2. Chemical Kinetics

Introduction:

- Thermodynamic laws allow determination of the equilibrium state of a chemical reaction system.
- If one assumes that the chemical reactions are fast compared to the other transport processes like diffusion, heat conduction, and flow,
- then, thermodynamics describe the system locally.
Introduction (Cont’d):

- In most combustion cases, however, chemical reactions occur on time scales comparable with that of the flow and the molecular transport processes.
- Then, information is needed about the rate of chemical reactions.
- Chemical reaction rates control pollutant formation, ignition, and flame extinction in most combustion processes.
Global & Elementary Reactions

• An *elementary* reaction is one that occurs on a molecular level exactly in the way which is described by the reaction equation.

\[
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}
\]

• The equation above is an elementary reaction. On the contrary, the following is not an elementary reaction:

\[
2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}
\]

• Above reaction is *global* or *overall* reaction.
A general global reaction mechanism involving overall reaction of $a$ moles of oxidizer with one mole of fuel to form $b$ moles of products:

$$F + a\text{Ox} \rightarrow b\text{Pr}$$  \hspace{1cm} (2.1)

Experimental observations yield the rate at which fuel is consumed as

$$\frac{d\lbrack F \rbrack}{dt} = -k_G(T)[F]^n[\text{Ox}]^m$$  \hspace{1cm} (2.2)
• \([X]\) denotes molar concentration of \(X\), e.g. \(\text{kmol/m}^3\).

• \(k_G(T)\) is the global rate coefficient.

• \(n\) and \(m\) relate to the reaction order.

• According to Eqn 2.2, reaction is
  - \(n\)th order with respect to fuel,
  - \(m\)th order with respect to oxidant, and
  - \((m + n)\)th order overall.

• \(m\) and \(n\) are determined from experimental data and are not necessarily integers.
• Use of global reactions to express chemistry is usually a black box approach and has limited use in combustion.

• It does not provide a basis for understanding what is actually happening.

• Let’s consider the following global reaction:

\[ 2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad (2.3) \]

• It implies that two moles of hydrogen molecule react with one mole of oxygen to form one mole of water, which is not strictly true.
In reality many sequential processes occur that involve several *intermediate species*. Following *elementary reactions*, among others, are important in conversion of $\text{H}_2$ and $\text{O}_2$ to water:

\[
\begin{align*}
\text{H}_2 + \text{O}_2 & \rightarrow \text{HO}_2 + \text{H} & (2.4) \\
\text{H} + \text{O}_2 & \rightarrow \text{OH} + \text{O} & (2.5) \\
\text{OH} + \text{H}_2 & \rightarrow \text{H}_2\text{O} + \text{H} & (2.6) \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} & (2.7)
\end{align*}
\]
• **Radicals** or **free radicals** or **reactive species** are reactive molecules, or atoms, that have unpaired electrons.

• To have a complete picture of the combustion of H\textsubscript{2} with O\textsubscript{2}, more than 20 elementary reactions can be considered.

• **Reaction mechanism** is the collection of elementary reactions to describe the overall reaction.

• Reaction mechanisms may involve a few steps or as many as several hundred (even thousands).

• (State-of-the-art).
Elementary Reaction Rates

- Using the concept of elementary reactions has many advantages.

- Reaction order is constant and can be experimentally determined.

- *molecularity of the reaction*: number of species that form the reaction complex.
  - Unimolecular
  - Bimolecular
  - Trimolecular / Termolecular
Bimolecular Reactions & Collision Theory

- Most combustion related elementary reactions are bimolecular:

\[ A + B \rightarrow C + D \quad (2.8) \]

- The rate at which the reaction proceeds is

\[ \frac{d[A]}{dt} = -k_{\text{bimolec}} [A][B] \quad (2.9) \]

- \( k_{\text{bimolec}} \propto f(T) \) and has a theoretical basis, unlike \( k_G \), rate coefficient of a global reaction.
Collision theory for bimolecular reactions has several shortcomings.

Approach is important for historical reasons and may provide a simple way to visualize bimolecular reactions.

