Homework (Apr 10)

9.4 The following reaction is found to be first order in A:

$$A \rightarrow B + C$$

If half of the starting quantity of A is used up after 56 s, calculate the fraction that will be used up after 6.0 min.

From the half-life (56 s), k can be determined:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{56\ \text{s}} = 1.24 \times 10^{-2}\ \text{s}^{-1}$$

The fraction of A that will remain after 6.0 min (3.6×10^2 s) is

$$\frac{[A]}{[A]_0} = e^{-kt} = e^{-\left(1.24\times10^{-2}\ \text{s}^{-1}\right)\left(3.6\times10^{2}\ \text{s}\right)} = 0.0115$$

Thus, the fraction that will be used up after 6.0 min is $1 - 0.0115 = 0.99$.

9.8 When the concentration of A in the reaction A → B was changed from 1.20 *M* to 0.60 *M*, the half-life increased from 2.0 min to 4.0 min at 25° C. Calculate the order of the reaction and the rate constant.

The half life is related to the initial concentration of A by

$$t_{1/2} \propto \frac{1}{[A]_0^{\,n-1}}$$

According to the data, the half-life doubled when $[A]_0$ was halved. This is only possible if the half-life is inversely proportional to $[A]_0$, or the reaction order, $n = 2$, indicating a second-order reaction.

The rate constant can be calculated using either $[A]_0 = 1.20\ M$ or $0.60\ M$ and the corresponding half-life.

$$k = \frac{1}{[A]_0 t_{1/2}} = \frac{1}{(1.20\ M)\ (2.0\ \text{min})} = 0.42\ M^{-1}\ \text{min}^{-1}$$

9.10 Cyclobutane decomposes to ethylene according to the equation

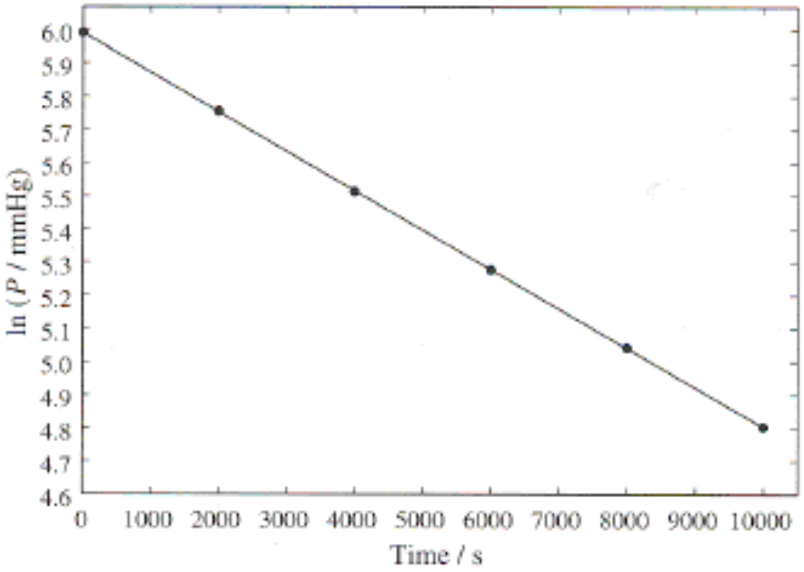
$$C_4H_8(g) \rightarrow 2C_2H_4(g)$$

Determine the order of the reaction and the rate constant based on the following pressures, which were recorded when the reaction was carried out at 430° C in a constant-volume vessel:

Time/s	$P_{C_4H_8}$/mmHg
0	400
2000	316
4000	248
6000	196
8000	155
10000	122

At constant temperature and volume, the pressure of cyclobutane is proportional to its concentration. A plot of ln P vs t shows a straight line with an equation of $y = -1.19 \times 10^{-4}x + 5.99$. Thus, the reaction is first order.

The slope of the line is $-k$. In other words, $k = 1.19 \times 10^{-4}\ \text{s}^{-1}$.



9.22 The following data were collected for the reaction between hydrogen and nitric oxide at 700° C:

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

Experiment	$[H_2]/M$	$[NO]/M$	Initial rate/$M \cdot s^{-1}$
1	0.010	0.025	2.4×10^{-6}
2	0.0050	0.025	1.2×10^{-6}
3	0.010	0.0125	0.60×10^{-6}

(a) What is the rate law for the reaction? **(b)** Calculate the rate constant for the reaction. **(c)** Suggest a plausible reaction mechanism that is consistent with the rate law. (*Hint:* Assume that the oxygen atom is the intermediate.) **(d)** More careful studies of the reaction show that the rate law over a wide range of concentrations of reactants should be

$$\text{rate} = \frac{k_1[NO]^2[H_2]}{1 + k_2[H_2]}$$

What happens to the rate law at very high and very low hydrogen concentrations?

