Express the rate of reaction with respect to each species in the following reactions:

(a) \(2\text{NO}(g) + \text{O}_2(g) \rightarrow \text{N}_2\text{O}_4(g)\)

(b) \(\text{H}_2(g) + \text{I}_2(g) \rightarrow 2\text{HI}(g)\)

(c) \(\text{ClO}(g) + \text{BrO}(g) \rightarrow \text{ClO}_2(g) + \text{Br}(g)\)

As discussed in the text, the total system pressure can be used to monitor the progress of a chemical reaction. Consider the following reaction: \(2\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_3(g) + \text{Cl}_2(g)\). The reaction is initiated, and the following data are obtained:

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>0</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
<th>15</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_{\text{Total}}) (kPa)</td>
<td>11.07</td>
<td>14.79</td>
<td>17.26</td>
<td>18.90</td>
<td>19.99</td>
<td>20.71</td>
</tr>
</tbody>
</table>

(a) Is the reaction first or second order with respect to \(\text{SO}_2\text{Cl}_2\)?
(b) What is the rate constant for this reaction?

The reaction rate as a function of initial reactant pressures was investigated for the reaction \(2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)\), and the following data were obtained:

<table>
<thead>
<tr>
<th>Run</th>
<th>(P_o) (\text{H}_2) (kPa)</th>
<th>(P_o) (\text{N}_2) (kPa)</th>
<th>Rate (kPa s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>53.3</td>
<td>40.0</td>
<td>0.137</td>
</tr>
<tr>
<td>2</td>
<td>53.3</td>
<td>20.3</td>
<td>0.033</td>
</tr>
<tr>
<td>3</td>
<td>38.5</td>
<td>53.3</td>
<td>0.213</td>
</tr>
<tr>
<td>4</td>
<td>19.6</td>
<td>53.3</td>
<td>0.105</td>
</tr>
</tbody>
</table>

What is the rate law expression for this reaction?

Consider the schematic reaction \(A \xrightarrow{k} P\).

(a) If the reaction is one-half order with respect to \([A]\), what is the integrated rate law expression for this reaction?
(b) What plot would you construct to determine the rate constant \(k\) for the reaction?
(c) What would be the half-life for this reaction? Will it depend on initial concentration of the reactant?

The growth of a bacterial colony can be modeled as a first-order process in which the probability of cell division is linear with respect to time such that \(\frac{dN}{N} = \zeta dt\), where \(dN\) is the number of cells that divide in the time interval \(dt\), and \(\zeta\) is a constant.
(a) Use the preceding expression to show that the number of cells in the colony is given by
\[ N = N_0 e^{\xi t} \]
where \( N \) is the number of cell colonies and \( N_0 \) is the number of colonies present at \( t = 0 \).

(b) The generation time is the amount of time it takes for the number of cells to double. Using
the answer to part (a), derive an expression for the generation time.

c) In milk at 37°C, the bacteria lactobacillus acidophilus has a generation time of about 75 min.
Construct a plot of the acidophilus concentration as a function of time for time intervals of 15,
30, 45, 60, 90, 120, and 150 minutes after a colony of size \( N_0 \) is introduced to a container of milk.

6) For the sequential reaction \( A \xrightarrow{k_1} B \xrightarrow{k_2} C \), the rate constants are \( k_A = 5 \times 10^6 \text{ s}^{-1} \) and \( k_B = 3 \times 10^6 \text{ s}^{-1} \). Determine the time at which \([B]\) is at a maximum.

7) Consider the following parallel 1st and 2nd order reactions:
- A \( \xrightarrow{k_1} B \)  First order reaction
- A \( \xrightarrow{k_2} C \)  Second order reaction

(a) Derive the integrated rate law expression for the concentration of reactant \([A]\) with time for
this parallel reaction considering that the starting concentration of \( A \) at \( t = 0 \) is \([A]_0\) and that of \( B \)
and \( C \) are zero.
(b) What are the limiting rate law expressions when \( k_2[A]_0 << k_1 \) and \( k_2[A]_0 >> k_1 \) with small
values of \( k_1t \)?

Note that
\[
\int \frac{dx}{x(ax + b)} = \frac{1}{b} \ln \left( \frac{x}{ax + b} \right)
\]

8) In the stratosphere, the rate constant for the conversion of ozone to molecular oxygen by
atomic chlorine is \( \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \) \([k = 1.7 \times 10^{10} \text{ M}^{-1} \text{s}^{-1})e^{-260K/T} \]

(a) What is the rate of this reaction at 20 km where \([\text{Cl}] = 5 \times 10^{-17} \text{ M}, [\text{O}_3] = 8 \times 10^{-9} \text{ M}, \) and \( T = 220 \text{ K}\)?
(b) The actual concentrations at 45 km are \([\text{Cl}] = 3 \times 10^{-15} \text{ M} \) and \([\text{O}_3] = 8 \times 10^{-11} \text{ M} \). What is
the rate of the reaction at this altitude where \( T = 270 \text{ K} \)?
(c) (Optional) Given the concentrations in part (a), what would you expect the concentrations at
45 km to be assuming that the gravity represents the operative force defining the potential
energy?

9) An experiment is performed on the branching reaction depicted in the text.
Two things are determined: (1) The yield for \( B \) at a given temperature is found to be 0.3 and (2)
the rate constants are described well by an Arrhenius expression with the activation to \( B \) and \( C \)
formation being 27 and 34 kJ \text{ mol}^{-1}, respectively, and with identical preexponential factors.
Demonstrate that these two statements are inconsistent with each other.
10) The rate constant for the reaction of hydrogen with iodine is $2.45 \times 10^{-4}$ M$^{-1}$ s$^{-1}$ at 302 °C and 0.950 M$^{-1}$ s$^{-1}$ at 508°C.

(a) Calculate the activation energy and Arrhenius preexponential factor for this reaction.
(b) What is the value of the rate constant at 400 °C?