10.1) The rate of formation of C in the reaction $2A + B \rightarrow 3C + 2D$ is $2.2 \text{ mol L}^{-1} \text{ s}^{-1}$.

State the rates of formation and consumption of A, B, and D.
rate of consumption of A = $2/3$ (rate of formation of C) = $1.5 \text{ mol L}^{-1} \text{ s}^{-1}$
rate of consumption of B = $1/3$ (rate of formation of C) = $0.73 \text{ mol L}^{-1} \text{ s}^{-1}$
rate of formation of D = $2/3$ (rate of formation of C) = $1.5 \text{ mol L}^{-1} \text{ s}^{-1}$

10.3) If the rate laws are expressed with (a) concentrations in molecules m$^{-3}$, (b) pressures in kPa, what are the units of the 2nd order and 3rd order rate constants?
In both cases, the units of the rate itself must be in concentration or pressure per second:

a) For 2nd order: $r = k[A]^2$, $k$ has units m$^3$ molecules$^{-1}$ s$^{-1}$
For 3rd order: $r = k[A]^3$, $k$ has units m$^6$ molecules$^{-2}$ s$^{-1}$
b) For 2nd order: $r = k(P_A)^2$, $k$ has units kPa$^{-1}$ s$^{-1}$
For 3rd order: $r = k(P_A)^3$, $k$ has units kPa$^{-2}$ s$^{-1}$

10.4) The following initial rate data were obtained on the rate of binding of glucose with the enzyme hexokinase present at a concentration of 1.34 mmol L$^{-1}$. What is (a) the order of reaction with respect to glucose, (b) the rate constant?

<table>
<thead>
<tr>
<th>$[\text{C}<em>6\text{H}</em>{12}\text{O}_6]$ (mmol L$^{-1}$)</th>
<th>1.00</th>
<th>1.54</th>
<th>3.12</th>
<th>4.02</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial rate (mol L$^{-1}$ s$^{-1}$)</td>
<td>5.0</td>
<td>7.6</td>
<td>15.5</td>
<td>20.0</td>
</tr>
</tbody>
</table>
The reaction of interest is:  \( \text{C}_6\text{H}_{12}\text{O}_6 + \text{HK} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6^-\text{HK} \)

The rate law is assumed to have the form:  \( r = k \left[ \text{C}_6\text{H}_{12}\text{O}_6 \right]^x \left[ \text{HK} \right]^y \)

In the method of initial rates, this rate law becomes:  \( r_0 = k \left[ \text{C}_6\text{H}_{12}\text{O}_6 \right]_0^x \left[ \text{HK} \right]_0^y \)

There are two ways to go about this problem, taking simple ratios and graphically.

1) For each possible combination of experiments, construct the ratio of the initial rates:

\[
e.g., \quad \frac{r_{01}}{r_{02}} = \frac{\left[ \text{C}_6\text{H}_{12}\text{O}_6 \right]_{01}^x}{\left[ \text{C}_6\text{H}_{12}\text{O}_6 \right]_{02}^x} \quad \text{(the } k\text{'s and the HK concentrations cancel out)}
\]

\[
\frac{r_{01}}{r_{02}} = \frac{5.0}{7.6} = \left( \frac{1.00 \times 10^{-3}}{1.54 \times 10^{-3}} \right)^x
\]

\[
\ln \left( \frac{5.0}{7.6} \right) = x \ln \left( \frac{1.00 \times 10^{-3}}{1.54 \times 10^{-3}} \right)
\]

\[
x = 0.97
\]

For the other combinations:

\[
r_{01}/r_{03}, \quad x=0.99
\]

\[
r_{01}/r_{04}, \quad x=1.00
\]

\[
r_{02}/r_{03}, \quad x=1.01
\]

\[
r_{02}/r_{04}, \quad x=1.01
\]

\[
r_{03}/r_{04}, \quad x=1.01
\]

AVG order with respect to glucose = 0.998 = 1  (1st order in glucose)

