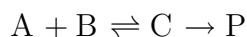


CYL110 2009-2010 More Kinetics Practice Problems

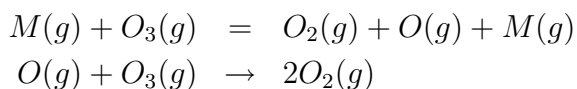
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1. The rate of decomposition of acetaldehyde can be studied by measuring the pressure in a system at constant volume and temperature. Express the rate of reaction in terms of the rate of change of the pressure. The overall reaction is $\text{CH}_3\text{CHO}(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$.
2. The decomposition of acetaldehyde given in problem 1 is second order. Formulate the rate law in terms of the total pressure of the system and integrate the result to express the pressure as a function of time.
3. The second order rate constant for the alkaline hydrolysis of ethyl formate in 85% ethanol (aqueous) at 29.86 °C is 4.53 L mol⁻¹ s⁻¹. (a) If the reactants are both present at 0.001 mol L⁻¹, what will be the half-life of the reaction? (b) If the concentration of one of the reactants is doubled and of the other is cut in half, how long will it take for half the reactant present at the lower concentration to react?
4. A gas reaction $2\text{A} \rightarrow \text{B}$ is second order in A and goes to completion in a reaction vessel of constant volume and temperature with a half life of 1h. If the initial pressure of A is 1 bar, what are the partial pressures of A, of B, and the total pressure at 1h, 2h, and at equilibrium? ($p_a = 0.5$, $p_b = 0.25$; 0.33, 0.33; 0, 0.5)
5. An autocatalytic reaction is one where one of the products catalyses the reaction. Derive an integrated rate law for the autocatalytic reaction $\text{A} \rightarrow \text{P}$ given that $-\text{d}[\text{A}]/\text{dt} = k[\text{A}][\text{P}]$ and initial $[\text{A}] = a$, $[\text{P}] = p$. [F00]
6. Consider the reaction mechanism



Write the expression for $\text{d}[\text{P}]/\text{dt}$, the rate of product formation. Assume equilibrium is established in the first reaction before any appreciable amount of product is formed, and show that $\text{d}[\text{P}]/\text{dt} = k_2K[\text{A}][\text{B}]$, where K is the equilibrium constant for the first step.

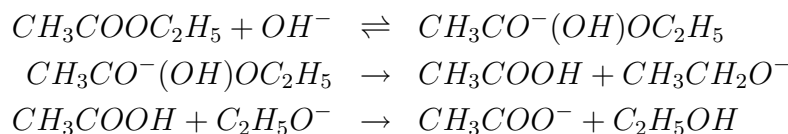
7. The decomposition of ozone $2\text{O}_3 \rightarrow 3\text{O}_2(\text{g})$ occurs by the reaction mechanism



where M is a molecule that can exchange energy with the reacting ozone molecule through a collision, but does not react. Use this mechanism to derive the rate law for $\text{d}[\text{O}_3]/\text{dt}$ assuming that O(g) can be treated by a steady state approximation (SSA) $(-1/2\text{d}[\text{O}_3]/\text{dt} = k_1k_2[\text{O}_3]^2[\text{M}]/(k_{-1}[\text{O}_2][\text{M}] + k_2[\text{O}_3])$

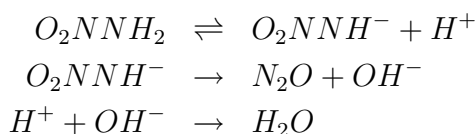
8. Explain why in the previous problem either (a) $v_{-1} \gg v_2$ and $v_{-1} \gg v_1$ or (b) $v_2 \gg v_{-1}$ and $v_2 \gg v_1$ must be true for the SSA to apply. The rate law for the decomposition reaction is found to be $\text{d}[\text{O}_3]/\text{dt} = -k[\text{O}_3][\text{M}]$. Is this rate law consistent with the conditions given by either (a) or (b) or both? ((b))

9. The rate law for the hydrolysis of ethyl acetate by aqueous sodium hydroxide at 298 K is $k_{\text{obs}}[\text{OH}^-][\text{CH}_3\text{COOC}_2\text{H}_5]$. The mechanism for the reaction is



Write the rates of formation of all the intermediate species? Under what conditions does this mechanism give the observed rate law? For these conditions, express k_{obs} in terms of the individual steps of the reaction mechanism. [F98] (fast equilibrium for step 1; $\frac{k_2 k_1}{k_{-1}}$)

10. The equilibrium constant for the reaction $\text{D}^+ + \text{OD}^- \rightleftharpoons \text{D}_2\text{O}$ is $4.08 \times 10^{16} \text{ mol}^{-1} \text{ dm}^3$. The rate constant for the reverse reaction is independently found to be $2.52 \times 10^{-6} \text{ s}^{-1}$. What would the relaxation time for a T-jump experiment be? The density of D_2O is 1.04 g cm^{-3} . (1.32×10^{-4})
11. Consider the chemical reaction described by $2\text{A} \rightleftharpoons \text{D}$ with forward and reverse rate constants given by k_1 and k_{-1} respectively. Obtain an expression for the response of this system to a temperature jump and express the relaxation time in terms of the two rate constants. ($\Delta[\text{D}] = \Delta[\text{D}]_0 e^{-t/\tau}$, $\tau = 1/(4k_1[\text{A}]_{2,\text{eq}} + k_{-1})$)
12. A proposed mechanism for the reaction of nitramide in water is



The experimentally observed rate law for the reaction is $\frac{k_{\text{obs}}[\text{O}_2\text{NNH}_2]}{[\text{H}^+]}$. (a) What is the overall reaction? (b) What are the units of k_{obs} ? (c) Under what conditions is this mechanism consistent with the rate law? (d) Express k_{obs} in terms of the rate constants of the elementary reactions. (e) With this mechanism as an example explain the concept of rate determining step. [F98]

13. A reaction $\text{A} + \text{B} + \text{C} \rightarrow \text{D}$ follows the mechanism (i) $\text{A} + \text{B} \rightleftharpoons \text{AB}$ (ii) $\text{AB} + \text{C} \rightarrow \text{D}$, in which the first step remains essentially in equilibrium. (a) Derive the expected rate law and express k_{obs} in terms of the rate constant of the elementary reactions. (b) If ΔH and E_a are the enthalpy change for the first step and the activation energy of the second step respectively, show that the dependence of k_{obs} on temperature is given by $k_{\text{obs}} = \text{A}e^{-(E_a + \Delta H)/RT}$. [F01]
14. (a) How do the dimensions of a pseudo first-order rate constant differ from those of a second order rate constant? (b) Give an example of the distinction between order and molecularity. (c) Explain the steady state approximation with an example. (d) Discuss the concept of the rate determining step with an example. [F98]
15. Consider the hypothetical, second order, kinetically irreversible reaction $2\text{A} \xrightarrow{k} \text{Products}$ at constant temperature and volume. Let the concentration c_t of A be given in terms of a measurable property P_t by $P_t = B \exp(b c_t)$ where B and b are constants depending only on temperature and t denotes the time. Derive an expression for the specific rate constant k in terms of t , P_t , B , and b . [M02]