LECTURE 3. REACTION MECHANISMS AND EVALUATION OF RATE FORMS

We have already seen that single reactions, in general, do not occur in one step; but that it is a particular sequence of elementary reactions (reaction mechanism) that leads to the overall reaction.

The knowledge of the reaction mechanism is extremely desirable since then the overall rate can be determined from first principles of the law of mass action which applies to every elementary step in the sequence. If such an attempt results in too complex algebraic expressions, at least experiments can be designed to test whether certain steps of the mechanism are rate limiting, which helps in finding a simplified rate form. Knowledge of the expected rate form helps in designing the right experiments for rate determination.

**Reaction Mechanism** - this sequence of elementary events represents the detailed pathway of transformation of the reactants through highly reactive intermediates (active centers) to final products.

Based on the structure of this sequence we can draw a more appropriate distinction between catalytic and noncatalytic processes.

An **open sequence** is one in which an active center is not reproduced in other steps of the sequence. The reaction is noncatalytic.

A **closed sequence** is one in which an active center is reproduced so that a cyclic pattern repeats itself, and a large number of molecules of products can be made from only one active center. Reaction is catalytic.

Let us consider some examples:

**Mechanism 1:**

\[
RCI \rightleftharpoons R^+ + Cl^- \\
R^+ + F^- \rightleftharpoons RF
\]

active center \( R^+ \); open sequence; noncatalytic

Overall stoichiometry:

\[
RCI + F^- \rightleftharpoons RF + Cl^-
\]
**Mechanism 2:**

\[ E + S \leftrightarrow ES^* \]  
active center \( ES^* \); closed sequence;  

\[ ES \leftrightarrow E + P \]  
catalytic  

--------------------
Overall stoichiometry:
\[ S = P \]
\[ E \]

This second mechanism above is the Michaelis-Menten mechanism for enzyme catalyzed reactions such as isomerization of glucose, etc.

We should be particularly careful to spot a closed sequence loop within a larger mechanistic path. For example, a typical chain propagation reaction follows **Mechanism 3** below:

\[
M_1 \rightarrow 2R_1^* \\
R_1^* + M_1 \rightarrow M_2 + R_2^* \\
R_2^* \rightarrow R_1^* + M_3 \\
2R_1^* \rightarrow M_1 \\
R_2^* + R_1^* \rightarrow M_4 \\
2R_2^* \rightarrow M_5
\]

Steps 2 and 3 of the above mechanism form a closed (catalytic) sequence in which the active centers (intermediates, radicals) \( R_1^* \) and \( R_2^* \) are repeatedly regenerated.

**Basic Rule:** Whenever a mechanism is hypothesized for a single reaction consisting of \( N \) elementary steps the weighted sum of the \( N \) steps (i.e. the sum of all steps each of them multiplied by an integer 1, 2, 3 etc.) must result in the overall stoichiometry for the reaction under consideration. If it does not, the mechanism is not consistent with stoichiometry and should be discarded.

The above Basic Rule has to be applied judiciously. It is certainly true for an open sequence mechanism. As a matter of fact, it can be used then to discard the steps that are incompatible. However, in mechanisms containing a closed sequence it is the steps of the closed sequence that must lead to the overall stoichiometry. In our mechanism 3 above, the stoichiometry is \( M_1 = M_2 + M_3 \). The fact that termination of active centers \( R_2^* \) may lead to \( M_4 \) or \( M_5 \) is immaterial since those would be present in an infinitesimal amount and would not affect the mass balance of the single reaction under consideration i.e.,

\[
\frac{\Delta n_1}{-1} = \frac{\Delta n_2}{1} = \frac{\Delta n_3}{1}.
\]
However, the "impurities" (e.g., $M_4$ and $M_5$) resulting from such a mechanism may be important from an environmental standpoint and we should strive to understand what they are and in what amounts they could form.

