HW 5 solutions

Ex 22.1a
• The rate of the reaction \( A + 2B \rightarrow 3C + D \) was reported as 1.0 mol dm\(^{-3}\) s\(^{-1}\). State the rates of formation and consumption of the participants.

\[
\begin{align*}
\text{Ex 22.1a} & \quad \text{The reaction has the form} \\
0 &= C - A - 2B \\
\text{Rate of formation of } C &= \frac{1.0 \text{ mol dm}^{-3} \text{ s}^{-1}}{3} = \frac{1}{3} \text{ mol dm}^{-3} \text{ s}^{-1} \\
\text{Rate of formation of } A &= \frac{1.0 \text{ mol dm}^{-3} \text{ s}^{-1}}{1} = 1.0 \text{ mol dm}^{-3} \text{ s}^{-1} \\
\text{Rate of formation of } B &= 0 \\
\end{align*}
\]

22.3a
• The rate law for the reaction in Exercise 22.1a was found to be \( v = k[A][B] \). What are the units of \( k \)? Express the rate law in terms of the rates of formation and consumption of (a) A, (b) C.

The rate is expressed in \( \text{mol dm}^{-3} \text{ s}^{-1} \); therefore

\[ \text{mol dm}^{-3} \text{ s}^{-1} = \left( \text{mol dm}^{-3} \right) \times \left( \text{mol dm}^{-3} \right) \times \left( \text{mol dm}^{-3} \right) \times \left( \text{mol dm}^{-3} \right) \]

where \([i]\) denotes units of \( i \), requires the units to be \( \text{mol dm}^{-3} \text{ s}^{-1} \).

(a) Rate of formation of \( A = v[A] \)
(b) Rate of formation of \( C = 3v[A][B] \)

22.5a
• At 518°C, the rate of decomposition of a sample of gaseous acetaldehyde, initially at a pressure of 363 Torr was 1.07 Torr s\(^{-1}\) when 5.0% had reacted and 0.76 Torr s\(^{-1}\) when 20.0% had reacted. Determine the order of the reaction.

\[
\begin{align*}
\text{Rate law} & = \frac{1}{2} = k \left( \frac{1}{2} \right) \\
\text{where } k & = k \left( \frac{1}{2} \right) \\
\text{Taking logarithms} & = \text{log} (1/2) \\
\text{or } \text{log} (k) & = \text{log} (0.5) \\
\text{Hence, the reaction is second-order.}
\end{align*}
\]

22.7a
• The rate constant for the first-order decomposition of \( \text{N}_2\text{O}_5 \) is \( 3.38 \times 10^{-5} \text{ s}^{-1} \) at 25°C. What will be the pressure, initially 500 Torr, after (a) 10 s, (b) 10 min after initiation of the reaction?

\[
\begin{align*}
\text{Rate law} & = \text{first order in } \text{N}_2\text{O}_5 \\
\text{Therefore, rate of consumption of } \text{N}_2\text{O}_5 & = -2 \times 25 \text{ Torr} \text{ min}^{-1} \\
\text{Therefore, the half life is} & = \frac{\ln 2}{-2 \times 25} \\
& = \frac{0.693}{-50} \\
& = 0.0138 \text{ min} \\
\end{align*}
\]

22.12a
• Show that \( \tau_{1/2} = 1/A^{n-1} \) for a reaction that is \( n \)th-order in \( A \).

The rate of change of \( [A] \) is

\[
-\frac{d[A]}{dt} = -k[A] \\
\frac{d[A]}{dt} = - \int_{t=0}^{t=1} k[A] \, dt \\
\therefore \quad \ln \left( \frac{1}{[A]} \right) = - \frac{1}{k[A]} \\
\text{Rate of change of } [A] & = - \frac{1}{k[A]} \\
\text{At } & = \frac{1}{[A]_0} = \frac{1}{k[1]} \\
\text{and } & = - \frac{1}{k[A]} \\
\text{Hence,} & = \frac{1}{[A]_0} \frac{1}{k[A]}
22.14a

- The rate constant for the decomposition of a certain substance is $2.80 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 30°C and $1.38 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 50°C. Evaluate the Arrhenius parameters of the reaction.

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

\[
\ln k_1 = \ln \frac{E_a}{R} - \frac{E_a}{R \times 303} = \ln \left(\frac{1.38 \times 10^{-2}}{2.80 \times 10^{-3}}\right)
\]

\[
E_a = 6.6 \text{ kJ mol}^{-1}
\]

For $A$, we rearrange eqn 22.31:

\[
A = k = \frac{E_a^{-RT}}{RT} = 2.80 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}
\]

22.16

- The second-order rate constants for the reaction of oxygen atoms with aromatic hydrocarbons have been measured (R. Atkinson and J.H. Pitts, J. Phys. Chem. 79, 295 (1975)). In the reaction with benzene, the rate constants are $1.44 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 300.3 K, $3.03 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 341.2 K, and $6.9 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ at 392.2 K. Find the pre-exponential factor and activation energy of the reaction.

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

\[
\ln k_1 = \ln \left(\frac{E_a}{R \times 300.3}ight) = 1.44
\]

\[
E_a = 13.0 \text{ kJ mol}^{-1}
\]

22.22

- Derive an integrated expression for a second-order rate law $v = k[A][B]$ for a reaction of stoichiometry $2A + 3B \rightarrow P$.

\[
v = \frac{d[P]}{dt} = k[A][B]
\]

Let the initial concentrations be $[A]_0 = A_0$, $[B]_0 = B_0$, and $[P]_0 = 0$. Then, when $P$ is formed or concentration $c$, the concentration of $A$ changes to $A_0 - 2c$ and that of $B$ changes to $B_0 - 3c$. Therefore:

\[
\frac{d[P]}{dt} = k(A_0 - 2c)(B_0 - 3c)\]

Simulation

- See Zhenfei's solution.