5. 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 determination of the apparent rate form at operating conditions of interest. Some pof the basic concepts are listed below.

Reaction Mechanism – is the sequence of elementary events that describes 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 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: $RCl \Leftrightarrow R^+ + Cl^-$ active center R^+; open sequence;

$R^+ + F^- \Leftrightarrow RF$ noncatalytic

Overall stoichiometry:

$RCl + F^- \Leftrightarrow RF + Cl^-$

Mechanism 2: $E + S \Leftrightarrow ES^*$ active center ES*; closed sequence;

$ES^* \Leftrightarrow E + P$ catalytic

Overall stoichiometry:

$$S \overset{E}{=} P$$

Nota Bene: There may be some confusion as to why the first mechanism is noncatalytic and the second is catalytic. In both cases, the active center is produced in the first reaction and consumed completely in the second reaction. However, the key to Mechanism 2 is species E: which is not part of the overall stoichiometry of the reaction, but is able to cycle through the reaction. E is consumed in step 1 to produce ES* and is then reproduced with P in step 2 from ES*. E can then again be used to form another molecule of ES*. This ability to reproduce the active center continuously makes Mechanism 2 catalytic. Upon examining Mechanism 1, there is no such cycle present, thus it is noncatalytic.

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:

$$M_1 \rightarrow 2R_1^*$$
$$R_1^* + M_1 \rightarrow M_2 + R_2^*$$
$$R_2^* \rightarrow R_1^* + M_3$$
$$2R_1^* \rightarrow M_1$$
$$R_2^* + R_1^* \rightarrow M_4$$
$$2R_2^* \rightarrow M_5$$
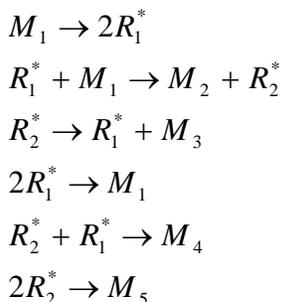
Steps 2 and 3 of the above mechanism form a closed (catalytic) sequence in which the active centers (intermediates, radicals) R_1^* *and* R_2^* are repeatedly regenerated.

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 for the single reaction under consideration which asserts that the change in moles of the reactants and products is tied by stoichiometry i.e molar extent X= $\dfrac{\Delta n_1}{-1} = \dfrac{\Delta n_2}{1} = \dfrac{\Delta n_3}{1}$. 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 or three steps. For example, if a single reaction stoichiometry is given by *2A = R* and the proposed two step mechanism is as shown below, then it is clear that the first step should be repeated twice (stoichiometric number $v^1 = 2$) in order to get the overall stoichiometry.

	Mechanistic Step	Stoichiometry of the Step	Stoichiometric Number
1.	$A + A \Leftrightarrow A^* + A$	$A = A^*$	2
2.	$A^* + A^* \Leftrightarrow R$	$2A^* = R$	1

Overall Stoichiometry: *2A = R*

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:

$$\sum_{j=1}^{S} v_j \, A_j = 0 \tag{1}$$

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:

$$\sum_{j=1}^{S^1} v_{ij} \, A_j = 0 \; \text{ for } \; i = 1, 2, 3...N \tag{2}$$

In order for the mechanism to be consistent with stoichiometry we must be able to find a set of stoichiometric numbers (multipliers) $v^i \; i = 1, 2,....N$ <u>not all zero</u> from the following set of linear equations:

$$\sum_{i=1}^{N} v^i \, v_{ij} = v_j \; \text{ for } \; j = 1, 2, 3...S^1 \tag{3}$$

where S^1 is the total number of species including active intermediates, <u>i.e.</u>, $S^1 = S + I$ where I is the total number of active intermediates. Naturally, the overall stoichiometric coefficients v_j for active intermediates $j = S + 1, S + 2, S + 3....., S^1 - 1, S^1$ must all be zero as they do not play a role in the overall reaction.

Example:

Mechanism:	Stoichiometry of each step:
$A + A \Leftrightarrow A^* + A$	$A = A^*$
$A^* + A^* \Leftrightarrow R$	$2A^* = R$
Overall Stoichiometry:	$2A = R$

A:	$-v^1 + 0 = -2$	$v^1 = 2$
R:	$0 + v^2 = 1$	$v^2 = 1$
I:	$v^1 - 2v^2 = 0$	

We now have a set of S^1 equations $\left(S^1 = S + I = 2 + 1 = 3\right)$ with N unknown mutipliers (stoichiometric numbers $\left(v^i \text{ for i} = 1,.., N\right) \, (N = 2)$. The nonzero solution exists if the matrix of stoichiometric coefficients v_{ij} has rank N. If that is the case, select N equations and solve for all v^i.