Finding the multipliers (stoichiometric numbers), by which certain steps of the mechanism have to be multiplied in order to lead to the overall stoichiometry upon summation, is a trivial matter for relatively simple mechanisms consisting of two to three steps. For example, if a single reaction stoichiometry is given by $2A = R$ and the mechanism is

<table>
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<th>Mechanistic Step</th>
<th>Stoichiometry of the Step</th>
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<tr>
<td>1. $A + A \leftrightarrow A^* + A$</td>
<td>$A = A^*$</td>
<td>2</td>
</tr>
<tr>
<td>2. $A^* + A^* \leftrightarrow R$</td>
<td>$2A^* = R$</td>
<td>1</td>
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Overall Stoichiometry: $2A = R$

it is clear that the first step should be repeated twice (stoichiometric number $v^1 = 2$) in order to get the overall stoichiometry.

For lengthy complex mechanisms simple inspection may not be the best way to proceed. If the reaction stoichiometry is given in such a way that all stoichiometric coefficients are integers (which can always be done by multiplying through with an appropriate number) then the reaction stoichiometry may be written as:

$$\sum_{j=1}^{S} v_j A_j = 0$$  \hspace{1cm} (1)

If the mechanism consists of $N$ steps, and the stoichiometric coefficient of species $j$ in step $i$ is $v_{ij}$, then the steps of the mechanism can be presented by a set of linear equations:

$$\sum_{j=1}^{S} v_{ij} A_j = 0 \hspace{0.5cm} \text{for} \hspace{0.5cm} i = 1, 2, 3...N$$  \hspace{1cm} (2)

In order for the mechanism to be consistent with stoichiometry we must be able to find a set of stoichiometric numbers (multipliers) $v^i$ $i = 1, 2, ..., N$ not all zero from the following set of linear equations:
\[
\sum_{i=1}^{N} v_i^j = v_j \quad \text{for} \quad j = 1, 2, 3 \ldots S^l
\] (3)

where \( S^l \) is the total number of species including active intermediates, i.e., \( S^l = S + I \) where \( I \) is the total number of active intermediates. Naturally the overall stoichiometric coefficients \( v_j \) for active intermediates \( j = S + 1, S + 2, S + 3 \ldots, S^l - 1, S^l \) must all be zero.

**Example:**

**Mechanism:**

\[
\begin{align*}
A + A & \rightleftharpoons A^* + A \\
A^* + A^* & \rightleftharpoons R
\end{align*}
\]

**Stoichiometry of each step:**

\[
\begin{align*}
A = A^* \\
2A^* = R
\end{align*}
\]

**Overall Stoichiometry:**

\[
\begin{align*}
A: & \quad -v^1 + 0 = -2 \\
R: & \quad 0 + v^2 = 1 \\
I: & \quad v^1 - 2v^2 = 0
\end{align*}
\]

Thus we have a set of \( S^l \) equations \((S^l = S + I = 2 + 1 = 3)\) with \( N \) unknowns \((v^j) (N = 2)\). The nonzero solution for \( v^j \) exists if the matrix of \( v_{ij} \) has rank \( N \). If that is the case select \( N \) equations and solve for \( v^j \).

In the above simple example we have one intermediate species \((A^*)\) so that \( I = 1 \) and we have two stable species \((A \text{ and } R)\) so that \( S = 2 \) and hence \( S^l = S + I = 3 \). The mechanism consists of two steps so that \( N = 2 \) and we need to determine the two stoichiometric numbers \( v^1 \) and \( v^2 \) by which step 1 and step 2, respectively, should be multiplied to arrive at the overall stoichiometry.