Uses the concepts of wall collision frequency, mean molecular speed, and mean free path.

The simpler approach is to consider a single molecule of diameter $\sigma$ travelling at constant speed $v$ and experiencing collisions with identical, but stationary molecules.
• If the distance travelled (mean free path) between collisions is large, then moving molecule sweeps out a cylindrical volume of \( u \pi \sigma^2 \Delta t \).

• For random distribution of stationary molecules with number density \( n/V \), number of collisions

\[
Z \equiv \text{collisions per unit time} = (n/V)u \pi \sigma^2 \quad (2.10)
\]

• For Maxwellian velocity distribution for all molecules

\[
Z_c = \sqrt{2}(n/V)\pi \sigma^2 \bar{v} \quad (2.11)
\]
• Eqn.2.11 applies to identical molecules. For different molecules, we can use $\sigma_A + \sigma_B \equiv 2\sigma_{AB}$

$$Z_c = \sqrt{2}(n_B/V)\pi\sigma_{AB}^2\bar{v}_A$$

which expresses frequency of collisions of a single A molecule with all B molecules.

• For all A molecules

$$Z_{AB}/V = (n_A/V)(n_B/V)\pi\sigma_{AB}^2(\bar{v}_A^2 + \bar{v}_B^2)^{1/2}$$

(2.13)
If we express mean molecular speed in terms of temperature,

\[ \frac{Z_{AB}}{V} = \left( \frac{n_A}{V} \right) \left( \frac{n_B}{V} \right) \pi \sigma_{AB}^2 \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \] (2.14)

\( k_B \) = Boltzmann constant.

\( \mu = \left( m_A m_B \right) / \left( m_A + m_B \right) = \text{reduced mass.} \)

\( T = \text{absolute temperature.} \)
• We can relate $Z_{AB}/V$ to reaction rates

$$\frac{-d[A]}{dt} = \left[\frac{\text{No. of collisons of A and B molecules per unit volume per unit time}}{\text{Probability that a collision leads to reaction}}\right] \cdot \left[\frac{\text{kmol of A}}{\text{No. of molecules of A}}\right]$$

(2.15a)

or

$$\frac{-d[A]}{dt} = \left(\frac{Z_{AB}}{V}\right)\mathcal{P}N_{AV}^{-1}$$

(2.15b)
The probability that a collision will lead to a reaction can be expressed as a product of two factors:

- an energy factor

\[
\exp \left[ -\frac{E_A}{(R_u T)} \right]
\]

which expresses the fraction of collisions that occur with an energy above the activation energy

- a geometrical or steric factor \( p \), that takes into account the geometry of collisions between A and B.
With substitutions $n_A/V = [A]N_{AV}$ and $n_B/V = [B]N_{AV}$, Eqn.2.15b becomes

$$- \frac{d[A]}{dt} = pN_{AV} \sigma_{AB}^2 \left[ \frac{8\pi k_B T}{\mu} \right]^{1/2} \exp \left[ -\frac{E_A}{(R_u T)} \right][A][B].$$

Comparing Eqn. 2.16 with 2.9

$$k(T) = pN_{AV} \sigma_{AB}^2 \left[ \frac{8\pi k_B T}{\mu} \right]^{1/2} \exp \left[ -\frac{E_A}{R_u T} \right]$$
Collision theory is not capable of providing any means to determine $E_A$ or $p$.

More advanced theories do allow calculation of $k(T)$ from first principles to a limited extent.

If the temperature range of interest is not too large, $k_{\text{bimolec}}$ can be expressed by the semi-empirical Arrhenius form

$$k(T) = A \exp \left[ -\frac{E_A}{R_u T} \right]$$

where $A$ is a constant termed \textit{pre-exponential factor} or \textit{frequency factor}. 

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Most of the time the experimental values for rate coefficients in Arrhenius form expressed as

\[ k(T) = AT^b \exp \left[ \frac{-E_A}{R_u T} \right] \quad (2.19) \]

where \( A, b, \) and \( E_A \) are three empirical constants.