In the above simple example we have only one intermediate species (A^*) so that $I = 1$ and we have two stable species (A and R) so that $S = 2$ so that $S^1 = S + I = 3$. The mechanism consists of two steps so that $N = 2$ and we need to determine 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:

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$$\left(v^1 \; v^2\right)\begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -2 \end{pmatrix} = \left(-2 \; 1 \; 0\right) \tag{3a}$$

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

$$\begin{pmatrix} -1 & 0 & 1 \\ 0 & 1 & -2 \end{pmatrix}$$

and the nonzero solution for the $\left(v^1 \; v^2\right)$ vector is guaranteed if that matrix has rank 2 which it clearly does. The matrix multiplication in eq. (3a) results in 3 columns that are presented above which generate the solution for v^1 and v^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)

5.1. 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 $S^1 = S + I$ can be formally written as:

$$\sum_{i=1}^{N} v_{ij} \; r_i = 0 = R_j \text{ for } j = S+1,..S^1 \tag{4}$$

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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 concentrations of intermediates into the expression for the rate of a desired component j

we obtain the required rate form for that component j as shown by eq.(5)

$$R_j = \sum_{i=1}^{N} v_{ij} \; r_i$$

$$j = 1, 2, ... S$$

(5)

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. This minimizes the amount of algebra required.   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

$$2 \, O_3 = 3 \, O_2$$

(6)

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1.   The proposed mechanism consists of 2 steps:

$$O_3 \; \underset{k_{1b}}{\overset{k_{1f}}{\rightleftharpoons}} \; O_2 + O^* \tag{7a}$$

$$O^* + O_3 \; \xrightarrow{k_2} \; O_2 + O_2 \tag{7b}$$

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, O^*.

3.   The net rate of formation of O^* is:

$$R_{O^*} = k_{1f} \, C_{O_3} - k_{1b} \, C_{O_2} \, C_{O^*} - k_2 \, C_{O^*} \, C_{O_3} = 0 \tag{8}$$

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

$$C_{O^*} = \frac{k_{1f} \, C_{O_3}}{k_{1b} \, C_{O_2} + k_2 \, C_{O_3}} \tag{9}$$

5.   Since both O_2 and O_3 appear in both steps of the mechanism we can set up the rate of disappearance of ozone directly

$$-R_{O_3} = k_{1f} \, C_{O_3} - k_{1b} \, C_{O^*} \, C_{O_2} + k_2 \, C_{O^*} \, C_{O_3} \tag{10}$$

Substituting the expression for C_{O^*}, and finding the common denominator, leads to:

$$-R_{O_3} = \frac{k_{1f} k_{1b} C_{O_3} C_{O_2} + k_{1f} \, k_2 \, C_{O_3}^2 - k_{1f} k_{1b} C_{O_3} C_{O_2} + k_{1f} \, k_2 \, C_{O_3}^2}{k_{1b} \, C_{O_2} + k_2 \, C_{O_3}}$$

$$-R_{O_3} = \frac{2 k_{1f} \, k_2 \, C_{O_3}^2}{k_{1b} \, C_{O_2} + k_2 \, C_{O_3}} \tag{11}$$

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 $k_{1b} \, C_{O_2} \gg k_2 \, C_{O_3}$ the rate simplifies to:

$$-R_{O_3} \approx \frac{2\,k_{1f}\,k_2}{k_{1b}}\,\frac{C_{O_3}^2}{C_{O_2}} \tag{12}$$

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:

$$A + B = R \tag{13}$$

and the experimentally determined rate is

$$-R_A = k\,C_A^2 \tag{14}$$

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

1. $$A + A \xrightarrow{\;k_1\;} I \tag{15a}$$

$$I + B \xrightarrow{\;k_2\;} R + A \tag{15b}$$

2.   The mechanism is obviously consistent with the overall stoichiometry since a straight forward addition of steps leads to it. The number of intermediates is one, I.