If we number \( A, R \) and \( A^* \) as species 1, 2, and 3, in that order, equation (3) can be written in the following matrix form:

\[
\begin{pmatrix} v^1 \\ v^2 \end{pmatrix} \begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -2 \end{pmatrix} = \begin{pmatrix} -2 \\ 1 \end{pmatrix} \] (3a)

The matrix of stoichiometric coefficient \((v_{ij})\) is:

\[
\begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -2 \end{pmatrix}
\]
and the nonzero solution for the \( \begin{pmatrix} \nu^1 & \nu^2 \end{pmatrix} \) vector is guaranteed if that matrix has rank 2 which it clearly does. The matrix multiplication in eq (3a) results in 3 rows that are presented above which generate the solution for \( \nu^1 \) and \( \nu^2 \). See any text on linear algebra or matrices for details if you encounter a problem of this nature. A good reference for chemical engineers is Amundson N.R., "Mathematical Methods in Chemical Engineering-Matrices and Their Applications", Prentice Hall, 1966.

When a consistent mechanism is proposed, the overall rate of reaction can be derived based on one of the following two assumptions:

1. Pseudo-steady state assumption (PSSA), also called Quasi-steady state assumption (QSSA)

2. Rate limiting step assumption (RLSA)
6.1. PSEUDO-STEADY STATE ASSUMPTION (PSSA)

Since the intermediates (active centers) which may be of various nature, (e.g., free radicals, ions, unstable molecules etc.) appear only in the mechanism but not in the overall stoichiometry for the reaction it can be safely assumed that their concentration is at all times small. If this was not so, then they would be detectable and would appear in the overall stoichiometry since a substantial portion of the reactants would be in that form at some point in time. Now, reasoning leads us to conclude that then the net rate of formation of these active intermediates must also always be small. If this was not true, and if at some point in time the net rate of formation was high, then the quantity of this intermediate would have to rise and we have already concluded that this cannot happen. Thus, the net rate of formation of all the active intermediates involved in the mechanism, but not appearing in the overall stoichiometry for the reaction, must be very small.

This is the basic hypothesis of the PSSA: The net rates of formation of all active intermediates are negligibly small and hence are approximately zero.

This requirement for a mechanism of \( N \) steps including \( S \) stable species that appear in overall reaction stoichiometry and \( I \) intermediates \( S^I = S + I \) can be formally written as:

\[
\sum_{i=1}^{N} v_{ij} r_i = 0 = R_j \quad \text{for } j = S + 1, \ldots S^I \quad (4)
\]

From these \( I \) linear expressions we can evaluate the \( I \) concentrations of the intermediates in terms of the rate constants and the \( S \) concentrations of stable species. Substituting these intermediate concentrations into the expression for the rate of a desired component \( j \)

\[
R_j = \sum_{i=1}^{N} v_{ij} r_i \quad j = 1, 2, \ldots S \quad (5)
\]

we obtain the required rate form for that component.
Thus, the procedure for applying the PSSA to a single reaction can be outlined as follows:

1. Write down the hypothesized mechanism and make sure that it is consistent with stoichiometry.

2. Count all the active intermediates.

3. Set up the net rate of formation for every active intermediate. Remember, since the steps in the mechanism are elementary, law of mass action applies in setting up rates of each step. Make sure to include the contribution of every step in which a particular intermediate appears to its net rate of formation.

4. Set all the net rates of active intermediates to be zero and evaluate from the resulting set of equations the concentrations of all active intermediates.

5. Set up the expression for the rate of reaction using a component which appears in the fewest steps of the mechanism (in order to cut down on the amount of algebra). Eliminate all the concentrations of active intermediates that appear in this rate form using the expressions evaluated in step 4. Simplify the resulting expression as much as possible.

6. If you need the rate of reaction for another component simply use the rate form evaluated in step 5 and the relationship between the rates of various components and their stoichiometric coefficients.

7. If there is solid theoretical or experimental information which indicates that certain terms in the rate form obtained in step 5 or 6 may be small in comparison to some other ones simplify the rate form accordingly.

8. Check the obtained rate form against experimental data for the rate.

9. Remember that even if the derived rate form agrees with experimental data that still does not prove the correctness of the proposed mechanism. However, your rate form may be useful especially if the reaction will be conducted under conditions similar to those under which experimental data confirming the rate form were obtained.

