# Chemical kinetics exercises with answers

1) The half-live 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.

R: ratio: [ 0.2 0.1 0.01] t/s: [ 515.468 737.468 1474.9361]

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

| $[glucose]_0/(mmol\ L^{-1})$ | | 1.00 | 1.54 | 3.12 | 4.02 |
|---|---|---|---|---|---|
| $v_0/(mol\ L^{-1}\ s^{-1})$ | (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-1, (b) 3.00 mmol L-1, (c) 10.0 mmol L -1. Find the orders of reaction with respect to glucose and hexokinase and the rate constant.

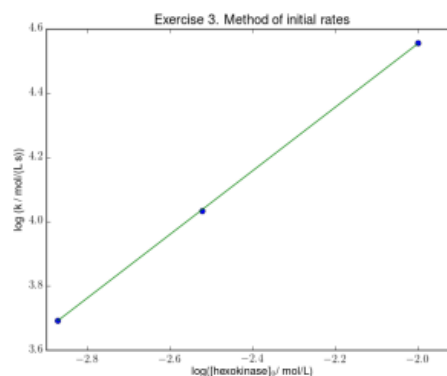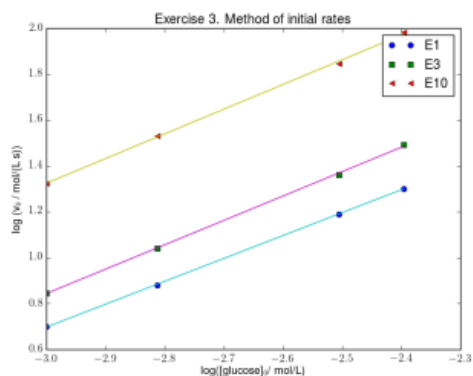For [hexokinase]= 0.00134 M, a= 0.999, log(k'/(M·s)^-1)= 3.692, k'= 4925 (M·s)^-1
For [hexokinase]= 0.00300 M, a= 1.063, log(k'/(M·s)^-1)= 4.033, k'= 1.078e+04 (M·s)^-1
For [hexokinase]= 0.01000 M, a= 1.077, log(k'/(M·s)^-1)= 4.556, k'= 3.594e+04 (M·s)^-1
Exponent for [Hexokinase] = 0.98964
log10(k)= 6.5 , k= 3.4e+6 L/(mol·s)

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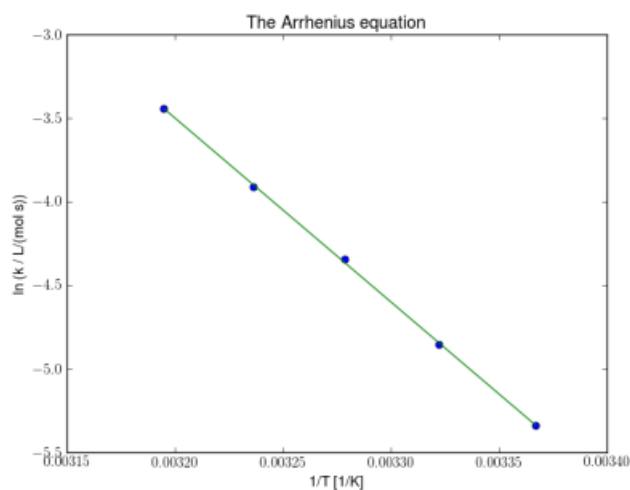
| T/K | 297 | 301 | 305 | 309 | 313 |
|---|---|---|---|---|---|
| $k/(10^{-3}$ L mol$^{-1}$ s$^{-1}$) | 4.8 | 7.8 | 13 | 20 | 32 |

**R:**
**Activation energy: Ea= 9.15e+04 J/mol**
**Pre-exponential factor: A= 6.01e+13 L/(mol s)**
**At 20 C, the rate constant is k= 0.00295 L/(mol s)**



The Arrhenius equation

4) For the second order reaction R → products, the initial concentration of the reactant was [R]0 = 0.55 M. After 11 minutes, the concentration of this reactant was determined to be [R]=0.24M.