3.   The net rate of formation of the intermediate is:

$$R_I = k_1\,C_A^2 - k_2\,C_I\,C_B = 0 \tag{16}$$

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

$$C_I = \frac{k_1\,C_A^2}{k_2\,C_B} \tag{17}$$

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

$$R_R = k_2\,C_I\,C_B \tag{18}$$

Eliminating C_I we get

$$R_R = k_1\,C_A^2 \tag{19}$$

6.   From stoichiometry

$$\frac{-R_A}{1} = \frac{R_R}{1} = k_1\,C_A^2 \tag{20}$$

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_1 on I. If we were to write the rate of disappearance of A,

$$- R_A = 2k_1\, C_A^2 - k_2\, C_I\, C_B \tag{21}$$

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_1 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_1 in step 3 and there would be no 2 but 1 in front of k_1 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 $- R_A$ in eq. (21) did not have a $2\,k_1$ but k_1, while R_I was as given, they would be identically equal to each other and thus asserting $R_I = 0$ would be asserting that $- R_A = 0$, which is absurd since $- R_A = R_R$ which is a respectable expression. This demonstrates the importance of <u>not</u> 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.

The application of PSSA to multiple reactions is a straightforward extension of the above procedure.
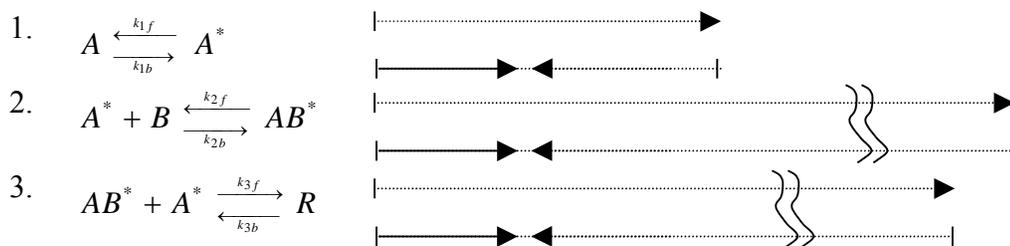

5.2   RATE LIMITING STEP ASSUMPTION (RLSA)

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 <u>rate limiting step</u> 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 ┄┄►, 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. $A \xrightleftharpoons[k_{1b}]{k_{1f}} A^*$

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

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

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 ($\longrightarrow$) in comparison to the total rate forward ($\cdots\cdots>$) and total reverse rate ($<\cdots\cdots$) 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 Christiansen 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:

$$2A = 2A^* \qquad\qquad v^1 = 2 \qquad\qquad\qquad\qquad\qquad\qquad (22a)$$

$$A^* + B = AB^* \qquad\quad v^2 = 1 \qquad\qquad\qquad\qquad\qquad\qquad (22b)$$

$$\underline{AB^* + A^* = R \; v^3 = 1 \qquad (22c)}$$

$$2A + B = R$$

2. Step 1 is rate limiting (given)

3. Set up equilibrium expressions for step 2 and 3

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

$$K_{C_3} = \frac{k_{3f}}{k_{3b}} = \frac{C_R}{C_{AB^*} \, C_{A^*}} = \frac{C_R}{K_{C_2} \, C_{A^*}^2 \, C_B} \qquad\qquad (23b)$$

4. Set up the rate for the rate limiting step

$$r_\ell = k_f \, C_A - k_{1b} \, C_{A^*} \qquad\qquad\qquad\qquad\qquad\qquad (24)$$

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

$$C_{A^*} = \sqrt{\frac{C_R}{K_{C_2} \, K_{C_3} \, C_B}}$$

$$r_\ell = k_{1f} \, C_A - \frac{k_{1b}}{\sqrt{K_{C_2} \, K_{C_3}}} \frac{C_R^{1/2}}{C_B^{1/2}} \qquad\qquad\qquad\qquad (24a)$$

5. The stoichiometric number of the rate limiting step is $v^\ell = s = 2$ as per (eq. 22a). Thus, since

$$R_R = \frac{v_R}{|v^\ell|} \, r_\ell$$

$$R_R = \frac{1}{2} \, r_\ell = \frac{k_{1f}}{2} \, C_A - \frac{k_{1b}}{2\sqrt{K_{C_2} \, K_{C_3}}} \frac{C_R^{1/2}}{C_B^{1/2}} \qquad\qquad (25)$$