The standard method for obtaining \( E_A \) is to graph experimental rate constant data versus inverse of temperature, i.e. \( \log k \) vs \( 1/T \). The slope gives \( E_A/R_u \).
Unimolecular Reactions:

- Involves single species

\[ A \rightarrow B \]  \hspace{1cm} (2.20)

\[ A \rightarrow B + C \]  \hspace{1cm} (2.21)

- Examples: \( O_2 \rightarrow O + O; \) \( H_2 \rightarrow H + H. \)

- First order at high pressures

\[ \frac{d[A]}{dt} = -k_{uni}[A] \]  \hspace{1cm} (2.22)
- At low pressures, the reaction rate may also depend on a third molecule that may exist within the reaction volume

\[
\frac{d[A]}{dt} = -k[A][M] \quad (2.23)
\]

**Termolecular Reactions:**

\[
A + B + M \rightarrow C + M \quad (2.24)
\]

- Termolecular reactions are third order

\[
\frac{d[A]}{dt} = -k_{ter}[A][B][M] \quad (2.25)
\]
Multistep Mechanisms

Net Production Rates

- Consider some of the reactions in \( \text{H}_2-\text{O}_2 \) system

\[
\begin{align*}
\text{H}_2 + \text{O}_2 & \xrightarrow{k_{f1}} \text{HO}_2 + \text{H} & \text{(R.1)} \\
\text{H} + \text{O}_2 & \xrightarrow{k_{f2}} \text{OH} + \text{O} & \text{(R.2)} \\
\text{OH} + \text{H}_2 & \xrightarrow{k_{f3}} \text{H}_2\text{O} + \text{H} & \text{(R.3)} \\
\text{H} + \text{O}_2 + \text{M} & \xrightarrow{k_{f4}} \text{HO}_2 + \text{M} & \text{(R.4)}
\end{align*}
\]
• The net production rate of any species, say X, involved is the sum of all of the individual elementary rates producing X minus all of the rates destroying X.

• Net production rate of \( \text{O}_2 \) is then,

\[
\frac{d[\text{O}_2]}{dt} = k_{r1}[\text{HO}_2][\text{H}] + k_{r2}[\text{OH}][\text{O}]
+ k_{r4}[\text{HO}_2][\text{M}] - k_{f1}[\text{H}_2][\text{O}_2]
- k_{f2}[\text{H}][\text{O}_2] - k_{f4}[\text{H}][\text{O}_2][\text{M}] \tag{2.26}
\]
Net production rate for H atoms:

\[
\frac{d[H]}{dt} = k_{f1}[H_2][O_2] + k_{r2}[OH][O]
\]

\[
+ k_{f3}[OH][H_2] + k_{r4}[HO_2][M]
\]

\[
- k_{r1}[HO_2][H] - k_{f2}[H][O_2]
\]

\[
- k_{r3}[H_2O][H] - k_{f4}[H][O_2][M]
\]

\[
\frac{d[X_i](t)}{dt} = f_i\{[X_1](t), [X_2](t), ..... [X_n](t)\}
\]

\[
[X_i](0) = [X_i]_0
\]

(2.27)

(2.28)
Compact Notation:

- Since mechanisms may involve many elementary steps and many species, a generalized compact notation has been developed for the mechanism and the individual species production rates.

- For the mechanism,

\[
\sum_{j=1}^{N} \nu'_{ji} X_j \Rightarrow \sum_{j=1}^{N} \nu''_{ji} X_j \quad \text{for } i = 1, 2, \ldots L \quad (2.29)
\]

where \( \nu'_{ji} \) and \( \nu''_{ji} \) are stoichiometric coefficients of reactants and products, respectively.
<table>
<thead>
<tr>
<th>( N )</th>
<th>Species</th>
<th>( L )</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O(_2)</td>
<td>1</td>
<td>R.1</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)</td>
<td>2</td>
<td>R.2</td>
</tr>
<tr>
<td>3</td>
<td>H(_2)O</td>
<td>3</td>
<td>R.3</td>
</tr>
<tr>
<td>4</td>
<td>HO(_2)</td>
<td>4</td>
<td>R.4</td>
</tr>
<tr>
<td>5</td>
<td>O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>H</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>M</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
• Stoichiometric coefficient matrices:

