

EXERCISE 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 $\text{CH}_3\text{CHO}(\text{g}) \longrightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g})$.

EXERCISE 2. Sulphuryl chloride decomposes according to the equation $\text{SO}_2\text{Cl}_2(\text{g}) \longrightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$. Determine the order of the reaction with respect to $\text{SO}_2\text{Cl}_2(\text{g})$ from the following initial rate data at 298 K.

$[\text{SO}_2\text{Cl}_2]_0/\text{mol dm}^{-3}$	0.10	0.37	0.76	1.22
$v_0/\text{mol dm}^{-3} \text{ s}^{-1}$	2.24×10^{-6}	8.29×10^{-6}	1.71×10^{-6}	2.75×10^{-5}

EXERCISE 3. A first order reaction has a rate constant of $2.24 \times 10^{-5} \text{ s}^{-1}$ at 320°C . Calculate the half-life of the reaction. What fraction of the sample remains after being heated for 5 h at 320°C ? How long will a sample have to be heated at 320°C to decompose 92% of the initial amount present.

EXERCISE 4. The reaction $\text{A} \longrightarrow \text{B}$ is n^{th} order (where $n = 1/2, 3/2, 2, 3$ etc.) and goes to completion to the right. Derive the expression for the half life in terms of k , n , and $[\text{A}]_0$. ($t_{1/2} = (2^{n-1} - 1)/(n - 1) k [\text{A}]_0^{n-1}$)

EXERCISE 5. The decomposition of acetaldehyde given in **Exercise 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.

EXERCISE 6. Consider the decomposition of C_4H_8 according to $\text{C}_4\text{H}_8(\text{g}) \rightarrow 2\text{C}_2\text{H}_4(\text{g})$. The rate is measured by observing the change in pressure (p) at constant T and V . (a) Express the rate of the reaction $\frac{1}{V} \frac{d\zeta}{dt}$ (where ζ is the extent of the reaction in terms of $\frac{dp}{dt}$). [Hint: Initially n_0 moles of C_4H_8 is present. Express the number of moles at any times t in terms of ζ]. (b) If p_i is the pressure when C_4H_8 is completely decomposed and the reaction is first order in C_4H_8 derive the relation between p and t . (c) If $k = 2.48 \times 10^{-1} \text{ s}^{-1}$, calculate $t_{1/2}$. (d) What is the value of p/p_i after 2 hours?

EXERCISE 7. 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 $P_t = B \exp(bc_t)$ 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 .

EXERCISE 8. The second order rate constant for the alkaline hydrolysis of ethyl formate in 85% ethanol (aqueous) at 29.86°C is $4.53 \text{ L mol}^{-1} \text{ s}^{-1}$. (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?

EXERCISE 9. 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)

EXERCISE 10. The reaction of *cis*-2-butene to *trans*-2-butene is first order in both directions. At 25°C , the equilibrium constant is 0.406 and the forward rate constant is $4.21 \times 10^{-4} \text{ s}^{-1}$. Starting with a sample of the pure *cis* isomer with $[\text{cis}]_0 = 0.115 \text{ mol dm}^{-3}$, how long would it take for half the equilibrium amount of the *trans* isomer to form.

EXERCISE 11. 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} .

EXERCISE 12. Consider the chemical reaction described by $2A \xrightleftharpoons[k_{-1}]{k_1} D$. 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. ($\Delta[D] = \Delta[D]_0 e^{-t/\tau}$, $\tau = 1/(4k_1[A]_{2,eq} + k_{-1})$)

EXERCISE 13. An autocatalytic reaction is one where one of the products catalyses the reaction. Derive an integrated rate law for the autocatalytic reaction $A \rightarrow P$ given that $-d[A]/dt = k[A][P]$ and initial $[A] = a$, $[P] = p$.

EXERCISE 14. Show that the ratio $t_{1/2}/t_{3/4}$, where $t_{1/2}$ is the half-life and $t_{3/4}$ is the time for the concentration of A to decrease to 3/4 of its initial value can be written as a function of n alone, and can therefore be used as a rapid assessment of the order of a reaction.

EXERCISE 15. The oxidation of HSO_3^- by O_2 in aqueous solution is a reaction of importance to the processes of acid rain formation. The reaction $2\text{HSO}_3^- + \text{O}_2 \longrightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$ follows the rate law $k[\text{HSO}_3^-]^2[\text{H}^+]^2$. Given a pH of 5.6 and an oxygen molar concentration of $2.4 \times 10^{-4} \text{ mol L}^{-1}$ (both presumed constant), an initial HSO_3^- concentration of $5 \times 10^{-5} \text{ mol L}^{-1}$, and a rate constant of $3.6 \times 10^6 \text{ L mol}^{-3} \text{ s}^{-1}$, what is the initial rate of the reaction? How long would it take for HSO_3^- to reach half its initial concentration?

EXERCISE 16. The rotational isomerization of a compound was studied by the T-jump method. At 20°C the deviation from equilibrium attains half its value at $t = 0$ in $6.93 \times 10^{-9} \text{ s}$. If the favored isomer is present to the extent of 80 %, determine the rate constants for the isomerization.