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:

$$K_{C1} = \frac{C_A^*}{C_A} = \frac{k_{1f}}{k_{1b}} \tag{26a}$$

$$K_{C3} = \frac{k_{3f}}{k_{3b}} = \frac{C_R}{C_{AB}^* C_A^*} \tag{26b}$$

and from these obtain the concentrations of the intermediates as

$$C_A^* = K_{C1} C_A \tag{27a}$$

$$C_{AB}^* = \frac{C_R}{K_{C1} K_{C3} C_A} \tag{27b}$$

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

$$r_\ell = k_{2f} C_{A^*} C_B - k_{2b} C_{AB^*} \tag{28}$$

$$r_e = k_{2f} K_{C1} C_A C_B - \frac{k_{2b}}{K_{C1} K_{C3}} \frac{C_R}{C_A} = \frac{k_{2f} K_{C1}^2 K_{C3} C_A^2 C_B - k_{2b} C_R}{K_{C1} K_{C3} C_A} \tag{28a}$$

$$R_R = r_e \text{ since } v^\ell = 1 \tag{29}$$

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 <u>nonlinear</u> 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 $\left(v^1 = 2\right)$ was rate limiting our rate form is given by

$$R_R = \frac{k_{1f}}{2} C_A - \frac{k_{1b}}{2\sqrt{K_{C2} K_{C3}}} \frac{C_R^{1/2}}{C_B^{1/2}} \tag{25}$$

$$= k_f C_A - k_b \frac{C_R^{1/2}}{C_B^{1/2}}$$

At equilibrium $R_R = 0$ so that

$$\frac{k_f}{k_b} = \frac{k_{1f}}{k_{1b}} \sqrt{K_{C2} K_{C3}} = \frac{C_R^{1/2}}{C_A C_B^{1/2}} \tag{30}$$

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

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

$$K_C = \frac{C_R}{C_A^2 \, C_B} \tag{31b}$$

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

$$\frac{k_f}{k_b} = K_{C1} \sqrt{K_{C2} \, K_{C3}} = K_C^{1/2} \tag{32}$$

Recall that $\dfrac{k_f}{k_b} = K_C^P = K_C^{\frac{1}{s}}$ where s is the stoichiometric number of the rate determining step. Here $s = v^1 = 2$. Hence,

$$K_C = K_{C1}^{\,2} \, K_{C2} \, K_{C3} \tag{33}$$

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

$$R_R = k_{2f} \, K_{C1} \, C_A \, C_B - \frac{k_{2b}}{K_{C1} \, K_{C3}} \frac{C_R}{C_A} \tag{28a}$$

$$= k_f \, C_A \, C_B - k_b \frac{C_R}{C_A}$$

so that at equilibrium $R_R = 0$

$$\frac{k_f}{k_b} = \frac{C_R}{C_A^{\,2} \, C_B} = K_C{}' \tag{33}$$

And $K_C{}' = \dfrac{k_{2f}}{k_{2b}} K_{C1}^{\,2} \, K_{C3} = K_{C1}^{\,2} \, K_{C2} \, K_{C3} \tag{33}$

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

$$K_{C1} = \frac{k_{1f}}{k_{1b}} = \frac{C_{O2} \, C_{o^*}}{C_{O3}} \tag{34a}$$

$$C_{o^*} = K_{C1} \frac{C_{O3}}{C_{O2}} \tag{34b}$$

$$r_\ell = k_2 C_{o^*} C_{O3} = k_2 K_{C1} \frac{C_{O3}^2}{C_{O2}} \tag{35}$$

Now $v^\ell = 1$ but $\left| v_{O_3} \right| = 2$

Thus, $-R_{O3} = 2k_2\ K_{C1} \dfrac{C_{O3}^2}{C_{O2}} = \dfrac{2k_{1f}\ K_2}{k_{1b}} \dfrac{C_{O3}^2}{C_{O2}}$ $\hspace{2cm}$ (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.

