 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 gelombang yang dapat diterima.

Tentukan sama ada operator yang berikut Hermitian atau tidak:

(i) x

(ii) $\frac{d}{dx}$

(iii) $\frac{d^2}{dx^2}$

(10 markah)

- (b) Nyatakan prinsip Ketidakpastian.

Suatu objek yang beratnya 10 kg bergerak pada halaju 1.5 m s^{-1} . Jika momentumnya dapat ditentukan di dalam kejituan $\pm 0.05 \%$, apakah ketidakpastian untuk menentukan kedudukannya? Apakah ketidakpastian jika nilai pemalar Planck, h , adalah 1 J s . Tafsirkan keputusan ini..

(10 markah)

7. Pertimbangkan suatu zarah yang jisimnya m bergerak di dalam sebuah kotak dua dimensi dengan sisi a dan b . Andaikan keupayaan adalah sifar di dalam kotak dan takrifkan di luar.

- (a) Tuliskan persamaan Schrödinger asas yang mesti diselesaikan bagi persoalan dua dimensi ini.

(5 markah)

- (b) Jika fungsi gelombang, ψ , dapat dinyatakan sebagai $\psi = X(x)Y(y)$, asingkan persamaan daripada (a) kepada dua persamaan yang masing-masing melibatkan $X(x)$ dan $Y(y)$.

(7 markah)

- (c) Tentukan ungkapan bagi $X(x)$ dan $Y(y)$.

(4 markah)

- (d) Perolehkan ungkapan bagi jumlah tenaga.

(4 markah)

(Diberikan: Fungsi gelombang bagi suatu zarah di dalam sebuah kotak satu dimensi dengan sisi a adalah $\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$)

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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		$\text{J K}^{-1} \text{mol}^{-1}$
		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 \AA	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			

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		