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?

**a)** $1/A_t = 1/A_0 + kt$

$k = 0.213\, M^{-1} min^{-1} = 0.00355\, M^{-1} s^{-1}$

**b)** $1/A_t = 1/A_0 + kt$    $2/A_0 = 1/A_0 + kt_{half}$    $t_{half} = \dfrac{1}{A_0 k}$

$t_{half} = \dfrac{1}{A_0 k} = 8.516\, min$

**c)** $t = (1/A_t - 1/A_0)/k = 30.5\, min$

**d)** $A_{7.5h} = 1/(1/A_0 + kt_{450\,min}) = 0.010\, M$

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 30ºC to 90ºC. Which is the activation energy of the reaction? If the half live of the reaction at 30ºC is 30 minutes, at which temperature the half live will be 10 minutes?

$k = A \exp(-E_a/RT)$

$k_{30C} = A \exp(-E_a/RT_{30C})$    $k_{90C} = A \exp(-E_a/RT_{90C})$

$k_{90C}/k_{30C} = 3$

$3 = \exp(-E_a/RT_{90C} + E_a/RT_{30C})$    Ea= 16759 J/mol

$t_{half} = \dfrac{1}{A_0 k}$

$k_{30C} = \dfrac{1}{A_0 t_{half}} = 1.01\, M^{-1} min^{-1}$

$k_T = \dfrac{1}{A_0 t_{half\,10\,min}} = 3.03\, M^{-1} min^{-1}$

$A = k_{30C}/\exp(-E_a/RT_{30C}) = 780\, M^{-1} min^{-1}$

Isolate T from $k_T = A \exp(-E_a/RT)$    T= 363 K = 90 C

6) In the reaction A + B → P + Q at 37ºC, the following data were obtained

| Experiment | $[A]_0/(mol\ L^{-1})$ | $[B]_0/(mol\ L^{-1})$ | $v_0/(mol\ L^{-1}s^{-1})$ |
|---|---|---|---|
| 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 37ºC.

b) In other experiment, it was prepared the following concentrations for [A]0 =0.01M and [B]0 =0.70M. Determine the rate constant of pseudo-first order. Calculate the concentration of A after 1 minute.

$$v=k[A]^\alpha[B]^\beta$$

$$\alpha=\frac{\ln\dfrac{v_1}{v_2}}{\ln\dfrac{[A]_1}{[A]_2}}\approx 1 \quad \beta=\frac{\ln\dfrac{v_2}{v_4}}{\ln\dfrac{[B]_2}{[B]_4}}\approx 2$$

$$v=k[A][B]^2$$

$$k_{37C}=0.051\,L^2\,mol^{-2}s^{-1}$$

b) $k_{app}=k[B]^2=2.5E\text{-}2\ s^{-1}$

$$\ln(A_t)=\ln(A_0)-k_{app}t$$

A$_t$=2.23E-3 M

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-1 to 56.0 mmol L-1 in 1.22·104 s at 25ºC and decreased in 6.2·103 s at 50ºC. a) Which is the rate constant of the reaction at 25ºC? Which is the rate constant of the reaction at 35ºC?

$$\ln(A_t)=\ln(A_0)-kt$$

$$k_{25C}=1.12\ 10^{-4}s^{-1} \quad k_{50C}=2.21\ 10^{-4}s^{-1}$$

$k=A\exp(-E_a/RT)$ Making a system with the two constants: Ea: 21667 J/mol

Again, knowing Ea and k25 we can obtain the constant at any temperature:
$$k_{35C}=1.49\ 10^{-4}s^{-1}$$

8) In the first order reaction A → products, the concentration of A is [A] = 0.816 M at the initial time of the reaction, and [A]=0.632 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?