5.3   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:

$$\left(-R_j \right) = kC_j^n \tag{37}$$

Then the **<u>characteristic reaction time</u>** is defined as $\tau_R = \dfrac{1}{kC_{jo}^{\,n-1}}$ and it is the time that it would take in a closed 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 $\dfrac{dC_j}{dt} = -R_j$. So when the reaction is not n-th order the characteristic reaction time can be defined as $\tau_R = \dfrac{C_{jo}}{-R_{jo}}$ 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

$$t_{1/2} = \int_o^{t_{1/2}} dt = \int_{\frac{C_{jo}}{2}}^{C_{jo}} \frac{dC_j}{-R_j} = \frac{C_{jo}}{-R_{jo}} \int_{\frac{1}{2}}^{1} \frac{d\bar{c}}{\bar{R}} = \tau_R \int_{\frac{1}{2}}^{1} \frac{d\bar{c}}{\bar{R}} \tag{38}$$

where $\bar{c} = C_j / C_{jo}$ and $\bar{R} = R_j / R_{jo}$.

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

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)C_{jo}^{n-1}} = \frac{2^{n-1} - 1}{(n-1)} \tau_R \tag{39}$$

For a first order process

$$t_{1/2} = \frac{\ln 2}{k} = \tau_R \ln 2 \tag{39a}$$

5.4   COMPARTMENTAL MODELING OF SINGLE PHASE SYSTEMS

We should note that in developing the rate forms based on mechanisms we have so far assumed that we deal with a system of constant mass consisting of fixed amounts of various atomic species. These atomic species are constituents of chemical species (components) that participate in elementary chemical reactions taking place in the system. These chemical species are either stable, and present in measurable concentrations (e.g. reactants and products), or are active intermediates present in much smaller concentrations. The volume of the system (i.e. of the invisible envelope that engulfs our constant mass) is small enough that molecules are free to interact by molecular motion so that concentration or temperature gradients can never develop in the system. Hence, the system is <u>well mixed</u>. Moreover, the system is <u>closed</u> since no exchange of mass occurs across system's boundaries.

We extend this approach now to modeling of isothermal, single phase systems of arbitrary volume. We assume that the volume of the system is perfectly mixed at all times so that there never are any spatial composition gradients in the system.

We can apply then the basic conservation law to quantities of the system that are conserved (e.g. mass, species mass, energy etc.) that states:

$$\left(\text{Rate of accumulation}\right) = \left(\text{Rate of input}\right) - \left(\text{Rate of output}\right) + \left(\text{Rate of generation}\right) \tag{40}$$

Such a well mixed system, to which we apply equation (40) often is called a compartment - hence, the name compartmental modeling. We can have closed systems (no exchange of mass across system's boundary) and open systems (that exchange mass with the surroundings).

Here we focus only on single phase systems and we start by developing the governing equation for a closed system.

A sketch of a closed system is shown below:

SYSTEM OF
- VOLUME V
- MASS M

At time $t = 0$ $c_j = c_{jo}$
At time $t = t$ $c_j(t)$

- Total mass of the system $M\ (kg) = const$
- Total volume of the system $V\ (m^3)$ may vary in time
- $c_j \left(\dfrac{mol\ j}{m^3} \right) = n_j / V$ molar concentration of species j in the system at time t

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$-\ R_j\left(\dfrac{mol}{m^3\,s}\right)$ = reaction rate of j

For a well mixed closed system the species mass balance for species j can be written as:

$$\frac{d(VC_j)}{dt} = VR_j \qquad ; \qquad t = 0,\ C_j = C_{jo} \tag{41}$$

where

$C_j\left(\dfrac{mol\ j}{L}\right)$ = molar concentration of j at time t

V(L) = volume of the system

t (s) = time

$R_j\left(\dfrac{mol\ j}{L\,s}\right)$ = reaction rate of production of species j (if j is a reactant $R_j < 0$)

$C_{jo}\left(\dfrac{mol\,j}{L}\right)$ = initial concentration of species j

Note: units of time instead of seconds could be minutes, hours or days; volume could be measured in m^3, etc.

If the volume of the system is constant V = const, eq. (41) is reduced to:

$$\frac{dC_j}{dt} = R_j \qquad ; \qquad t = 0,\ C_j = C_{jo} \tag{41a}$$

If we have R reactions occurring in the system, then their stoichiometry is given by:

$$\sum_{j=1}^{s} \upsilon_{ij} A_j = 0 \ ; \ i = 1,2,...R \tag{42}$$

here υ_{ij} = stoichiometric coefficient of species j in reaction i (recall $\upsilon_{ij} > 0$ products, $\upsilon_{ij} < 0$ reactants) and S = total number of stable species in the system.