\[
\nu'_{ji} = \begin{bmatrix}
1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 & 1 & 0 \\
1 & 0 & 0 & 0 & 0 & 1 & 0 & 1
\end{bmatrix} \tag{2.30a}
\]

\[
\nu''_{ji} = \begin{bmatrix}
0 & 0 & 0 & 1 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 & 1 & 0 \\
0 & 0 & 1 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 & 0 & 0 & 1
\end{bmatrix} \tag{2.30b}
\]
• Net production rate of each species in a multistep mechanism:

\[ \frac{d[X_j]}{dt} \equiv \dot{\omega}_j = \sum_{i=1}^{L} \nu_{ji} q_i \quad \text{for} \quad j = 1, 2, \ldots, N \]  

(2.31)

where

\[ \nu_{ji} = (\nu_{ji}'' - \nu_{ji}') \quad (2.32) \]

\[ q_i = k_{fi} \prod_{j=1}^{N} [X_j]^{\nu_{ji}'} - k_{ri} \prod_{j=1}^{N} [X_j]^{\nu_{ji}''} \quad (2.33) \]
• For example, $q_i (= q_1)$ for reaction R.1 is

$$q_i = \dot{k_f}_1 [O_2]^1 [H_2]^1[H_2O]^0 [HO_2]^0 [O]^0 [H]^0 [OH]^0 [M]^0$$

$$- k_{r1} [O_2]^0[H_2]^0[H_2O]^0$$

$$[HO_2]^1 [O]^0 [H]^1[OH]^0 [M]^0$$

$$= \dot{k_f}_1 [O_2][H_2] - k_{r1} [HO_2][H]$$

(2.34)

• Writing similar expressions for $i = 2, 3, \text{and } 4$ and summing completes the total rate expression for $\dot{\omega}_j$. 

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Rate Coefficients and Equilibrium Constants:

- At equilibrium forward and reverse reaction rates must be equal.

\[ A + B \xrightleftharpoons[{k_f \over k_r}]{} C + D \quad (2.35) \]

- Formation rate of species A:

\[ \frac{d[A]}{dt} = -k_f [A][B] + k_r [C][D] \quad (2.36) \]

- For equilibrium, time rate of change of [A] must be zero. Same goes for B, C, and D.
Then, Eqn. 2.36

\[ 0 = -k_f [A][B] + k_r [C][D] \]  \hspace{1cm} (2.37)

arranging

\[ \frac{[C][D]}{[A][B]} = \frac{k_f(T)}{k_r(T)} \]  \hspace{1cm} (2.38)

Previously we have defined equilibrium constant as,

\[ K_p = \frac{(P_C/P^o)^c(P_D/P^o)^d \ldots}{(P_A/P^o)^a(P_B/P^o)^b \ldots} \]  \hspace{1cm} (2.39)
• Since molar concentrations are related to mol fractions and partial pressures as,

\[ [X_i] = \chi_i P/(R_u T) = P_i/(R_u T) \quad (2.40) \]

we can define an equilibrium constant based on molar concentrations, \( K_c \) and relate it to \( K_p \),

\[ K_p = K_c (R_u T/P^o)^{c+d+...-a-b...} \quad (2.41a) \]

or

\[ K_P = K_c (R_u T/P^o)^{\Sigma\nu''-\Sigma\nu'} \quad (2.41b) \]
where, $K_c$ is defined as,

$$K_c = \frac{[C]^c[D]^d \cdots}{[A]^a[B]^b \cdots} = \frac{\prod \text{prod} [X_i]^\nu_i''}{\prod \text{react} [X_i]^\nu_i'} \quad (2.42)$$

- So that,

$$\frac{k_f(T)}{k_r(T)} = K_c(T) \quad (2.43)$$

- For bimolecular reactions $K_c = K_p$. 

2. Chemical Kinetics
**Steady-State Approximation**

- Analysis of reactive systems can be simplified by applying steady-state approximation to the reactive species or radicals.

