

## Chemical kinetics exercises with answers

1) The half-life of pyruvic acid in the presence of an aminotransferase enzyme (which converts it to alanine) was found to be 221 s. How long will it take for the concentration of pyruvic acid to fall to 1/5, 1/10 or 1/100 of its initial value in this first-order reaction.

2) The following data were obtained on the initial rate of binding of glucose to the enzyme hexokinase:

$[\text{glucose}]_0 / (\text{mmol L}^{-1})$		1.00	1.54	3.12	4.02
$v_0 / (\text{mol L}^{-1} \text{ s}^{-1})$	(a)	5.0	7.6	15.5	20.0
	(b)	7.0	11.0	23.0	31.0
	(c)	21.0	34.0	70.0	96.0

The enzyme concentrations are (a) 1.34 mmol L<sup>-1</sup>, (b) 3.00 mmol L<sup>-1</sup>, (c) 10.0 mmol L<sup>-1</sup>. Find the orders of reaction with respect to glucose and hexokinase and the rate constant.

3) The rate constant of the acid hydrolysis of sucrose varies with temperature as follows. Find the activation energy and the pre-exponential factor. Predict the value of the rate constant at 20 °C.

T/K	297	301	305	309	313
$k / (10^{-3} \text{ L mol}^{-1} \text{ s}^{-1})$	4.8	7.8	13	20	32

4) For the second order reaction  $R \rightarrow \text{products}$ , the initial concentration of the reactant was  $[R]_0 = 0.55 \text{ M}$ . After 11 minutes, the concentration of this reactant was determined to be  $[R] = 0.24 \text{ M}$ .

a) Determine the value of the rate constant.

b) Using the integrated expression of the velocity, deduce the analytical expression of the half life for this reaction, and calculate its value.

c) At which time the concentration of  $[R]$  will be 0.12 M?

d) Which will be the concentration of  $[R]$  at 7.5 h?

5) For a second order reaction in which the initial concentration of the reactant is 0.033 M, the rate constant increases three times when the temperature increases from 30°C to 90°C. Which is the activation energy of the reaction? If the half live of the reaction at 30°C is 30 minutes, at which temperature the half live will be 10 minutes?

6) In the reaction  $A + B \rightarrow P + Q$  at 37°C, the following data were obtained

Experiment	$[A]_0/(\text{mol L}^{-1})$	$[B]_0/(\text{mol L}^{-1})$	$v_0/(\text{mol L}^{-1} \text{s}^{-1})$
1	0.12	0.14	$1.20 \cdot 10^{-4}$
2	0.09	0.14	$9.00 \cdot 10^{-5}$
3	0.16	0.14	$1.60 \cdot 10^{-4}$
4	0.09	0.42	$8.10 \cdot 10^{-4}$

a) Determine the partial order of A and B, and the rate constant at 37°C.

b) In other experiment, it was prepared the following concentrations for  $[A]_0 = 0.01\text{M}$  and  $[B]_0 = 0.70\text{M}$ . Determine the rate constant of pseudo-first order. Calculate the concentration of A after 1 minute.

7) In a study of the alcohol-dehydrogenase-catalyzed oxidation of ethanol, the molar concentration of ethanol decreased in a first-order reaction from 220 mmol L<sup>-1</sup> to 56.0 mmol L<sup>-1</sup> in  $1.22 \cdot 10^4$  s at 25°C and decreased in  $6.2 \cdot 10^3$  s at 50°C. a) Which is the rate constant of the reaction at 25°C? Which is the rate constant of the reaction at 35°C?

8) In the first order reaction  $A \rightarrow \text{products}$ , the concentration of A is  $[A] = 0.816\text{ M}$  at the initial time of the reaction, and  $[A] = 0.632\text{ M}$  after 16 minutes. a) Determine the value of the rate constant b) Deduce the analytical expression of the half life for this reaction, and calculate its value. c) At which time the concentration of  $[A]$  will be 0.235 M? Which will be the concentration of  $[A]$  at 2.5 h?

9) In the reaction  $2 A + B \rightarrow C$  at 500K, the following data were obtained

Experiment	$[A]_0/(\text{mol L}^{-1})$	$[B]_0/(\text{mol L}^{-1})$	$V_0/(10^{-3} \text{ mol L}^{-1} \text{s}^{-1})$
1	0.26	0.26	5.4
2	0.52	0.26	10.8
3	0.52	0.52	21.6

a) Determine the partial order of A and B, and the rate constant at 500K.

b) In other experiment, if the concentration of  $[A]_0 = 0.4\text{M}$  and  $[B]_0 = 0.004\text{M}$ . Determine the rate constant of pseudo-first order. Calculate the concentration of B after 1 minute.