Often, in chemical as well as in environmental systems such as encountered in air or water pollution, the set of R reactions is extended to include all active intermediate species (their total number is S' previously we called the total number of intermediates I) that are linked among themselves and with stable species via a large set of R' elementary reactions based on the proposed mechanism. (Note $R' >$ R).

This augmented set of R' elementary reactions arising from the mechanism can be written as

$$\sum_{j=1}^{S+S'} \upsilon_{ij}^m A_j = 0 \ ; \ i = 1,2,...R' \tag{43}$$

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where υ_{ij}^{m} is the stoichiometric coefficient of chemical species j (including both stable species and active intermediates for j=1, 2,, S, S+1, S+2, ..S') in the mechanistic step involving reaction i for i=1, 2,..R' .

There are two ways now to proceed.

a)   An <u>exact</u> solution can be obtained by solving equation (41a) for all the S + S' species, stable as well as active intermediates, <u>i.e</u> for j = 1,2,3...S,S+1, S+2...S+S'. This can be stated as:

$$\frac{dC_j}{dt} = R_j = \sum_{i=1}^{R'} \upsilon_{ij}^{m} r_i \quad ; \quad t = 0, \; C_j = C_{jo} \tag{44}$$

For j = 1,2,...S, S + 1... (S' + S)

where r_i is the reaction rate of the elementary reaction i in the proposed mechanism for which the rate constant is evaluated from transition state theory (TST) or by other appropriate means. For each of the stable compounds (j = 1, 2,...S) the initial concentration, C_{jo}, is known, for all active intermediates (j = S + 1, S + 2...S + S') the initial concentration is zero, $C_{jo} = 0$.

This set of S'+ S differential equations given by eq. (44)) results in a **stiff system** of differential equations which must be solved by an appropriate computer package. Numerical solution is almost always required. The stiffness (vastly different eigenvalues) is caused by a wide range of time constants for various reactions. The results can be displayed for active intermediates as well as stable compounds as functions of time.

b)   An <u>approximate</u> solution can be obtained by using PSSA. For all active intermediates we set

$$R_j = \sum_{i=1}^{R'} v_{ij}^{m} r_i = 0 \qquad \text{for j = S + 1, S + 2,...S + S'} \tag{45}$$

From the resulting S' algebraic equations (often nonlinear) we evaluate the S' concentrations of active intermediates which then can be substituted into the rate forms for stable species. Only S differential equations given by eq.(46) below, of the type given above by eq. (44), need to be solved now instead S+S':

$$\frac{dC_j}{dt} = R_j = \sum_{i=1}^{R} \upsilon_{ij} r_i^{o} \quad ; \quad t = 0, \; C_j = C_{jo} \tag{46}$$

    only for the S stable species (j = 1,2,3...S).

The reaction rate for reaction i among stable species, r_i^{o} , is now obtained from the mechanism by applying PSSA and eliminating the concentrations of active intermediates. These expressions for r_i^{o} can be of rather complex form depending on the relationship between concentrations of active intermediates and those of stable species which result from the solution of algebraic equations Eq.(45). Upon solution of the differential equations (46) for the concentrations of the stable species these can be displayed as function of time. The concentrations of the active intermediates can then be calculated from the solution of equation (45) and are constant in time. <u>Nota bene</u>: More complex dynamic behavior with limit cycles, etc., can also be encountered. Concentrations of active intermediates are always small.

2.   **Open System**

A sketch of the open system is shown below:

$$\begin{array}{ccc} \xrightarrow{\quad Q_{in}\quad} & \boxed{\begin{array}{c}\text{SYSTEM OF}\\ \text{MASS } M\\ \text{VOLUME } V\end{array}} & \xrightarrow{\quad Q_{out}\quad}\\ C_{jin} & & C_{jout} \end{array}$$
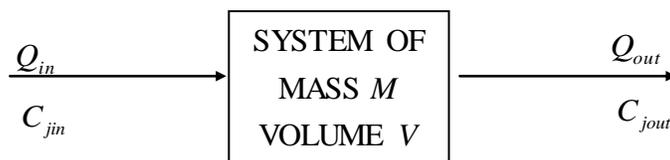
-     $Q_{in}\left(m^3/s\right)$ = volumetric flow rate in
-     $Q_{out}\left(m^3/s\right)$ - volumetric flow rate out
-     $C_{j\,out} \equiv C_j$ for all j. Outlet of perfectly mixed system is representative of system's content.

