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:

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

where k_r and $K_c^{\neq}$ are the rate constant and equilibrium constant, respectively, for the process

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

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

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

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

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

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 3.95×10^{-4} dm^3 mol^{-1} s^{-1} and 120.0 kJ mol^{-1}, respectively, at 298.15 K. Calculate, at 298.15 K, the pre-exponential factor, A, the enthalpy of activation, $\Delta^{\neq}H^{\circ}$, the Gibbs energy of activation, $\Delta^{\neq}G^{\circ}$, and the entropy of activation, $\Delta^{\neq}S^{\circ}$.

(10 marks)

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

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

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,

$$2HI\,(g) \underset{k'}{\overset{k}{\rightleftharpoons}} H_2\,(g) + I_2\,(g)$$

the measured rate constants as a function of temperatures are:

T/K	647	666	683	700	716	781
k / 10^{-3} dm^3 mol^{-1} s^{-1}	0.086	0.220	0.512	1.157	2.502	39.53
k' / 10^{-3} dm^3 mol^{-1} 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:

$$d_{HI} = d_{H_2} = d_{I_2} = 0.35 \text{ nm.}$$

(20 marks)

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

$$A + B \rightleftharpoons [AB]^{\neq} \rightarrow \text{products}$$

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)

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

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

where ψ_m and ψ_n are acceptable wave functions. Determine whether the following operations are Hermitian or not :

(i) x

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

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

(10 marks)

(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 ± 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:

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

dengan k_r dan $K_c^{\neq}$ masing-masing ialah pemalar kadar dan pemalar keseimbangan bagi proses

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

yang mana kompleks yang diaktifkan dibentukkan daripada bahan tindak balas.
Bermula daripada persamaan:

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

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

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

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 x 10^{-4} dm^3 mol^{-1} s^{-1} dan 120.0 kJ mol^{-1}, pada 298.15 K. Pada 298.15 K, kiralah faktor pra-eksponen, A, entalpi pengaktifan, $\Delta^{\neq}H^{\circ}$, tenaga pengaktifan Gibbs, $\Delta^{\neq}G^{\circ}$, dan entropi pengaktifan, $\Delta^{\neq}S^{\circ}$.

(10 markah)

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

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

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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,

$$2HI\,(g) \underset{k'}{\overset{k}{\rightleftharpoons}} H_2\,(g) + I_2\,(g)$$

pemalar kadar tersebut diberi sebagai satu fungsi terhadap suhu:

T/K	647	666	683	700	716	781
k / 10^{-3} dm^3 mol^{-1} s^{-1}	0.086	0.220	0.512	1.157	2.502	39.53
k' / 10^{-3} dm^3 mol^{-1} 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:

$$d_{HI} = d_{H_2} = d_{I_2} = 0.35\text{ nm}.$$

(20 markah)

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

$$A + B \rightleftharpoons [AB]^{\neq} \rightarrow \text{hasil}$$

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

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) Pertimbanan 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 partisi translasi $q_t = \left(2\pi mkT/h^2\right)^{3/2} V$, 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

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

dengan ψ_m dan ψ_n adalah fungsi gelombang yang dapat diterima.

Tentukan sama ada operator yang berikut Hermitian atau tidak:

(i) x

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

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

(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 ± 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 $\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$)

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	1.60218×10^{-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		

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