The effective 1sts order rate constant is obtained by substitution for each combination,  \( \text{AVG } k = 4920 \text{ mol}^{-1} \text{ L s}^{-1} \) (assumes the enzyme is in excess)

2) For a graphical (better) solution, plot \( \ln r_0 \) vs. \( \ln[\text{C}_6\text{H}_{12}\text{O}_6] \). After fitting to a straight line, the slope will be \( x \) and the y-intercept will correspond to \( \ln k \).
Therefore:

\[ x = 0.9986 = 1 \quad \text{and} \quad k = \exp(8.50215) = 4925 \, \text{mol}^{-1} \, \text{L} \, \text{s}^{-1} \]

(Note that these agree with the values obtained with the ratio method)

10.6) The rate constant for the 1st order decomposition of N₂O₅ in the reaction 2N₂O₅ (g) \(\rightarrow\) 4NO₂(g) + O₂(g) is \(k = 3.38 \times 10^{-5} \, \text{s}^{-1}\) at 25°C.

a) What is the half-life of N₂O₅? What will be the total pressure, initially 500 Torr for the pure N₂O₅ vapor, a) 10 s, b) 10 min after initiation of the reaction?

a) For a 1st order reaction, \(t_{\frac{1}{2}} = \frac{\ln 2}{k}\)

So, \(t_{\frac{1}{2}} = \frac{\ln 2}{3.38 \times 10^{-5}} = 2.05 \times 10^4 \, \text{s}\)

b & c) For a 1st order reaction, \([A] = [A]_0 e^{-kt}\), or in the present case if we assume the volume and temperature are held constant: \(P_{N₂O₅} = P_{N₂O₅}^{t=0} e^{-kt}\) since then pressure is directly proportional to the number of moles of N₂O₅ (perfect gas).
After 10 s, the pressure due to N₂O₅ will be reduced to:

\[ P_{\text{N}_2\text{O}_5} = (500 \text{ Torr}) \ e^{-kt} = (500) \exp[-(3.38 \times 10^{-5})(10)] = 499.8 \text{ Torr} \]

From the stoichiometry of the reaction, a loss of 0.2 Torr of N₂O₅ will be accompanied by an increase of \( \frac{5}{2} \times 0.2 \text{ Torr} = 0.5 \text{ Torr} \) for the products

\[ P(\text{total}) = 499.8 + 0.5 = 500.3 \text{ Torr} \ (\text{essentially unchanged}) \]

After 10 min = 600 s,

\[ P_{\text{N}_2\text{O}_5} = (500) \exp[-(3.38 \times 10^{-5})(600)] = 490 \text{ Torr} \]

The loss of 10 Torr of N₂O₅ is matched by an increase of \( \frac{5}{2}(10) = 25 \text{ Torr} \) in the products.

\[ P(\text{total}) = 490 + 25 = 515 \text{ Torr} \]

Note that you could also work this problem in terms of the fraction of N₂O₅ dissociated.

10.7) In the 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 \( 1.22 \times 10^4 \text{ s} \). What is the rate constant of the reaction?

For a 1st order reaction, \([A] = [A]_0 e^{-kt}\) or \(\ln[A] = \ln[A]_0 - kt\)

Hence,

\[ k = \frac{1}{t} \left( \ln[A]_0 - \ln[A] \right) \]

\[ = \frac{1}{1.22 \times 10^4} \left[ \ln(220) - \ln(56) \right] = 1.12 \times 10^{-4} \text{ s}^{-1} \]
10.11) The formation of NOCl from NO in the presence of a large excess of chlorine is pseudosecond-order in NO. In an experiment to study the reaction, the partial pressure of NOCl increased from zero to 100 Pa in 522 s. What is the rate constant of the reaction given that the initial partial pressure of NO is 300 Pa?

The balanced reaction is: \( \text{NO} + \frac{1}{2} \text{Cl}_2 \rightarrow \text{NOCl} \)

The rate for the production of NOCl is: \( \frac{d[\text{NOCl}]}{dt} = k[\text{NO}]^2 \), where \( k \) is the pseudo 2nd-order rate constant and Cl\(_2\) is in large excess.