In the open system all the species are brought in and out across the system's boundary. We will assume here that this happens by convection only, and that the volumetric flow rate in and out is the same, $Q\left(L/s\right)=Q_{in}=Q_{out}$.

The species balance which is based on the basic conservation equation (40) can be written as:

$$V\frac{dC_j}{dt} = R_j V + Q\left(C_{j_{in}} - C_j\right); t = 0, C_j = C_{jo} \tag{47}$$

where $C_{j_{in}}\left(\dfrac{mol\,j}{L}\right)$ is the concentration of species j in the incoming (feed) flow. Due to the assumption of perfect mixing the concentration of j in the exit flow is the same as the concentration C_j of j at that time in the system. The rate R_j is given as before. Again one can go for the exact solution by applying eq (47) to all species, j = 1, 2, 3...S + S'. Or one can attempt a PSSA solution by setting $R_j = 0$ for j = S + 1, S + 2,...S + S' and by solving eq (47) for j = 1, 2...S for the stable species only.
An open system can reach steady state when $\dfrac{dC_j}{dt} = 0$ and then

$$(-R_j)V = Q\left(C_{j_{in}} - C_j\right) \tag{47a}$$

In complex reaction networks true steady state may never be reached as cycles set in.

We can apply now the compartmental single phase model to gaseous systems contained in a vessel, in a room, urban atmosphere or in the whole atmosphere. The underlying assumption is then that in the volume we have chosen mixing is perfect so that no composition spatial gradients occur at any time. Otherwise we must divide the system into a number of compartments and describe the flows between them.

Let us consider some gas phase atmospheric reactions next.

5.5   GAS-PHASE ATMOSPHERIC REACTIONS

Atmosphere is an oxidizing environment with abundance of solar energy (during day time hours) so that the pollutants are continuously brought to a higher and higher oxidation state. Hydrocarbons are reacted to aldehydes, then acids, then CO_2. Sulfur containing compounds are oxidized to SO_2 and ultimately to H_2SO_4. Ammonia and other nitrogen containing species are oxidized to NO, then NO_2 and HNO_3.

5.5.1   <u>Atmospheric Photochemical Reactions</u>

These are initiated by absorption of a photon by an atom, molecule, radical or ion.

$$A + h\nu \xrightarrow{\ k\ } A^*$$
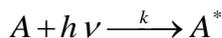
The excited activated molecule (radical), A^*, can participate in four different reaction types

dissociation	$A^* \xrightarrow{\ k_1\ } B_1 + B_2$	(1)
direct reaction	$A^* + B \xrightarrow{\ k_2\ } C_1$	(2)
fluorescence	$A^* \xrightarrow{\ k_3\ } A + h\nu$	(3)
collisional deactivation	$A^* + M \xrightarrow{\ k_4\ } A + M$	(4)

Reactions (1) and (2) lead to chemical change while (3) and (4) return the molecule to its ground state.

The quantum yield, ϕ_i , of a process (i = 1 to 4) is defined as the ratio of the number of radicals A^* reacting by that process to the number of photons absorbed.

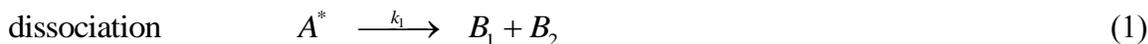The active intermediate A^* is short lived so that PSSA applies

$$0 = R_{A^*} = k[A] - k_1\left[A^*\right] - k_2\left[A^*\right][B] - k_3\left[A^*\right] - k_4\left[A^*\right][M]$$

$$\left[A^*\right] = \frac{k[A]}{k_1 + k_2[B] + k_3 + k_4[M]}$$

The rate of formation of [A^*] by absorption of light is $k[A]$ where k is the specific absorption rate (k first order rate constant independent of [A]).

Using the quantum yield definition for the above four processes we can write

$$R_{B_1} = k_1\left[A^*\right] = \phi_1 k[A]$$
$$R_{C_1} = k_2\left[A^*\right][B] = \phi_2 k[A]$$
$$R_A = k_3\left[A^*\right] = \phi_3 k[A]$$
$$R_A = k_4\left[A^*\right][M] = \phi_4 k[A]$$

So that $\displaystyle\sum_{i=1}^{4} \phi_i = 1$.

