

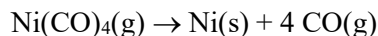
Exercise 1. Indicate which of the following statements are TRUE or FALSE:

- For a reaction with a very large equilibrium constant, the rate constant of the forward reaction is much higher than the rate constant of the reverse reaction.
 - At equilibrium, the rate constants of the forward and reverse reactions are equal.
 - Increasing the concentration of a reactant increases the rate of a reaction by increasing the rate constant in the forward direction.
 - Increasing the concentration of a product, increases the rate of the reverse reaction, and so the rate of the forward reaction must then increase, too.
 - If $Q < K_{eq}$, the reaction will proceed towards generating more products until equilibrium is reached.
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Exercise 2. Consider a reaction in which reactant R is converted into a product P at constant temperature. If the initial concentration of R is 1 mol/L, the half-life is 10 minutes. If the initial concentration is doubled, the half-life is two times lower.

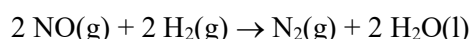
- What is the order of this reaction?
 - What is the rate constant of this reaction?
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Exercise 3. Consider the following decomposition reaction:



- How is the rate of Ni(CO)_4 consumption related to the rate of CO production? Provide the equation.
 - If the rate of CO production is $2.4 \cdot 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$ what is the rate of Ni(CO)_4 consumption at the same moment.
-

Exercise 4. You are studying the kinetics of the following reaction:



And by changing the ratio of starting reactant concentrations, the following experimental results were obtained:

Measurement #	$[\text{NO}]_0$ ($\text{mol}^{-1}\text{L}^{-1}$)	$[\text{H}_2]_0$ ($\text{mol}^{-1}\text{L}^{-1}$)	Rate of N_2 production ($\text{mol L}^{-1} \text{ min}^{-1}$)
1	1.0	1.0	0.15
2	1.0	2.0	0.30
3	1.0	3.0	0.45
4	2.0	3.0	1.80
5	3.0	3.0	4.05

- Determine the partial reaction order for each reactant.
- Determine the global reaction order for the entire reaction.
- Write the equation that describes the reaction rate as a function of NO and H_2 concentrations?

Exercise 5. Consider the decomposition reaction below:



The reaction takes place at $T = 318 \text{ K}$, with the rate constant of $5.0 \cdot 10^{-4} \text{ s}^{-1}$. The activation energy for this reaction is 100 kJ/mol .

- What is the order of this reaction?
- What percentage of the starting amount of $\text{N}_2\text{O}_5(\text{g})$ decomposes after 45 min at 318 K?
- Calculate the rate constant at 332 K.
- What is the time of half-life at 332 K?

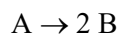
Given values: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Exercise 6. Consider a chemical reaction in which reactant A is converted into product B following first-order kinetics. At the start of the reaction, the initial concentration of A is: $[\text{A}]_0 = 0.1 \text{ mol/L}$. After 1 hour at 25°C , 40% of reactant A has been converted into product B. To speed up the process, the temperature of the reaction mixture is then raised to 35°C and the reaction is continued for 1 more hour. After this time interval (1 h at 25°C + 1 h at 35°C) it is observed that the concentration of A is equal to 0.01 mol/L .

- Calculate the rate constant of this reaction at 25°C and at 35°C .
- Calculate the temperature at which you must continue this reaction so that only 10^{-3} mol/L of A remains in the reaction mixture after an additional 30 minutes of reaction. *Hint:* You may have to first calculate the rate constant of the reaction at that temperature and its activation energy.

Given values: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

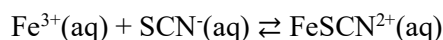
Exercise 7. Consider the following second-order reaction:



Assume that the volume and temperature do not change during the reaction. For the following initial conditions, $[\text{A}]_0 = 0.5 \text{ mol/L}$ and $[\text{B}]_0 = 0 \text{ mol/L}$, it is observed that the half-life of A is 15 min.

- Calculate the rate constant (k).
- Assuming that the same reaction described in the text above is still running, calculate the reaction rate (v) at the time point when the concentration of B increases to $[\text{B}] = 0.5 \text{ mol/L}$.
- Assuming that the same reaction described in the text above is still running, calculate the time needed for the concentration of B to increase from $[\text{B}] = 0.5 \text{ mol/L}$ to $[\text{B}] = 0.8 \text{ mol/L}$.