Let us apply this to an example.
Consider the decomposition of ozone. We want to know its rate. The overall stoichiometry is

\[ 2 \text{O}_3 = 3 \text{O}_2 \]  

\[ (6) \]

1. The proposed mechanism consists of 2 steps:

\[ \text{O}_3 \xrightarrow{k_{1f}} \text{O}_2 + \text{O}^* \]  

\[ (7a) \]

\[ \text{O}^* + \text{O}_3 \xrightarrow{k_2} \text{O}_2 + \text{O}_2 \]  

\[ (7b) \]

The mechanism is obviously consistent with the overall stoichiometry, the stoichiometric number of both steps being one.

We have already assumed that the last step is irreversible since it is highly unlikely that two oxygen molecules would spontaneously "collide" to produce an active oxygen atom and ozone.

2. Counting the active intermediates we find one, namely, \( \text{O}^* \).

3. The net rate of formation of \( \text{O}^* \) is:

\[ R_{\text{O}^*} = k_{1f} \text{C}_{\text{O}_3} - k_{1b} \text{C}_{\text{O}_2} \text{C}_{\text{O}^*} - k_2 \text{C}_{\text{O}_3}^2 = 0 \]  

\[ (8) \]

4. According to PSSA the above rate must be zero. From the above equation we get

\[ \text{C}_{\text{O}^*} = \frac{k_{1f} \text{C}_{\text{O}_3}}{k_{1b} \text{C}_{\text{O}_2} + k_2 \text{C}_{\text{O}_3}} \]  

\[ (9) \]

5. Since both \( \text{O}_2 \) and \( \text{O}_3 \) appear in both steps of the mechanism we can set up the rate of disappearance of ozone directly

\[ -R_{\text{O}_3} = k_{1f} \text{C}_{\text{O}_3} - k_{1b} \text{C}_{\text{O}^*} \text{C}_{\text{O}_2} + k_2 \text{C}_{\text{O}_3}^2 \text{C}_{\text{O}_3} \]  

\[ (10) \]

Substituting the expression for \( \text{C}_{\text{O}^*} \), and finding the common denominator, leads to:
\[-R_{O_3} = \frac{k_{1f}k_{ib}C_{O_3}C_{O_2} + k_{1f}k_2C_{O_3}^2 - k_{1f}k_{ib}C_{O_3}C_{O_2} + k_{1f}k_2C_{O_3}^2}{k_{ib} C_{O_2} + k_2 C_{O_3}}\]  
\[-R_{O_i} = \frac{2k_{1f}k_2C_{O_3}^2}{k_{ib} C_{O_2} + k_2 C_{O_3}}\]  

This is a complete rate expression based on the hypothesized mechanism.

7. Concentration of ozone is orders of magnitude smaller than the concentration of oxygen. It also appears that the second step in the mechanism is slow. Thus, when \( k_{ib} C_{O_3} \gg k_2 C_{O_3} \), the rate simplifies to:

\[-R_{O_3} \approx \frac{2k_{1f}k_2C_{O_3}^2}{k_{ib} C_{O_2} + k_2 C_{O_3}}\]

8. The experimentally found rate under these conditions of low \( O_3 \) is \( R_{O_3} = k C_{O_3}^2 C_{O_2}^{-1} \). Agreement seems to exist between the proposed mechanism and data.

Consider another example. The overall reaction stoichiometry is given as:

\[A + B = R\]  
(13)

and the experimentally determined rate is

\[-R_A = k C_A^2\]  
(14)

It is desired to determine whether the mechanism outlined below is consistent with the observed rate.