10) The rate constant of a reaction is double when the temperature increases from 50°C to 80°C. Which is the activation energy of the reaction? If the reaction follows a first-order rate law, explain what happens with its half-life when the temperature is increased from 50°C to 80°C.

11) The decomposition of  $\text{H}_2\text{O}_2(\text{aq})$  at 25°C follows a first order kinetics. Determine the percentage of  $\text{H}_2\text{O}_2$  decomposed in the first 10 minutes after the reaction was initiated. The kinetic constant of this reaction at 25°C is  $k = 7.3 \cdot 10^{-4} \text{ s}^{-1}$

12) A reaction  $\text{R} \rightarrow \text{P}$  has a kinetic constant of  $k = 1.24 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate how many hours are required for the concentration of R to change from  $0.450 \text{ mol L}^{-1}$  to  $0.033 \text{ mol L}^{-1}$ . The units of the kinetic constant indicates that is a second order reaction.

13) For the  $2 \text{ NO} + \text{O}_2 \rightarrow 2 \text{ NO}_2$  reaction in gas phase the initial velocity of formation of  $\text{O}_2$  was measured at 25°C

Find the orders of the reaction with respect to NO and  $\text{O}_2$ . Find the rate constant at 25°C

14)

a) In the collision theory, it is supposed that an activated complex is in equilibrium with the reactants. Indicate if this sentence is true or false. If it is false indicate why.

b) The Boltzmann distribution gives the numbers of molecules in each state of a system at any temperature. Indicate if this sentence is true or false. If it is false indicate why.

15) The half-life of pyruvic acid in the presence of an aminotransferase enzyme (which converts it to alanine) was found to be 221 s. How long will it take for the concentration of pyruvic acid to fall to  $1/64$  of its initial value in this first order reaction?

16) The following kinetic data ( $v_0$  is the initial rate) were obtained for the reaction  $2 \text{ ICl}(\text{g}) + \text{H}_2 \rightarrow \text{I}_2(\text{g}) + 2 \text{ HCl}(\text{g})$ :

Experiment	$[\text{ICl}]_0 / (\text{mmol dm}^{-3})$	$[\text{H}_2]_0 / (\text{mmol dm}^{-3})$	$v_0 / (\text{mol dm}^{-3} \text{ s}^{-1})$
1	1.5	1.5	$3.7 \times 10^{-7}$
2	3.0	1.5	$7.4 \times 10^{-7}$
3	3.0	4.5	$22 \times 10^{-7}$
4	4.7	2.7	?

a) Write the rate law for the reaction.

b) Determine the value of the rate constant

c) Use the data to predict the reaction rate for experiment 4.

17) The Arrhenius parameters for the reaction of decomposition of cyclobutane  $\text{C}_4\text{H}_8(\text{g}) \rightarrow 2 \text{C}_2\text{H}_4(\text{g})$  are  $\log(A/\text{s}^{-1})=15.6$  and  $E_a= 261 \text{ kJ mol}^{-1}$ . What is the half-life of this first-order reaction at  $20^\circ\text{C}$  and  $500^\circ\text{C}$ ?

18) Pharmacokinetics is the study of the rates of absorption and elimination of drugs by organisms. In most cases, elimination is slower than absorption and is a more important determinant of availability of a drug for binding to its target. A drug can be eliminated by many mechanism, such as metabolism in the liver, intestine, or kidney followed by excretion of breakdown products through urine or feces. Consider the elimination of beta adrenergic blocking agents (beta blockers), drugs used in the treatment of hypertension. After intravenous administration of a beta blocker, the blood plasma of a patient was analysed for remaining drug, and the data are shown below, where  $c$  is the drug concentration measured at time  $t$  after injection at  $310 \text{ K}$ .

<b>t/min</b>	30	60	120	150	240	360	480
<b>c/(ng/mL)</b>	699	622	413	292	152	60	24

a) Identify the order of the elimination process of beta blockers. Plot zero, first and second order representations.

b) Determine the kinetic constant and the half live.

c) Determine the concentration of the drug at 0 h.

d) Determine the concentration of the drug at 10 h.