(a) Comparing Experiment 1 and Experiment 2, the concentration of NO is constant and the concentration of H_2 has decreased by one-half. The initial rate has also decreased by one-half. Therefore, the initial rate is directly proportional to the concentration of H_2. That is, the reaction is first order in H_2.

Comparing Experiment 1 and Experiment 3, the concentration of H_2 is constant and the concentration of NO has decreased by one-half. The initial rate has decreased by one-fourth. Therefore, the initial rate is proportional to the squared concentration of NO. That is, the reaction is second order in NO.

Therefore, the rate law is

$$\text{Rate} = k[NO]^2[H_2]$$

(b) Using Experiment 1 to calculate the rate constant,

$$k = \frac{\text{Rate}}{[NO]^2[H_2]} = \frac{2.4 \times 10^{-6}\ M\ s^{-1}}{(0.025\ M)^2\ (0.010\ M)} = 0.38\ M^{-2}\ s^{-1}$$

(c) The rate law suggests that the slow step in the reaction mechanism will probably involve one H_2 molecule and two NO molecules. Additionally, the hint suggests that the O atom is an intermediate. A plausible mechanism is

$$H_2 + 2NO \longrightarrow N_2 + H_2O + O \quad \text{slow step}$$
$$O + H_2 \longrightarrow H_2O \quad \text{fast step}$$

(d) At very high hydrogen concentrations, $k_2\,[H_2] \gg 1$. Therefore, the rate law becomes

$$\text{rate} = \frac{k_1[NO]^2[H_2]}{k_2[H_2]} = \frac{k_1}{k_2}[NO]^2$$

At very low hydrogen concentrations, $k_2\,[H_2] \ll 1$. Therefore, the rate law becomes

$$\text{rate} = k_1[NO]^2[H_2]$$

9.57 Oxygen for metabolism is taken up by hemoglobin (Hb) to form oxyhemoglobin (HbO_2) according to the simplified equation

$$\mathrm{Hb}(aq) + \mathrm{O_2}(aq) \xrightarrow{k} \mathrm{HbO_2}(aq)$$

where the second-order rate constant is $2.1 \times 10^6\ M^{-1}\,\mathrm{s}^{-1}$ at 37° C. For an average adult, the concentrations of Hb and O_2 in the blood in the lungs are $8.0 \times 10^{-6}\ M$ and $1.5 \times 10^{-6}\ M$, respectively. **(a)** Calculate the rate of formation of HbO_2. **(b)** Calculate the rate of consumption of O_2. **(c)** The rate of formation of HbO_2 increases to $1.4 \times 10^{-4}\ M\,\mathrm{s}^{-1}$ during exercise to meet the demand of an increased metabolic rate. Assuming the Hb concentration remains the same, what oxygen concentration is necessary to sustain this rate of HbO_2 formation?

(a)

$$\begin{aligned}\text{Rate of formation of } \mathrm{HbO_2} &= \frac{d\,[\mathrm{HbO_2}]}{dt} = k[\mathrm{Hb}][\mathrm{O_2}] \\ &= \left(2.1 \times 10^6\ M^{-1}\,\mathrm{s}^{-1}\right)\left(8.0 \times 10^{-6}\ M\right)\left(1.5 \times 10^{-6}\ M\right) \\ &= 2.5 \times 10^{-5}\ M\,\mathrm{s}^{-1}\end{aligned}$$

(b) The rate of consumption of O_2 is

$$-\frac{d\,[\mathrm{O_2}]}{dt} = \frac{d\,[\mathrm{HbO_2}]}{dt} = 2.5 \times 10^{-5}\ M\,\mathrm{s}^{-1}$$

(c)

$$\text{Rate of formation of } \mathrm{HbO_2} = k[\mathrm{Hb}][\mathrm{O_2}]$$

$$\begin{aligned}[\mathrm{O_2}] &= \frac{\text{Rate of formation of } \mathrm{HbO_2}}{k[\mathrm{Hb}]} \\ &= \frac{1.4 \times 10^{-4}\ M\,\mathrm{s}^{-1}}{\left(2.1 \times 10^6\ M^{-1}\,\mathrm{s}^{-1}\right)\left(8.0 \times 10^{-6}\ M\right)} \\ &= 8.3 \times 10^{-6}\ M\end{aligned}$$

Thus, 5.6 times as much oxygen is required to sustain the increase in metabolism.