1. \( A + A \xrightarrow{k_1} I \)  
(15a)

\[I + B \xrightarrow{k_2} R + A\]  
(15b)

2. The mechanism is obviously consistent with the overall stoichiometry since a straightforward addition of steps leads to it. The number of intermediates is one, \( I = I \).
3. The net rate of formation of the intermediate is:

\[ R_i = k_1 C_A^2 - k_2 C_i C_B = 0 \]  

(16)

4. And according to PSSA is equal to zero. The concentration of \( I \) is then

\[ C_I = \frac{k_1 C_A^2}{k_2 C_B} \]  

(17)

5. Since \( A \) appears in both steps of the mechanism and \( R \) only in one, set up the rate of formation of \( R \) for convenience

\[ R_R = k_2 C_I C_B \]  

(18)

Eliminating \( C_I \) we get

\[ R_R = k_1 C_A^2 \]  

(19)

6. From stoichiometry

\[- \frac{R_A}{1} = \frac{R_R}{1} = k_1 C_A^2 \]  

(20)

7. The rate agrees with the experimentally determined one. (Compare eq. (20) and (14)). The mechanism may be right.

**NOTE:** In writing the net rate of formation of \( I, R_i \), in step 3 we used the equivalent rate and thus based the rate constant \( k_i \) on \( I \). If we were to write the rate of disappearance of \( A \),

\[- R_A = 2k_1 C_A^2 - k_2 C_i C_B \]  

(21)

notice that the first term has to be multiplied by the stoichiometric coefficient of \( A \) in the 1st step, which is two, since the rate of disappearance of \( A \) in the 1st step is twice the rate of appearance of \( I \) in that step. If we followed a different convention we would have based \( k_i \) on the left hand side from where the arrow originates i.e., we would have based it on a component \( A \). In that case a factor 1/2 would have appeared with \( k_i \) in step 3 and there would be no 2 but 1 in front of \( k_i \) in the expression for \(- R_A\). This seemingly trivial point often causes a lot of errors.
and grief. Just notice that if we forgot the proper stoichiometric relationship, and the expression for $-R_d$ in eq. (21) did not have a $2k_1$ but $k_1$, while $R_f$ was as given, they would be identically equal to each other and thus asserting $R_f = 0$ would be asserting that $-R_d = 0$, which is absurd since $-R_d = R_R$ which is a respectable expression. This demonstrates the importance of not forgetting the stoichiometric coefficients in setting up rates.

At the end it should be mentioned that the PSSA fortunately does not only rest on the verbal arguments presented at the beginning of this section (can you find any fault with this?) but has solid mathematical foundations originating in the theory of singular perturbations. This will be illustrated in an Appendix since the same theory is applicable to many other situations.

The application of PSSA to multiple reactions is a straightforward extension of the above procedure.
6.2 RATE LIMITING STEP ASSUMPTION (RLSA)

This approach is less general than the previous one, in the sense that we must know more about the mechanism than just its form in order to apply it. The rate expression obtained from RLSA represents thus a limiting case of the one that could be obtained using PSSA.

The basic hypothesis of the RLSA is as follows:

1. One step in the mechanism is much slower than the others and thus that rate limiting step determines the overall rate.

2. With respect to the rate limiting step all other steps may be presumed in equilibrium.

This is best explained based on an example. Consider a reaction $2A + B = R$. Suppose that we want to find its rate form based on the mechanism shown below. In addition, it is known that the 1st step is the slowest. If we then depict the magnitude of the forward and reverse rates for each step with $\rightarrow$, and the magnitude of the net forward rate by a solid arrow, and if we keep in mind that the net rate must be of the same magnitude in all the steps (which is required by PSSA) because otherwise the active intermediates would accumulate someplace, we get the picture presented to the right of the hypothesized mechanism below.