Exercise 8. You are characterizing the reversible reaction below:



The equilibrium constant for this reaction at 25 °C is $K=140$. In 1.0 L of water at 25 °C you prepare the following combination of reagents:

$$\begin{aligned} [\text{Fe}^{3+}]_0 &= 0.20 \text{ mol/L} \\ [\text{SCN}^{-}]_0 &= 0.10 \text{ mol/L} \end{aligned}$$

- Is the system in equilibrium? If not, in which direction will the reaction proceed?
 - Calculate the equilibrium concentrations of all species?
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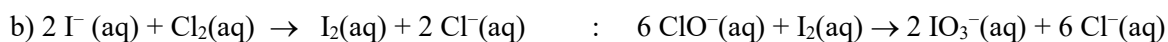
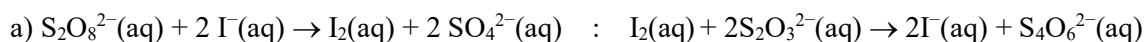
Exercise 9. You are interested in developing cleaning products based on hydrogen peroxide (H_2O_2). However, most water sources will have small amounts of iron oxide (rust), which can catalyze degradation of H_2O_2 . From the literature, you find that the activation energy for spontaneous decomposition of H_2O_2 is 75.3 kJ/mol and in the presence of iron oxide, that value is reduced to 67.8 kJ/mol. This change seems relatively small, but you still want to check the impact on the rate constant.

What is the ratio of H_2O_2 decomposition rates in the presence and absence of iron oxide?

Given values:

$$\begin{aligned} R &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\ T &= 25^\circ\text{C} \end{aligned}$$

Exercise 10. Below are two examples of reaction cascades involving iodine (1st reaction followed by a 2nd). Does iodine act as a catalyst in either cascade reaction? Explain.



Quick Answers:

1.

- a) True
- b) False
- c) False
- d) True
- e) True

2.

- a) 2nd order
- b) $k = 0.1 \text{ L mol}^{-1} \text{ min}^{-1}$

3.

- a) $v = -\frac{d[\text{Ni}(\text{CO})_4]}{dt} = +\frac{1}{4}\frac{d[\text{CO}]}{dt}$
- b) $6 \cdot 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$

4.

- a) 1 for H₂; 2 for NO;
- b) 3 for the entire reaction;
- c) $v = k [\text{NO}]^2[\text{H}_2]$;

5.

- a) 1st order
- b) 74.08% decomposes
- c) $2.46 \cdot 10^{-3} \text{ s}^{-1}$
- d) $t_{1/2} = 281 \text{ s}$

6.

- a) $k_1 (25^\circ\text{C}) = 1.42 \cdot 10^{-4} \text{ s}^{-1}$; $k_2 (35^\circ\text{C}) = 4.98 \cdot 10^{-4} \text{ s}^{-1}$;
- b) $T_3 = 316 \text{ K } (\sim 43^\circ\text{C})$; $k_3 (\sim 43^\circ\text{C}) = 1.28 \cdot 10^{-3} \text{ s}^{-1}$; $E_a = 95.9 \text{ kJ/mol}$;

7.

- a) $k = 0.133 \text{ L mol}^{-1} \text{ min}^{-1}$ (or $2.22 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$)
- b) $v = 8.33 \cdot 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ (or $1.39 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$)
- c) $t = 45 \text{ min}$

8.

- a) No; The reaction will proceed towards the generation of products.
- b) $[\text{FeSCN}^{2+}]_{\text{eq}} = 0.0937 \text{ mol/L}$; $[\text{Fe}^{3+}]_{\text{eq}} = 0.1063 \text{ mol/L}$; $[\text{SCN}^-]_{\text{eq}} = 0.0063 \text{ mol/L}$;

9.

$$k_{(\text{cat})}/k_{(\text{uncat})} = 20.6$$

10.

- a) Yes. It is regenerated by the 2nd reaction
- b) No. The 2nd reaction just makes a new species.