- Steady-state approximation is justified when the reaction forming the intermediate species is slow, while the reaction destroying the intermediate species is very fast.

- As a result the concentration of the radical is small in comparison with those of the reactants and products.
• Example (Zeldovich mechanism for NO formation):

\[
\begin{align*}
O + N_2 & \overset{k_1}{\rightarrow} NO + N \\
N + O_2 & \overset{k_2}{\rightarrow} NO + O
\end{align*}
\]

First reaction is slow (rate limiting); while second is fast.

• Net production rate of N atoms,

\[
\frac{d[N]}{dt} = k_1[O][N_2] - k_2[N][O_2] \quad (2.44)
\]
• After a rapid transient allowing buildup of $N$, $d[N]/dt$ approaches zero.

$$0 = k_1 [O][N_2] - k_2 [N]_{ss}[O_2]$$  \hspace{1cm} (2.45)

$$[N]_{ss} = \frac{k_1 [O][N_2]}{k_2 [O_2]}$$  \hspace{1cm} (2.46)

• Time rate of change of $[N]_{ss}$ is

$$\frac{d[N]_{ss}}{dt} = \frac{d}{dt} \left[ \frac{k_1 [O][N_2]}{k_2 [O_2]} \right]$$  \hspace{1cm} (2.47)
Mechanism for Unimolecular Reactions

- Let’s consider a three-step mechanism:

\[ A + M \xrightarrow{k_e} A^* + M \]  \hspace{1cm} (2.48a)

\[ A^* + M \xrightarrow{k_{de}} A + M \]  \hspace{1cm} (2.48b)

\[ A^* \xrightarrow{k_{unim}} \text{products} \]  \hspace{1cm} (2.48c)

- In step 1: kinetic energy transferred to A from M; A has increased internal vibrational and rotational energies and becomes an energized A molecule, A*.
Two possible scenarios for \( A^* \):
- \( A^* \) may collide with another molecule and goes back to \( A \) (2.48b)
- \( A^* \) may decompose into products (2.48c)

The rate at which products are formed:

\[
\frac{d[\text{products}]}{dt} = k_{\text{unim}}[A^*] \quad (2.49)
\]

Net production rate of \( A^* \):

\[
\frac{d[A^*]}{dt} = k_e[A][M] - k_{\text{de}}[A^*][M] - k_{\text{unim}}[A^*] \quad (2.50)
\]
• Steady-state approximation for $A^*$, i.e. $\frac{d[A^*]}{dt} = 0$,

$$[A^*] = \frac{k_e[A][M]}{k_{de}[M] + k_{unim}} \quad (2.51)$$

• Substitute Eqn. 2.51 into 2.49,

$$\frac{d[\text{products}]}{dt} = \frac{k_e[A][M]}{(k_{de}/k_{unim})[M] + 1} \quad (2.52)$$
Another form of writing the overall rate of production of *products* for the overall reaction:

\[
\text{A} \xrightarrow{k_{\text{app}}} \text{products} \quad (2.53)
\]

\[
-\frac{d[A]}{dt} = \frac{\text{products}}{dt} = k_{\text{app}}[A] \quad (2.54)
\]

\(k_{\text{app}}\) is an apparent unimolecular rate coef.

Equating Eqns. 2.52 and 2.54 yields

\[
k_{\text{app}} = \frac{k_e[M]}{(k_{de}/k_{\text{unim}})[M] + 1} \quad (2.55)
\]
• Eqn.2.55 lets us to explain pressure dependence of unimolecular reactions:

- At high enough pressures \((k_{de}[M]/k_{unim}) \gg 1\) because \([M]\) increases as the pressure is increased; then

\[
k_{\text{app}}(P \to \infty) = k_{unim}k_e/k_{de} \tag{2.56}
\]

- At low enough pressures \((k_{de}[M]/k_{unim}) << 1\), then

\[
k_{\text{app}}(P \to 0) = k_e[M] \tag{2.57}
\]
**Chain and Chain-Branching Reactions:**