1. $A \xrightleftharpoons[k_{b1}]{k_{a1}} A^*$

2. $A^* + B \xrightleftharpoons[k_{b2}]{k_{a2}} AB^*$

3. $AB^* + A^* \xrightleftharpoons[k_{b3}]{k_{a3}} R$

Clearly the magnitude (length) of the arrows indicating forward and reverse rates is the smallest in step 1, this step is the slowest and limits the rate. At the same time the magnitude of the net rate forward is almost $1/2$ of the total rate forward in step 1 and that step clearly is not in equilibrium while the magnitude of the net rate forward ($\rightarrow$) in comparison to the total rate forward ($\leftarrow$) and total reverse rate ($\leftarrow$) in steps 2 and 3 is negligible. Thus, in these two steps rates forward and backward are approximately equal, and in comparison to step 1 these two steps have achieved equilibrium.

Thus, the procedure for applying the RLSA to a single reaction can be outlined as follows:
1. Write down the hypothesized mechanism and make sure that it is consistent with stoichiometry.

2. Determine which is the rate determining step. This should be done based on experimental information. Often various steps are tried as rate limiting due to the lack of information in order to see whether the mechanism may yield at all a rate form compatible with the one found experimentally.

3. Set up the net rates of all the steps, other than the rate limiting one, to be zero, i.e., set up equilibrium expressions for all other steps.

4. Set up the rate form based on the law of mass action for the rate determining step, and eliminate all concentrations of intermediates using the expressions evaluated in step 3.

5. Using the stoichiometric number of the rate determining step relate its rate to the desired rate of a particular component.

6. Check the obtained rate form against the experimentally determined rate.

7. Remember that the agreement or disagreement between the derived and experimental rate form does not prove or disprove, respectively, the validity of the hypothesized mechanism and of the postulated rate limiting step. If the two rate forms disagree try another rate limiting step and go to step 3. If the two rate forms agree use the rate form with caution.

The greatest limitation of the rate forms based on RLSA is that they are much less general than those developed from PSSA and they do not test the mechanism in its entirety. The rate forms based on RLSA may be valid only in narrow regions of system variables (e.g., $T$, concentrations) since with the change in variables (i.e., concentrations, $T$) the rate limiting step may switch from one step in the mechanism to another. Clearly, the magnitude of our arrows representing the rates depends on concentration levels, temperature, pressure etc. and may change rapidly as conditions change. An example in the shift of the rate limiting step is the previously covered Lindemann's-Christensen mechanism for unimolecular reactions.
Suppose that we want to evaluate the rate of formation of $R$ for the reaction given above and under the assumptions made.

1. We first test the compatibility of the proposed mechanism with stoichiometry. By inspection we find:

\[
\begin{align*}
2A &= 2A^* & v^1 &= 2 \\ 
A^* + B &= AB^* & v^2 &= 1 \\ 
AB^* + A &= R & v^3 &= 1 \\ 
2A + B &= R
\end{align*}
\] (22a)

2. Step 1 is rate limiting (given)

3. Set up equilibrium expressions for step 2 and 3

\[
K_{C_2} = \frac{k_{2f}}{k_{2b}} = \frac{C_{AB^*}}{C_{A^*}C_B}
\] (23a)

\[
K_{C_3} = \frac{k_{3f}}{k_{3b}} = \frac{C_R}{C_{AB^*}C_{A^*}} = \frac{C_R}{K_{C_2}C_A^*C_B}
\] (23b)

4. Set up the rate for the rate limiting step

\[
\begin{align*}
r_t &= k_f C_A - k_{1b} C_{A^*} \\
&= \frac{k_{1f}}{\sqrt{K_{C_2}K_{C_3}C_B}} \left( \frac{C_R^{1/2}}{C_R} \right)
\end{align*}
\] (24)