$\ln(A_t)=\ln(A_0)-kt$

$k=0.016\,min^{-1}$

$t_{1/2}=\ln(2)/R=2603\,s$

$t=4668\,s$

$[A]=0.074\,M$

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

| Experiment | $[A]_0/(mol\ L^{-1})$ | $[B]_0/(mol\ L^{-1})$ | $V_0/(10^{-3}\ mol\ L^{-1}s^{-1})$ |
|---|---|---|---|
| 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 =0.4M and [B]0 =0.004M. Determine the rate constant of pseudo-first order. Calculate the concentration of B after 1 minute.

a) $v=k[A]^{\alpha}[B]^{\beta}$

$\alpha=\ln(v_2/v_1)/\ln(A_2/A_1)=1$

$\beta=\ln(v_3/v_2)/\ln(A_3/A_2)=1$

$k=0.080\,L/(mol\ s)$

b) $k_{app}=k[A]=0.032\,s^{-1}$

$\ln(B_t)=\ln(B_0)-k_{app}t$

$B_{1\,min}=5.810^{-4}\,M$

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

$$k_{50}=A\,e^{\frac{-Ea}{RT_{50}}} \qquad k_{80}=A\,e^{\frac{-Ea}{RT_{80}}} \qquad 2=e^{\frac{-Ea}{RT_{80}}}/e^{\frac{-Ea}{RT_{50}}} \qquad E_a=21922\,J/mol$$

11) The decomposition of H2O2(aq) at 25ºC follows a first order kinetics. Determine the percentage of H2O2 decomposed in the first 10 minutes after the reaction was initiated. The kinetic constant of this reaction at 25ºC is k= 7.3·10-4 s-1

$$\ln A=\ln A_0-kt$$

Remaining percentage of A =100*A/A_0=100 exp( -k t)= 64.5 %

Percentage of A decomposed =100-Remaining percentatge of A=35.5 %

12) A reaction R → P has a kinetic constant of k =1.24 cm3 mol-1 s-1. Calculate how many hours are required for the concentration of R to change from 0.450 mol L-1 to 0.033 mol L-1 . The units of the kinetic constant indicates that is a second order reaction.

$$\frac{1}{A}=\frac{1}{A_0}+kt \qquad t=6.3\,h$$

13) For the 2 NO + O2 → 2 NO2 reaction in gas phase the initial velocity of formation of O2 was measured at 25°C

| $[O_2]$ (mmol L$^{-1}$) | $[NO]$ (mmol L$^{-1}$) | $d[O_2]/dt$ (mol L$^{-1}$ s$^{-1}$) |
|---|---|---|
| 1.44 | 0.28 | -6.9 x 10$^{-7}$ |
| 1.44 | 0.93 | -7.5 x 10$^{-6}$ |
| 1.44 | 2.69 | -6.0 x 10$^{-5}$ |
| 0.066 | 2.69 | -3.0 x 10$^{-6}$ |

Find the orders of the reaction with respect to NO and O2. Find the rate constant at 25°C

$$v = k[NO]^{\alpha}[O_2]^{\beta}$$

$$\alpha = \frac{\ln \dfrac{v_1}{v_2}}{\ln \dfrac{[NO]_1}{[NO]_2}} \approx 2 \qquad \beta = \frac{\ln \dfrac{v_3}{v_4}}{\ln \dfrac{[O_2]_3}{[O_2]_4}} \approx 1$$

$$v = k[NO]^2[O_2]$$

$$k = 6112 \, L^2 mol^{-2} s^{-1}$$

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.

FALSE. The activated complex is defined in the TST (Transition State Theory) not in the Collision Theory.

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. TRUE.