- *Chain reactions* produce one or more radical species that subsequently react to produce another radical(s).
- To learn some of the features of chain reactions, we consider a hypothetical chain mechanism, which is globally represented as

\[ A_2 + B_2 \rightarrow 2AB \]

- *Chain initiation:*

\[ A_2 + M \xrightarrow{k_1} A + A + M \quad \text{(C.1)} \]
• *Chain-propagating reactions* involving free radicals A and B:

\[ A + B_2 \xrightarrow{k_2} AB + B \quad (C.2) \]

\[ B + A_2 \xrightarrow{k_3} AB + A \quad (C.3) \]

• *Chain-terminating reaction* is

\[ A + B + M \xrightarrow{k_4} AB + M \quad (C.4) \]

where AB is the stable product.
• Concentrations of A and B are small throughout the course of reaction, so is AB at initial stages; thus we ignore reverse reactions and determine reaction rates for stable species as:

\[
\frac{d[A_2]}{dt} = -k_1[A_2][M] - k_3[A_2][B] \tag{2.58}
\]

\[
\frac{d[B_2]}{dt} = -k_2[B_2][A] \tag{2.59}
\]

\[
\frac{d[AB]}{dt} = k_2[A][B_2] + k_3[B][A_2] + k_4[A][B][M] \tag{2.60}
\]
• If we use the steady-state approximation for free radicals A and B:

\[
\frac{d[A]}{dt} = 2k_1[A_2][M] - k_2[A][B_2] \\
+ k_3[B][A_2] - k_4[A][B][M] = 0
\]  

\[
\frac{d[B]}{dt} = k_2[A][B_2] \\
- k_3[B][A_2] - k_4[A][B][M] = 0
\]  

• Simultaneous solution of Eqns. 2.61 and 2.62 for A:
\[ [A] = \frac{k_1}{2k_2} \frac{[M][A_2]}{[B_2]} + \frac{k_3}{k_4} \frac{[A_2]}{[M]} \cdot \left\{ 1 + \left( \frac{k_1 k_4}{2k_2 k_3} \frac{[M]^2}{[B_2]} \right)^2 \right\}^{1/2} - 1 \]  

2.63

- A similar expression can be written for [B].
- With the steady-state values for [A] and [B],

\[ \frac{d[A_2]}{dt}, \frac{d[B_2]}{dt}, \text{ and } \frac{d[AB]}{dt} \]

can be found for initial values of [A_2] and [B_2].
• If we consider the simplest of the three, \( \frac{d[B_2]}{dt} \):

\[
\frac{d[B_2]}{dt} = -\frac{k_1}{2} [A_2][M] - \frac{k_2 k_3}{k_4} \frac{[A_2][B_2]}{[M]}
\]

\[
\left\{ 1 + \left( \frac{k_1 k_4}{2 k_2 k_3} \frac{[M]^2}{[B_2]} \right)^2 \right\}^{1/2} - 1 \quad (2.64)
\]

• The last two Eqns can be further simplified:

\[
k_1 k_4 [M]^2 / (2k_2 k_3 [B_2]) << 1
\]
since $k_2$ and $k_3$ must be much larger than $k_1$ and $k_4$ for steady-state approximation to apply.

- Eqns. 2.63 and 2.64 can be approximated as:

\[
[A] \approx \frac{k_1}{2k_2} \frac{[M][A_2]}{[B_2]} + \frac{k_1^2 k_4}{8k_2^2 k_3} \frac{[M]^3[A_2]}{[B_2]^2} \quad (2.65)
\]

\[
\frac{d[B_2]}{dt} \approx -\frac{k_1}{2} [A_2][M] - \frac{k_1^2 k_4}{4k_2 k_3} \frac{[M]^3[A_2]}{[B_2]} \quad (2.66)
\]

- First term in both Eqns. dominates at low pressures.
• Concentration of A depends on the ratio $k_1/k_2$.
• Rate at which $B_2$ dissapears is governed by $k_1$.
• Increasing $k_2$ and $k_3$ increases radical concentration, but has no effect on production rate of products.
• $[A]$ and $[B]$ are directly proportional to $P$.
• Reaction rates of major species scale with pressure squared.
  - provided that second terms in Eqns.2.65 and 2.66 remain small.
• At high pressures, the second terms in Eqns. 2.65 and 2.66 become important (they increase with pressure faster than the first terms do).

