

## Reaction Kinetics I: Homogeneous Systems

P85. The rate of a reaction was measured by monitoring the absorbance ( $A$ ) of the solution:

Time /min	0.0	18.0	57.0	130	240	337	398
$A$	1.39	1.26	1.03	0.706	0.398	0.251	0.180

Assuming the validity of Beer's law, show that the reaction is first-order and calculate the rate constant. ( $\ln A$  versus  $t$  is a straight line.  $k = 8.52 \cdot 10^{-5} \text{ s}^{-1}$ )

P86. The kinetic decomposition of the  $^{14}\text{C}$  radioactive isotope with a nuclear energy of 0.160 MeV has a half-life of 5730 years. The  $^{14}\text{C}$  isotope content of the wood of an archaeological sample is 72% of that in living trees. How old is the sample? (2716 year)

P87. Sucrose is hydrolyzed in acidic solution: the conversion is 57% after 57 minutes. Assuming that the reaction is kinetically first-order, calculate the time required for 75% hydrolysis. (93.6 min)

P88. The bromination reaction of acetone in an aqueous solution is controlled by the enolization step. In the case of  $[(\text{CH}_3)_2\text{CO}]_0 \gg [\text{Br}_2]_0$ , the reaction rate is:

$$-\frac{d[\text{Br}_2]}{dt} = k [(\text{CH}_3)_2\text{CO}].$$

At 23.0 °C and 0.040 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> concentration, the initial concentrations of the other reagents are as follows:  $[(\text{CH}_3)_2\text{CO}]_0 = 0.645 \text{ mol dm}^{-3}$  and  $[\text{Br}_2]_0 = 0.0193 \text{ mol dm}^{-3}$ . Use the following spectrophotometric data ( $A$ ) to determine the value of  $k$ . ( $k = 6.1 \cdot 10^{-6} \text{ s}^{-1}$ )

Time /s	0.0	600	1200	3600	4800	6000	9000
$A$	0.201	0.257	0.313	0.558	0.665	0.683	0.683

P89. The following data are measured for the „CH + O<sub>2</sub> → product(s)“ reaction under pseudo-first-order conditions, where  $[\text{CH}] \ll [\text{O}_2]$ .

$10^7 \cdot [\text{O}_2] / (\text{mol dm}^{-3})$	2.56	6.41	9.19	13.12	17.28	21.43	24.09
$k_{\Psi} / \text{s}^{-1}$	19600	29850	34590	45700	59700	64700	80700

Determine the second-order  $k$  rate constant. ( $k = 2.7 \cdot 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

P90. The thermal decomposition of dimethyl ether ( $(\text{CH}_3)_2\text{O} \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$ ) was monitored by measuring the increase of pressure versus time. The following data were found at 777 K temperature and 312 Hgmm (torr) initial pressure.

Time /s	390	777	1195	2000	3155
Increase of pressure /Hgmm	96	179	250	363	467

Show that the reaction is first-order and determine the rate constant. ( $k = 4.38 \cdot 10^{-4} \text{ s}^{-1}$ )

P91. Butadiene dimerizes in a second-order reaction according to the following stoichiometry:  $2 \text{ C}_4\text{H}_6 \rightarrow \text{C}_8\text{H}_{12}$ . The rate constant of the reaction is  $4.90 \cdot 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . Calculate what percentage of butadiene is dimerized after 30.0 minutes if the initial concentration is  $0.050 \text{ mol dm}^{-3}$ . (46.9%)

- P92. The following data were obtained by flash photolysis for the reaction of sulfate ion radicals in the presence of formate ion excess:

Time / $\mu\text{s}$	10	20	30	40	50	60	70	80
$I_{\text{abs}}/I_0$	0.0218	0.0191	0.0163	0.0143	0.0121	0.0107	0.0094	0.0078

After starting the reaction, the concentration of sulfate ion radicals was measured in time using absorption spectroscopy. Draw a proper diagram to show that the process is first-order and determine the pseudo-first-order rate constant. ( $\ln(I_{\text{abs}}/I_0)$  versus  $t$  is a straight line.  $k = 14487 \text{ s}^{-1}$ )

- P93. Methyl acetate was hydrolyzed in an excess of  $0.050 \text{ mol dm}^{-3}$  hydrochloric acid at  $25.0^\circ\text{C}$ . The volume of sodium hydroxide solution used to neutralize  $25.0 \text{ cm}^3$  samples from the reaction mixture was the following:

Time /min	0.0	21.0	75.0	119.0	$\infty$
Titrant / $\text{cm}^3$	24.4	25.8	29.3	31.7	47.2

Show that the reaction is pseudo-first-order under these conditions and calculate the half-life of the reaction. ( $212.75 \text{ min}$ )