Using eq. (23b) and eliminating $C_{A^*}$ we get

\[
C_{A^*} = \sqrt{\frac{C_R}{K_{C_2}K_{C_3}C_B}}
\]

\[
r_t = k_{1f} C_A - \frac{k_{1b}}{\sqrt{K_{C_2}K_{C_3}C_B}} \frac{C_R^{1/2}}{C_R}
\] (24a)
5. The stoichiometric number of the rate limiting step is \( v' = s = 2 \) as per (eq. 22a). Thus, since \( R_R = \frac{v_R}{v'} r_i \)

\[
R_R = \frac{1}{2} r_i = \frac{k_{1f}}{2} C_A - \frac{k_{1b}}{2} \frac{C_R^{1/2}}{\sqrt{K_{C_2} K_{C_3}}} \frac{C_B^{1/2}}{C_B^{1/2}}
\]

(25)

6. Information not available.

Now suppose that in the same mechanism step 2 was rate limiting (i.e. arrows for the rate of step 2 now being much shorter than those in step 1 and 3).

We can quickly write the equilibrium relationships for step 1 and 3:

\[
K_{C1} = \frac{C_A^*}{C_A} = \frac{k_{1f}}{k_{1b}}
\]

(26a)

\[
K_{C3} = \frac{k_{3b}}{k_{3b}} = \frac{C_R}{C_A^* C_A^*}
\]

(26b)

and from these obtain the concentrations of the intermediates

\[
C_A^* = K_{C1} C_A
\]

(27a)

\[
C_{AB}^* = \frac{C_R}{K_{C1} K_{C3} C_A}
\]

(27b)

The rate for the rate limiting step (step 2) is:

\[
r_i = k_{2f} C_A^* C_B - k_{2b} C_{AB}
\]

(28)

\[
r_e = k_{2f} K_{C1} C_A C_B - k_{2b} \frac{C_R}{K_{C1} K_{C3} C_A} = \frac{k_{2f}}{K_{C1}} \frac{K_{C3}}{K_{C3}} \frac{C_R}{K_{C1} K_{C3} C_A} C_B - k_{2b} C_R
\]

(28a)

\[
R_R = r_e \text{ since } v' = 1
\]

(29)
Clearly this is an entirely different rate form than obtained previously based on step 1 being rate limiting.

**NOTA BENE 1:** It would be quite tedious to find the rate form for the above mechanism based on PSSA since when the net rates of formation of intermediates are set to zero we get nonlinear equations due to the product $C_{AB}^* C_A^*$ resulting from the rate forward in step 3. Try it anyway for an exercise.

**NOTA BENE 2:**

If the first step \( v^1 = 2 \) was rate limiting our rate form is given by

\[
R_R = \frac{k_{1f}}{2} C_A - k_{1b} \frac{C_B^{3/2}}{2 \sqrt{K_{C2} K_{C3}}} \frac{C_C^{3/2}}{C_B^{3/2}}
\]  

\[
= k_f C_A - k_b \frac{C_B^{3/2}}{C_B^{3/2}}
\]  

At equilibrium \( R_R = 0 \) so that

\[
\frac{k_f}{k_b} = \frac{k_{1f}}{k_{1b}} \sqrt{K_{C2} K_{C3}} = \frac{C_B^{1/2}}{C_A^{1/2} C_C^{1/2}}
\]  

Recall that \( \frac{k_{1f}}{k_{1b}} = K_{C1} \) \( (31a) \)

and that for the reaction \( 2A + B = R \) the equilibrium (concentration units) constant \( K_C \) is given by

\[
K_C = \frac{C_R}{C_A^2 C_B}
\]  

\( (31b) \)

Substituting eqs. \( 31a \) and \( 31b \) into eq. \( 30 \) we get

\[
\frac{k_f}{k_b} = K_{C1} \sqrt{K_{C2} K_{C3}} = K_C^{1/2}
\]  

\( (32) \)
Recall that \( \frac{k_f}{k_b} = K_c^p = K_c^{1/s} \), where \( s \) is the stoichiometric number of the rate determining step. Here \( s = v^1 = 2 \). Hence,

\[
K_c = K_{C_1}^2 K_{C_2} K_{C_3}
\]  \hspace{1cm} (33)

