CML101: Introduction to Chemistry (Mid-sem Exam)

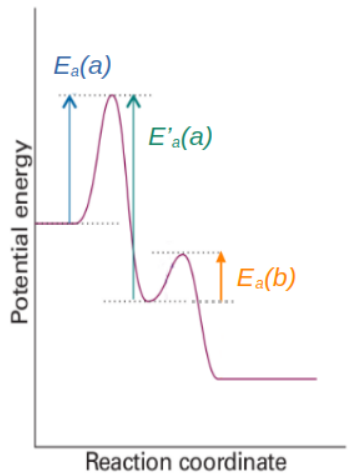
Date: 15 Sept 2023 Time: 13:00 - 15:00 pm Total Marks: 25 Questions: Q1-Q13

Q1: The gas-phase decomposition of acetic acid at 1189 K proceeds by way of two parallel reactions:

(1) $CH_3COOH \rightarrow CH_4 + CO_2$ $k_1 = 3.74\ s^{-1}$
(2) $CH_3COOH \rightarrow CH_2CO + H_2O$ $k_2 = 4.65\ s^{-1}$

(i) Derive an expression to calculate the concentration of the ketene $[CH_2CO]$ from the integrated rate law equations. (ii) What is the percentage yield of the ketene CH_2CO obtainable at this temperature when the reaction reaches completion (almost)? (2+1 marks)

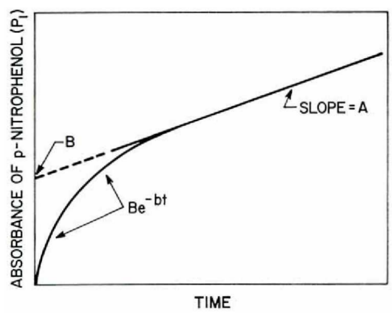
Q2: For a composite reaction involving pre-equilibrium first step a, followed by step b, the observed rate constant (k_{obs}) is $k_{obs} = \frac{k_a k_b}{k'_a}$, where k_a and k'_a are the rate constants associated with the forward and backward reactions of the step a, and k_b is the rate constant of the forward reaction of the second step, b. The activation energies, $E_a(a)$, $E'_a(a)$, and $E_a(b)$ correspond to the barriers for the different steps (see Figure).
(i) Write down a possible mechanism of the reaction corresponding to the given potential energy profile.
(ii) Assuming that each of these rate constants has Arrhenius-like temperature dependence, express the total activation energy of the reaction in terms of the activation energies of the elementary reactions. (0.5+1.5 marks)



Q3: Alpha-chymotrypsin is an important enzyme that catalyses protein hydrolysis. Furthermore, it catalyses various carboxylic acid derivatives, amides, and esters. An experiment studying the hydrolysis of p-nitrophenylacetate (ester) catalyzed by α-chymotrypsin has the following steps,

$$E + S \overset{K_s}{\rightleftharpoons} E.S \xrightarrow{k_2} ES' + P_1 \xrightarrow{k_3} E + P_2$$

where P_1 is the p-nitrophenol, and P_2 is an acetate. The concentration of P_1, follows the curve depicted on the right side Figure. As you notice in the Fig., the calculation of the concentration of P_1 involves three constants, A, B, and b that are given as,



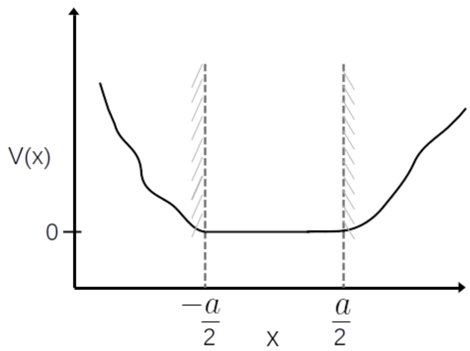
$$A = \frac{\frac{k_2 k_3}{k_2+k_3}[E]_0[S]_0}{[S]_0 + \frac{K_S k_3}{k_2+k_3}} \qquad B \cong [E]_0 \qquad b \cong \frac{(k_2+k_3)[S]_0}{[S]_0 + K_S} \quad (1)$$