- P94. Substances A and B result in the same P product in independent reactions. The rate constants are as follows:  $k_A = 2.44 \cdot 10^{-3} \text{ s}^{-1}$  and  $k_B = 6.78 \cdot 10^{-4} \text{ s}^{-1}$ . Suppose that in a reaction mixture  $[A]_0 = 6.24 \cdot 10^{-4} \text{ mol dm}^{-3}$  and  $[B]_0 = 3.42 \cdot 10^{-4} \text{ mol dm}^{-3}$ . Calculate [P], (and for questions b. and c.,  $t$  also)
- after 1500 s, ( $8.262 \cdot 10^{-4} \text{ mol dm}^{-3}$ )
  - when  $[A] = 1.00 \cdot 10^{-4} \text{ mol dm}^{-3}$  and ( $750.4 \text{ s}$  and  $6.604 \cdot 10^{-4} \text{ mol dm}^{-3}$ )
  - when  $[A] = [B]$ . ( $341.3 \text{ s}$  and  $4.233 \cdot 10^{-4} \text{ mol dm}^{-3}$ )

- P95. The rate constant for the  $\text{CH}_3\text{COOC}_2\text{H}_5(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{C}_2\text{H}_5\text{OH}(\text{aq})$  second-order reaction is  $0.110 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . How much is the ester concentration after 10.0 minutes if the initial concentration of the ester was  $0.1 \text{ mol dm}^{-3}$  and the initial concentration of base was  $0.050 \text{ mol dm}^{-3}$ ? ( $0.05094 \text{ mol dm}^{-3}$ )

- P96. Substance A decomposes in the following reaction:  $2\text{A} \rightarrow \text{B}$ . The rate constant of the kinetically second-order decomposition is  $k = 2.62 \cdot 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ . What is the half-life of the decomposition when the initial concentration of A is  $[A]_0 = 1.70 \text{ mol dm}^{-3}$ ? ( $112 \text{ s}$ )

- P97. The rate equation of a reaction is  $v = k [A]^2$ . At  $[A]_0 = 0.240 \text{ mol dm}^{-3}$ , after 92 min, the reaction is 75.0 % complete. In the same reaction with  $[A]_0 = 0.146 \text{ mol dm}^{-3}$ , how much time is needed for the concentration of A to reach  $0.043 \text{ mol dm}^{-3}$ ? ( $120.75 \text{ min}$ )

- P98. For the  $2\text{A} \rightarrow \text{P}$  reaction, the rate equation is second-order with  $k = 3.5 \cdot 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . Calculate the time needed to decrease the concentration of A from  $0.26 \text{ mol dm}^{-3}$  to  $0.011 \text{ mol dm}^{-3}$ . ( $34.55 \text{ hour}$ )

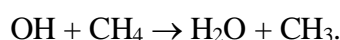
- P99. An ester of a monovalent organic acid is reacted with a monovalent base. The initial concentration of the ester in the solution was  $0.25 \text{ mol dm}^{-3}$ . Samples of  $10.00 \text{ cm}^3$  from the reaction mixture were titrated with  $1.0 \text{ mol dm}^{-3} \text{ HCl}$ . At  $t = 0$ , the volume of the titrant was  $5.05 \text{ cm}^3$ , and  $3.65 \text{ cm}^3$  titrant volume was determined after 5.0 min. Calculate the rate constant if the saponification of the ester is considered to be a second-order reaction. ( $k = 6.488 \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )

- P100. The kinetics of recombination of iodine has been studied in the presence of argon. The method of initial rates was used to determine the reaction orders. The initial rate of iodine formation  $v_0$  ( $\text{M s}^{-1}$ ) changes with reactant concentration as follows:

	$10^5 \cdot [\text{I}]_0 / (\text{mol dm}^{-3})$			
$10^3 \cdot [\text{Ar}]_0 / (\text{mol dm}^{-3})$	1.00	2.00	4.00	6.00
1.00	0.00087	0.00348	0.0139	0.0313
5.00	0.00435	0.01740	0.0692	0.1570
10.0	0.00869	0.03470	0.1380	0.3130

Calculate the reaction order for iodine and argon and calculate the rate constant of the reaction. ( $v = 8.687 \cdot 10^9 \text{ M}^{-2} \text{ s}^{-1} [\text{I}]^2 [\text{Ar}]$ )

- P101. Methane is an important trace element of the upper part of the atmosphere (called troposphere). The most important methane consuming reaction is the following:



The temperature of the troposphere decreases with height. Calculate the relative decrease of the reaction rate constant from the surface of the Earth ( $T = 295 \text{ K}$ ) to the upper limit of the troposphere ( $T = 220 \text{ K}$ ). The activation energy of the reaction is:  $19.5 \text{ kJ mol}^{-1}$ . (0.066507-times slower)