If the 2nd step \( (v^2 = 1) \) is rate limiting the rate form is given by eq. (28a)

\[
R_R = k_{2f} K_{C_1} C_A C_B - \frac{k_{2b}}{K_{C_1} K_{C_3} C_A} \frac{C_R}{C_A}
\]  \hspace{1cm} (28a)

\[
= k_f C_A C_B - k_b \frac{C_R}{C_A}
\]

so that at equilibrium \( R_R = 0 \)

\[
\frac{k_f}{k_b} = \frac{C_R}{C_A^2 C_B} = K_c
\]  \hspace{1cm} (33)

and \( K_c = \frac{k_{2f}}{k_{2b}} K_{C_1}^2 K_{C_3} = K_{C_1}^2 K_{C_2} K_{C_3} \)  \hspace{1cm} (33)

Let us go back to the reaction of decomposition of ozone \( 2O_3 = 3O_2 \). The mechanism was given before and let us assume that the 2nd step is rate limiting.

Then

\[
K_{C_1} = \frac{k_{1f}}{k_{1b}} = \frac{C_{O_2}}{C_{O_3}} \]  \hspace{1cm} (34a)

\[
C_{O^*} = K_{C_1} \frac{C_{O_3}}{C_{O_2}} \]  \hspace{1cm} (34b)

\[
r_i = k_2 C_{O^*} C_{O_3} = k_2 K_{C_1} \frac{C_{O_3}^2}{C_{O_2}} \]  \hspace{1cm} (35)
Now $v' = 1$ but $|v_{o_1}| = 2$

Thus, $-R_{o_3} = 2k_2 K_c C_{o_3}^2 \frac{C_{o_2}}{C_{o_2}} = \frac{2k_{i,f} K_2}{k_{b'}} C_{o_3}^2$ \hspace{2cm} (36)

Notice that this is the rate form obtained when using PSSA after certain additional assumptions were made. The rate form generated by the use of PSSA without additional assumptions is much more general. The above expression is its limiting case.

For multiple reactions, rate forms can be obtained by RLSA by the straightforward extension of the above rules.
6.3 HALF LIFE AND CHARACTERISTIC REACTION TIME

Based on either PSSA or RLSA we are usually able to derive a rate form for a particular reaction. Often n-th order rate form is obtained, say for reactant \(j\):

\[
(-R_j) = kC_j^n
\]

Then the characteristic reaction time is defined as \(\tau_g = \frac{1}{kC_j^{n-1}}\) and it is the time that it would take in a close system (batch) for the concentration \(C_j\) to decay to \(e^{-1}\) of its original value \(C_{jo}\).

The balance for reactant \(j\) in a closed system is \(\frac{dC_j}{dt} = -R_j\). So when the reaction is not n-th order the characteristic reaction time can be defined as \(\tau_g = \frac{C_{jo}}{R_{jo}}\) where the rate \(R_{jo}\) is evaluated at initial conditions.

**Half-life** is the time needed for the reactant (species) concentration to be reduced to half of its original value in a closed system. Integration of the species balance yields

\[
t_{1/2} = \int_{C_j}^{\bar{C}_j} \frac{dC_j}{R_j} = \int_{C_j}^{R_{jo}} \frac{dC_j}{R_{jo}} \left(\frac{1}{\overline{R}}\right) = \tau_g \int_{1}^{\bar{C}_j} \frac{dC_j}{\overline{R}}
\]

where \(\bar{C} = C_j / C_{jo}\) and \(\overline{R} = R_j / R_{jo}\).

The integration is performed by substituting into the above expression all concentrations in terms of \(C_j\) using the stoichiometric relations. For an n-th order reaction we get

\[
t_{1/2} = \frac{2^{n-1} - 1}{k(n - 1)C_j^{n-1}} = \frac{2^{n-1} - 1}{(n-1)\tau_g}
\]

For a first order process

\[
t_{1/2} = \frac{\ln 2}{k} = \tau_R \ln 2
\]