• So, $k_4$ has some influence at high pressures, although it does not have much influence on radical concentrations or overall reaction rate at lower pressures.

• *Chain-branching reactions* involve the formation of two radical species from a reaction that consumes only one radical.

\[
O + H_2O \rightarrow OH + OH
\]
**Chemical Time Scales:**

- Magnitude of chemical times relative to convective or mixing times is of importance in combustion.

- *Unimolecular reactions*

\[ A \xrightarrow{k_{\text{app}}} \text{products} \quad (2.53) \]

\[ -\frac{d[A]}{dt} = \frac{\text{products}}{dt} = k_{\text{app}}[A] \quad (2.54) \]

- Integrating at constant \( T \) for \([A](t = 0) = [A]_0\),
\[ [A](t) = [A]_0 \exp [-k_{\text{app}} t] \quad (2.67) \]

- Characteristic chemical time can be defined as the time required for the concentration of A to fall from its initial value to a value equal to $1/e$ times the initial value,

\[ \frac{[A](\tau_{\text{chem}})}{[A]_0} = 1/e \quad (2.68) \]

- Combining Eqns. 2.67 and 2.68 yields,
\[ 1/e = \exp \left( -k_{\text{app}} \tau_{\text{chem}} \right) \] (2.69)

or

\[ \tau_{\text{chem}} = \frac{1}{k_{\text{app}}} \] (2.70)

- **Bimolecular Reactions**

\[ A + B \overset{k_{\text{bimolec}}}{\rightarrow} C + D \] (2.8)

\[ \frac{d[A]}{dt} = -k_{\text{bimolec}}[A][B] \] (2.9)
• For this single reaction [A] and [B] are related by stoichiometry. Any change in [A] has a corresponding change in [B],

\[ x \equiv [A]_0 - [A] = [B]_0 - [B] \]  \hspace{1cm} (2.71)

\[ [B] = [A] + [B]_0 - [A]_0 \]  \hspace{1cm} (2.72)

• Substituting Eqn.4.71 into 4.9 and integrating,

\[ \frac{[A](t)}{[B](t)} = \frac{[A]_0}{[B]_0} \exp \left\{ \left( [A]_0 - [B]_0 \right) k_{\text{bimolec}} t \right\} \]  \hspace{1cm} (2.73)
Substitute Eqn.2.72 into 2.73, and set:

\[
[A]/[A]_0 = 1/e \quad \text{when} \quad t = \tau_{\text{chem}}
\]

gives

\[
\tau_{\text{chem}} = \frac{\ln \left[ e + (1 - e)([A]_0/[B]_0) \right]}{([B]_0 - [A]_0)k_{\text{bimolec}}} \quad (2.74)
\]

If \([B]_0 >> [A]_0\),

\[
\tau_{\text{chem}} = \frac{1}{[B]_0 k_{\text{bimolec}}} \quad (2.75)
\]
• **Termolecular Reactions**

\[ A + B + M \overset{k_{\text{ter}}}{\longrightarrow} C + M \]  \hspace{1cm} (2.24)

• For a simple system at constant \( T \), \([M]\) is constant

\[ \frac{d[A]}{dt} = (-k_{\text{ter}}[M])[A][B] \]  \hspace{1cm} (2.9)

where \((-k_{\text{ter}}[M])\) plays the same role as \(k_{\text{bimolec}}\) does for a bimolecular reaction.
• Then, the characteristic time for termolecular reactions is,

\[ \tau_{\text{chem}} = \frac{\ln \left[ e + (1 - e) \left( \frac{[A]_0}{[B]_0} \right) \right]}{([B]_0 - [A]_0) k_{\text{ter}}[M]} \]  

(2.77)

And, when \([B]_0 >> [A]_0\),

\[ \tau_{\text{chem}} = \frac{1}{[B]_0 (k_{\text{ter}}[M])} \]  

(2.78)