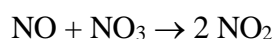
- P102. The rate of a reaction doubles when the temperature rises from  $290 \text{ K}$  to  $300 \text{ K}$ . Calculate the activation energy. (50.14 kJ/mol)

- P103. The rate constant of a particular reaction at  $30.0 \text{ }^\circ\text{C}$  is  $2.80 \cdot 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , and at  $50 \text{ }^\circ\text{C}$   $1.38 \cdot 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . Calculate the activation energy of the reaction. (65.0 kJ/mol)

- P104. For the  $\text{N}_2\text{O}_5 + \text{NO} \rightarrow 3 \text{NO}_2$  reaction, the following rate equation was found to be valid:

$$-\frac{dp(\text{N}_2\text{O}_5)}{dt} = k \cdot p(\text{N}_2\text{O}_5).$$

Using the Bodenstein principle (*steady-state* approximation), show that the rate equation is consistent with the following reaction mechanism:



What can you say about the relationship between the rate constants of the individual elementary step? ( $k_2[\text{NO}] \gg k_{-1}[\text{NO}_2]$  and  $k_2[\text{NO}] \gg k_1$ )

- P105. The following rate equation was found to be valid for the kinetics of ferricyanide and iodide ions:

$$\frac{d[\text{I}_2]}{dt} = k \frac{[\text{Fe}(\text{CN})_6^{3-}]^2 [\text{I}^-]^2}{[\text{Fe}(\text{CN})_6^{4-}]}$$

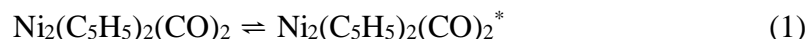
Suggest a mechanism that results in this rate equation. ( $\text{Fe}(\text{III}) + \text{I}^- \rightleftharpoons \text{Fe}(\text{II}) + \text{I}$  (fast);  $\text{I} + \text{I}^- \rightleftharpoons \text{I}_2^-$  (fast);  $\text{Fe}(\text{III}) + \text{I}_2^- \rightarrow \text{Fe}(\text{II}) + \text{I}_2$  (rate determining))

- P106. One possible mechanism for the  $\text{Fe}^{\text{III}} + \text{V}^{\text{III}} = \text{Fe}^{\text{II}} + \text{V}^{\text{IV}}$  reaction is as follows:



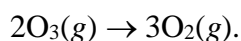
Determine the steady-state rate equation and its form at  $k_{-1}[\text{Fe}^{\text{II}}] \gg k_2[\text{V}^{\text{III}}]$ . ( $v = k_1 k_2 [\text{Fe}^{\text{III}}][\text{V}^{\text{III}}][\text{V}^{\text{IV}}] / \{k_{-1}[\text{Fe}^{\text{II}}] + k_2[\text{V}^{\text{III}}]\} = k_1 k_2 [\text{Fe}^{\text{III}}][\text{V}^{\text{III}}][\text{V}^{\text{IV}}] / \{k_{-1}[\text{Fe}^{\text{II}}]\}$ )

P107. When  $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{CO})_2$  reacts with diphenylacetylene (dpa), both of the two CO molecules can be replaced. The following mechanism is assumed:



Determine the rate equation using the steady-state approximation for the intermediate  $\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{CO})_2^*$ . At  $[\text{dpa}] \gg [\text{Ni}]$ , how would you express the  $k_{\Psi}$  pseudo-first-order rate coefficient? ( $v = k_1 k_2 [\text{Ni}_2(\text{C}_5\text{H}_5)_2(\text{CO})_2][\text{dpa}] / \{k_{-1} + k_2[\text{dpa}]\}$ ;  $k_{\Psi} = k_1 k_2 [\text{dpa}] / \{k_{-1} + k_2[\text{dpa}]\}$ )

P108. One of the most important reactions in the atmosphere can be described by the following stoichiometric equation:



The following experimental data are known:

$p(\text{O}_3) / \text{torr}$	0.20	0.20	0.40
$p(\text{O}_2) / \text{torr}$	0.50	1.00	1.00
$v_0 / (\text{torr s}^{-1})$	6.0	3.0	12.0

Suppose that the rate equation can be written in the following form:

$$v_0 = k \cdot p(\text{O}_3)^\alpha \cdot p(\text{O}_2)^\beta.$$

- What is the value of  $\alpha$  and  $\beta$ ? ( $\alpha = 2$  and  $\beta = -1$ )
- What is the average value of the rate constant? ( $75 \text{ s}^{-1}$ )
- What is the kinetic effect of  $\text{O}_2$  under these conditions? (auto-inhibitor)
- Which of the following five mechanisms is suitable for interpreting the rate equation? (3 and 5)