Using the integrated rate law for a 2nd-order reaction: \( [\text{NOCl}] = \frac{kt[\text{NO}]^2}{1 + kt[\text{NO}]} \)

But for constant volume, the partial pressures are directly proportional to the molar concentrations, so we can use these directly in this expression:

\[
P_{\text{NOCl}} = \frac{ktP_{\text{NO},0}^2}{1 + ktP_{\text{NO},0}}
\]

Solving for the rate constant \( k \),

\[
k = \frac{P_{\text{NOCl}}}{t(P_{\text{NO},0}^2 - P_{\text{NOCl}}P_{\text{NO},0})} = \frac{100 \text{ Pa}}{522(300^2 - (100)(300))}
\]

\[
= 3.19 \times 10^{-6} \text{ Pa}^{-1} \text{s}^{-1}
\]
10.15) The half-life for $^{90}\text{Sr} = 28.1 \text{ yr}$. How much of 1.00 $\mu\text{g}$ will remain after (a) 19 yr. and (b) 75 yr.

Each half-life decreases the concentration by 1/2:

$$[\text{A}]_t = \left(\frac{1}{2}\right)^n [\text{A}]_0$$

where $n$ is the number of half-lives

Taking the natural log of both sides:

$$\ln[A] = n \ln \frac{1}{2} + \ln[A]_0$$

a) 19 yr = 0.6762 half-lives

$$\ln x = (0.6762)\ln \frac{1}{2} + \ln(1.00) = -0.4687$$

$$x = 0.63 \mu\text{g}$$

b) 75 yr. = 2.669 half-lives

$$\ln x = (2.669)\ln \frac{1}{2} + \ln(1.00) = -1.832$$

$$x = 0.16 \mu\text{g}$$

10.19) A rate constant is $1.78 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$ at 19ºC and $1.38 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 37ºC. Evaluate the Arrhenius parameters of the reaction.

Starting from the relation derived from the Arrhenius equation (note: you should be able to easily derive this yourself!)

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$E_a = \frac{R \ln \frac{k_1}{k_2}}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)} = \frac{(8.3145) \ln \frac{1.78 \times 10^{-4}}{1.38 \times 10^{-3}}}{\left( \frac{1}{310} - \frac{1}{292} \right)}$$

$$= 85.63 \times 10^3 \text{ J} / \text{mol} = 85.6 \text{ kJ} / \text{mol}$$

using the 19ºC data:

$$A = \frac{k}{e^{E_a/RT}} = \frac{1.78 \times 10^{-4}}{85.63 \times 10^3} = 3.70 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$$
10.20) The activation energy for the decomposition of benzene diazonium chloride is 99.1 kJ/mol. At what temperature will the rate be 10% greater than its rate at 25°C?

Starting with the relation:
\[
\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]

if \( k_2 = 1.10(k_1) \):
\[
\ln \left(\frac{1.10k_1}{k_1}\right) = \ln(1.10) = \frac{E_a}{R} \left( \frac{1}{298} - \frac{1}{T_2} \right)
\]

Rearranging to solve for \( T_2 \):
\[
T_2 = \frac{E_a}{\frac{E_a}{298} - R \ln 1.10}
\]
\[
= \frac{99.1 \times 10^3}{\frac{99.1 \times 10^3}{298} - (8.3145) \ln 1.10}
= 299 \text{ K}
\]

10.23) Food rots about 40 times more rapidly at 25°C than when it is stored at 4°C. Estimate the overall activation energy for the processes responsible for its decomposition.

rate @ 25°C = 40 x rate @ 4°C :
\[
\ln \frac{40k_4}{k_4} = \frac{E_a}{R} \left( \frac{1}{277} - \frac{1}{298} \right)
\]
\[
E_a = \frac{R \ln 40}{\left( \frac{1}{277} - \frac{1}{298} \right)} = 1.21 \times 10^5 \text{ J/mol} = 121 \text{ kJ/mol}
\]