15) The half-live 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?

$$k = \frac{\ln 2}{t_{1/2}} = 3.1 \cdot 10^{-3} s^{-1}$$

$$A_0/64 = A_0 * e^{-k t_{1/64}} \qquad t_{1/64} = 1326 \, s$$

16) The following kinetic data (v0 is the initial rate) were obtained for the reaction 2 ICl(g) + H2 → I2 (g) + 2 HCl(g):

| Experiment | $[ICl]_0/$ (mmol dm$^{-3}$) | $[H_2]_0/$ (mmol dm$^{-3}$) | $v_0/$ (mol dm$^{-3}$ s$^{-1}$) |
|---|---|---|---|
| 1 | 1.5 | 1.5 | 3.7 x 10$^{-7}$ |
| 2 | 3.0 | 1.5 | 7.4 x 10$^{-7}$ |
| 3 | 3.0 | 4.5 | 22 x 10$^{-7}$ |
| 4 | 4.7 | 2.7 | ? |

a) Write the rate law for the reaction.

$$v_1 = k[ICl]_1^\alpha [H\_2]_1^\beta$$
$$v_2 = k[ICl]_2^\alpha [H\_2]_2^\beta$$
$$v_3 = k[ICl]_3^\alpha [H\_2]_3^\beta$$
$$v_4 = k[ICl]_4^\alpha [H\_2]_4^\beta$$

$$\alpha = \frac{\ln\frac{v_1}{v_2}}{\ln\frac{[ICl]_1}{[ICl]_2}} \qquad \beta = \frac{\ln\frac{v_2}{v_3}}{\ln\frac{[ICl]_2}{[ICl]_3}} \simeq 1$$

Rate law:  $v = k[ICl][H\_2]$

b) Determine the value of the rate constant

$$k = \frac{v_1}{[ICl]_1[H\_2]_1} = 0.16\frac{dm^3}{mol \cdot s}$$

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

$$v_4 = k[ICl]_4[H\_2]_4 = 2.1 \cdot 10^{-6}\frac{mol}{dm^3 \cdot s}$$

17) The Arrhenius parameters for the reaction of decomposition of cyclobutane C4H8(g) → 2 C2H4(g) are log(A/s-1)=15.6 and Ea= 261 kJ mol-1. What is the half-live of this first-order reaction at 20ºC and 500ºC?

$$k=A\,e^{\frac{-Ea}{RT}}$$

$$k_{20\,°C}=1.2\cdot10^{-31}\,s^{-1} \qquad t_{1/2}=\frac{\ln2}{k_{20°C}}=6.2\cdot10^{30}\,s$$

$$k_{500\,°C}=9.0\cdot10^{-3}\,s^{-1} \qquad t_{1/2}=\frac{\ln2}{k_{500°C}}=77\,s$$

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 at time t after injection at 310 K.

| t/min | 30 | 60 | 120 | 150 | 240 | 360 | 480 |
|---|---|---|---|---|---|---|---|
| c/(ng/mL) | 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.
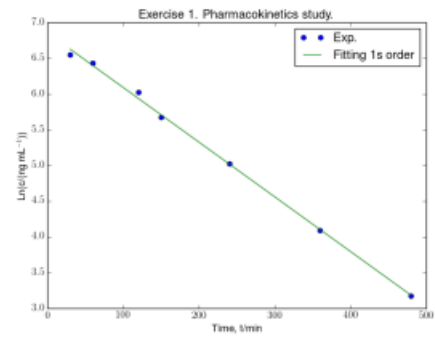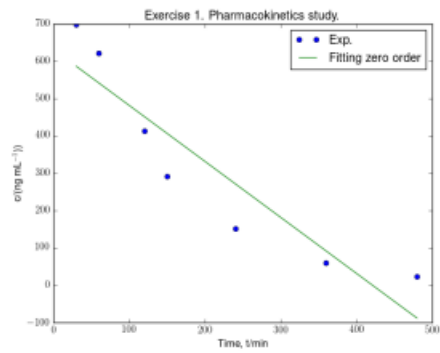
**The constant is 0.0076498 min$^{-1}$**
**The Half live is 90.6098 min**
**Conc. 0h: 959 ng/ml**
**Conc. 10h: 9.6 ng/ml**