First Semester Examination
Academic Session 2020/2021

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KFT431 – Physical Chemistry III

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Duration : 2 hours
[Masa : 2 jam]

Please check that this examination paper consists of **EIGHT (8)** pages of printed material before you begin the examination.

Instructions:

This paper has **FIVE (5)** questions in **Sections A** and **B**.

Please answer **FOUR (4)** questions only. Answer **TWO (2)** questions from **Section A** and **any TWO (2) questions** from **Section B**.

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

Appendix: Fundamental constants in Physical Chemistry

SECTION A

Answer **ALL** questions.

1. (a) Consider a particle moving in a 1-D box, the wavefunction, ψ is given by:

$$\psi = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$$

where L is the dimension of the box and n is the quantum number.

(i) The quantum number for the particle-in-a-box system cannot be zero. Explain this statement.

(ii) Starting with the operators for position and momentum, interpret the commutability of these two operators for this system and its implication.

(13 marks)

(b) A system comprising of one mole of distinguishable and non-interacting molecules has a two-fold degenerate ground energy level, a two-fold degenerate excited energy level at 1237 cm^{-1} and a nondegenerate excited energy level at 2010 cm^{-1} at 300 K and 1 atm. Calculate

(i) the partition function, q.

(ii) the number of molecules in each energy level.

(iii) the change in the ratio of the molecules in the first excited energy level with respect to the ground energy level when the temperature increases by 10-fold.

(iv) the total energy, E.

(v) the partition function when $T = \infty$.

(12 marks)

2. (a) The competitive inhibition can be described as follows: (CLO1)

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

$$ES \xrightarrow{k_2} E + P$$

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} EI$$

In this mechanism, I, is the inhibitor, EI is the enzyme-inhibitor complex and the other species are identical to those employed in the standard enzyme kinetic scheme.

(i) Demonstrate that the rate of product formation is (C3)

$$r = \frac{k_2[S][E]_o}{[S] + K_m\left(1 + \frac{[I]}{K_i}\right)}$$

where $K_i = \frac{[E][I]}{[EI]}$.

(ii) Derive the Lineweaver-Burk equation if a new apparent Michaelis-Menten constant is defined as

$$K_m^* = K_m\left(1 + \frac{[I]}{K_i}\right)$$

(10 marks)

(b) The following data is collected from an enzyme-catalysed reaction:

Concentration of substrate, [S]/mol dm^{-3}	Rate, υ/mol m^{-3} s^{-1}
2.5 x 10^{-4}	2.3 x 10^{-4}
5.0 x 10^{-4}	7.8 x 10^{-4}

The concentration of the enzyme is 2 g dm^{-3} and its molecular weight is 50,000 g mol^{-1}. Calculate the Michaelis constant, K_m, and the limiting rate, V, for this reaction.

(5 marks)

(c) The Eyring constant, k_r , equation is given as

$$k_r = \left(\frac{k_B T}{h}\right)\kappa_c^{\neq}$$

where $\kappa^{\neq}{}_c$ is the equilibrium constant, k_B is the Boltzmann constant and T is temperature.

Starting from the equation:

$$\frac{d\ln\kappa_c^{\neq}}{dT} = \frac{\Delta^{\neq}U^o}{RT^2}$$

Derive

$$E_a = \Delta^{\neq}H^o + RT(1-\Delta^{\neq}n)$$

where $\Delta^{\neq}U^o$ is the increase in internal energy in passing from the initial state to the activated state, E_a is the experimental activation energy, $\Delta^{\neq}H^o$ is the enthalpy change and Δn is the change in the number of molecules when the activated complex is formed from the reactants.

(10 marks)

SECTION B

Answer **any TWO (2)** questions

3. Consider a particle moving in a 2-D box of dimensions a and b. The wavefunction, ψ, is given by

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

(a) Starting from the Hamiltonian operator, show that the expression of energy for this system $E = \frac{h^2}{8m}\left(\frac{n_x{}^2}{a^2} + \frac{n_y{}^2}{b^2}\right)$

(10 marks)

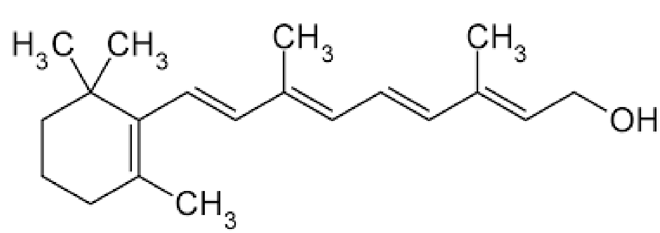
(b) If the box is a square,

(i) prepare a table showing the quantum numbers, the energy levels and the degree of degeneracy for each energy level for the energy level up to $9E_1$, where E_1 is the ground state energy.

(ii) determine the number of energy level and state from the answers obtained from (b)(i).

(15 marks)

4. (a) The molecular structure of vitamin A is shown in figure below. Its conjugated π-electron system can be described using the particle-in-a-box system.



Given that the average bond distance, ℓ_C = 140 pm and the penetration term, p = 140 pm, determine the wavelength corresponding to the first transition.

(10 marks)

(b) Starting from the expression of entropy, S, for a distinguishable system:

$$S_{dis} = k\left[N \ln\frac{q}{N} + \frac{E}{kT} + N \ln N\right]$$

(i) derive the expression for Helmholtz free energy, A.

(ii) Consider a system of 1 mole of CO (g) molecules. The internuclear distance is 1.128×10^{-10} m, the vibrational wavenumber is 2170 cm^{-1} and the ground electronic level is nondegenerate. Calculate the total free energy of 1 mole of CO (g) molecules at 298 K and pressure 1 bar.

Given:

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

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

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

(15 marks)

5. Using the Transition State Theory, calculate the rate constant for the reaction:

$$H + D_2 \rightarrow HD + D$$

The classical barrier height or the maximum path of the reaction, E_o, is 40.2 kJ mol^{-1} at 327 ^oC. The transition-state structure is an unsymmetric, linear arrangement of three atoms with an internuclear distance of 9.30 x 10^{-11} m. The HD_2 activated complex has vibrational wavenumbers of 1762 cm^{-1} (symmetric bending) and 694 cm^{-1} (doubly degenerate). Assume that the internuclear distance of H-D in the activated complex is equal to the internuclear distance of D-D.

D_2 has only one vibrational mode and its vibrational wavenumber is 3112 cm^{-1}. The D_2 internuclear distance is 7.41 x 10^{-11} m. The electronic degeneracies are 2 for H and HD_2 and unity for D_2, respectively.

Given:

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

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

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

(25 marks)

APPENDIX

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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	1.60218	10^{-19}	C
Faraday constant	$F = N_A e$	9.64853	10^{4}	C mol^{-1}
Boltzmann constant	k	1.38065	10^{-23}	J K^{-1}
Mass of electron	m_e	9.10938356	10^{-31}	kg
Gas constant	$R = N_A k$	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**

Conversion factors		Useful relation	Unit relations	
1 eV	1.60218×10^{-19} J 96.485 kJ mol^{-1} 8065.5 cm^{-1}	2.303 RT/F = 0.0591 V at 25 °C	Energy	1 J = 1 kg m^2 s^{-2} = 1 A V s
			Force	1 N = 1 kg m s^{-2}
1 cal	4.184 J		Pressure	1 Pa = 1 N m^{-2} = 1 kg m^{-1} s^{-2} = 1 J m^{-3}
1 atm	1.013 bar 101.325 kPa 760 Torr			
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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