(i) At high substrate concentration, P_1 gets produced much faster than P_2. These conditions will help you write down a reduced form the expression of A, and from there, calculate k_3. Given: the initial enzyme concentration, $[E]_0 = 1.15 \times 10^{-5}$ M and $A = 1.94 \times 10^{-9}$ M $\sec^{-1}$. (ii) If $K_S = 1.6 \times 10^{-3}$ M, the substrate concentration, $[S]_0 = 5.72 \times 10^{-5}$ M, and $b = 1.13 \times 10^{-3} sec^{-1}$, calculate k_2. (iii) What is the functional form of the curve corresponding to the variation of $[P_1]$ with time? (1+1+1 marks)

Q4: The wave function of a H-like atom's electron is given as, $\psi = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$. Where is the electron most likely to be found? Find out its dependence with Z. (2 marks)

Q5: Write the Schrödinger equation of a particle of mass m with a non-zero potential $V(x)$. Determine if the momentum operator commutes with the potential energy operator. Comment on your observation. (1.5 + 0.5 marks)

Q6: A quantum system has an arbitrary potential V(x) as shown in Fig. 3. Let's assume that we have found a region $-a/2 \leq x \leq a/2$ in which the potential is zero (marked on Fig. 3), and the potential rises immediately to infinity at the two boundaries, $-a/2$ and $a/2$.



For this system,
(i) Unlike the particle in 1D-box wavefunction that we discussed in the class, here the ground-state and the first excited states wave functions are, $\psi_0(x) = \sqrt{2/a}\cos\frac{\pi x}{a}$ and $\psi_1(x) = \sqrt{2/a}\sin\frac{2\pi x}{a}$, respectively.
(i) Why are the forms of the wavefunctions different than what we discussed in the class?
(ii) Derive an outcome if you measure 'x' several times using the ground-state wavefunction of this system. Explain.
(2+2 marks)

Q7: The ground-state wave function of a quantum harmonic oscillator is given as,

$$\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{1/4} e^{-\alpha x^2/2},$$

where $\alpha = \frac{m\omega}{\hbar}$, $\omega = 2\pi\nu$ is the angular frequency, and $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

(i) What is the classically forbidden region of the ground state?

(ii) Find out the probability of finding the particle in the classically forbidden region?
$\Big[$*Hint: You might need an integration,* $\int_{1/\alpha}^{\infty} e^{-\beta x^2}dx = \frac{\sqrt{\pi}}{2}\frac{1}{\alpha}\left[1 - \mathrm{Erf}(1)\right]$, and $\mathrm{Erf}(1) = 0.8427\Big]$ (1+1 marks)

Q8: Suppose we write a quantum particle's total wavefunction (ψ) as a linear sum of a few wavefunctions (ϕ_i) as, $\psi = \sum_i \alpha_i \phi_i$, where α_i are the coefficients. Write down the formula to calculate the expectation of Q. If each ϕ_i is an eigenfunction of its corresponding operator $\hat{Q}$ with eigenvalue λ_i. Assuming ϕ_i are orthonormal, derive an expression of the expectation value of Q. (0.5+1.5 marks)

Q9. Calculate CFSE of $[Co(bpy)_3]^{3+}$ and $[CuCl_4]^{2-}$ (bpy = 2,2'-bipyridine). (1 mark)

Q10. Which type of spinal is $ZnCr_2O_4$? Give a reason for your answer. (1 mark)

Q11. In an octahedral weak ligand field, categorize the following metal ions in ascending order of their ionic radii.

Cr^{3+}, Fe^{3+}, Mn^{3+} (1 mark)

Q12. Between two complexes, $[CrCl_6]^{4-}$ and $[Cr(NH_3)_6]^{2+}$, which one will have a more axially distorted structure? Explain your answer. (1 mark)

Q13. The observed effective magnetic moment (μ_{eff}) of an iron(II) complex is 5.4 μ_B, which much higher than the expected value. Explain. (1 mark)

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