Chapter 33

1) Consider a collection of gas particles confined to translate in two dimensions (for example, a gas molecule on a surface). Derive the Maxwell speed distribution for such a gas.

2) Compute $\nu_{mp}$, $\nu_{ave}$, and $\nu_{rms}$ for O$_2$ at 300 and 500 K. How would your answers change for H$_2$?

3) The speed of sound is given by $v_{sound} = \sqrt{\frac{\gamma kT}{m}} = \sqrt{\frac{\gamma RT}{M}}$, where $\gamma = C_p/C_v$.
   a) What is the speed of sound in Ne, Kr, and Ar at 1000 K?
   b) At what temperature will the speed of sound in Kr equal the speed of sound in Ar at 1000 K?

4) For N$_2$ at 298 K, what fraction of molecules has a speed between 200 and 300 m s$^{-1}$? What is this fraction if the gas temperature is 500 K?

5) (a) Starting with the Maxwell speed distribution, demonstrate that the probability distribution for translational energy for $\varepsilon_{Tr} >> kT$ is given by:

   $$f(\varepsilon_{Tr})d\varepsilon_{Tr} = 2\pi \left(\frac{1}{\pi kT}\right)^{1/2} e^{-\varepsilon_{Tr}/kT} \varepsilon_{Tr}^{1/2} d\varepsilon_{Tr}$$

   (b) Using the above distribution of particle translational energy, derive expressions for the average and most probable translational energies for a collection of gaseous particles.

6) (a) A sample of cesium is heated to 500 °C in an oven. In one wall there is a small hole and the atoms emerge to form an atomic beam. What is their average velocity?
   (b) How many collisions does a single Cs atom make inside the oven in each second? How many collisions per second do all the atoms inside the 50 cm$^3$ oven make? (The vapor pressure of Cs at 500 °C is 80 mm Hg. For calculating the cross-section, use diameter d = 540 pm (0.540 nm)).

7) You are a NASA engineer faced with the task of ensuring that the material on the hull of a spacecraft can withstand puncturing by space debris. The initial cabin air pressure in the craft of 1 atm can drop to 0.7 atm before the safety of the crew is jeopardized. The volume of the cabin is 100 m$^3$, and the temperature in the cabin is 285 K. Assuming it takes the space shuttle about 8 hours from entry into orbit until landing, what is the largest circular aperture created by a hull puncture that can be safely tolerated assuming that the flow of gas out of the spaceship is
effusive? Can the escaping gas from the spaceship be considered as an effusive process? (You can assume that the air is adequately represented by N₂.)

**Chapter 35**

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

2) As discussed in the text, the total system pressure can be used to monitor the progress of a chemical reaction. Consider the following reaction: \(2\text{SO}_2\text{Cl}_2(g) \rightarrow \text{SO}_2(g) + \text{Cl}_2(g)\). 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?

3) 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_0) (\text{H}_2) (kPa)</th>
<th>(P_0) (\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?

4) Consider the schematic reaction \(A \rightarrow^k P\).

(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 \[ \frac{dN}{dt} = \zeta dt, \] 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 \[ N = N_0 e^{\zeta t}, \] 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.

For the sequential reaction \( AB \xrightarrow{k_1} A + BC \xrightarrow{k_2} \), 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.

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

(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?

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 mol\(^{-1}\), respectively, and with identical preexponential factors. Demonstrate that these two statements are inconsistent with each other.

The rate constant for the reaction of hydrogen with iodine is \( 2.45 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1} \) at 302 °C and \( 0.950 \text{ M}^{-1} \text{ s}^{-1} \) 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?

Consider the following parallel 1st and 2nd order reactions:

\[ A \xrightarrow{k_1} B \quad \text{First order reaction} \]
\[ A \xrightarrow{k_2} C \quad \text{Second order reaction} \]
(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 \(k_2[A]_0 \ll k_1\) and \(k_2[A]_0 \gg k_1\)?

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