The solar flux, or actinic irradiance, F , (photons/cm^{2}s) is the radiation intensity striking a unit area of surface per unit time.

$$dF = I(\lambda)\,d\lambda$$

where $I(\lambda)d\lambda$ = actinic irradiance in the wave length range (λ *to* $\lambda + d\lambda$) so that the actinic irradiance density $I(\lambda)$ is in (photons/cm³s).

We are most interested in dissociation reactions for which the first order rate constant is given by

$$k_1 = \int_{\lambda_1}^{\lambda_2} \sigma_A(\lambda,T)\,\phi_A(\lambda,T)\,I(\lambda)\,d\lambda$$

where

$\sigma_A(\lambda,T)$ = absorption cross-section of A at wave length λ and temperature T

$\phi_A(\lambda,T)$ = the quantum yield or probability that molecule A decomposes on absorbing radiation of wave length λ at temperature T.

The integral is usually approximated by summation. In the troposphere the wave lengths of interest are 280 nm $< \lambda <$ 730 nm. Stratosphere O_2 and O_3 block out most small wave lengths $\lambda <$ 280 nm. No chemistry occurs at $\lambda >$ 730 nm. Absorption cross-sections and quantum yields are measured in laboratory. (Examples are shown in Figures 1 and 2). The major variable is the intensity change that occurs as a function of time of day, latitude, time of year and state of the atmosphere (e.g. humidity, cloudiness, particulates, etc.). Solar flux as a function of λ is shown in Figure 3. In the US maximum noontime, intensity in summer months is about 2×10^{16} (photons/cm²s) in the 300-400 nm range and is close to this value for 4-6 hours. In winter, 0.7×10^{16} to 1.5×10^{16} (photons/cm²s) are typical values depending on the latitude.

Major photo dissociating species in the lower atmosphere are summarized in Table 1.

FIGURE 1:   **Absorption cross section for O_3 and NO_2 in the uv and visible regions of the spectrum (Luther and Gelinas, 1976)**

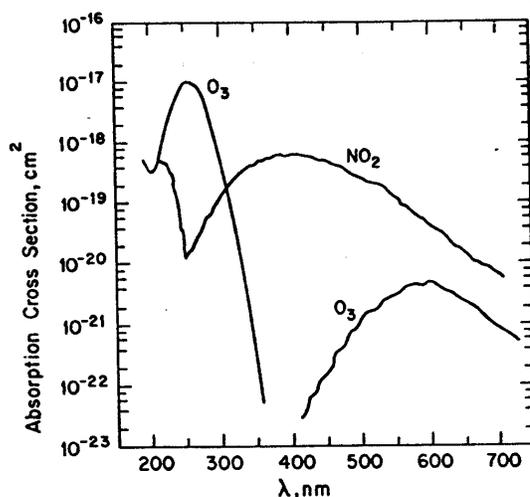**FIGURE 2:** **Experimental quantum yield data for the production of atomic oxygen (O) from the photolysis of NO$_2$ as a function of wavelength. The dashed line represents the quantum yields suggested by Demerjian et al. 1980).**
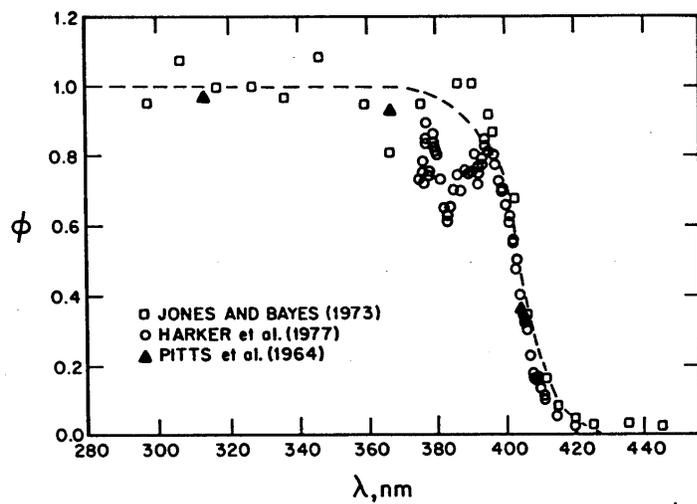
FIGURE 3:   Direct solar flux at 0 and 15 km as a function of wavelength (National Center for Atmospheric Research, 1982).
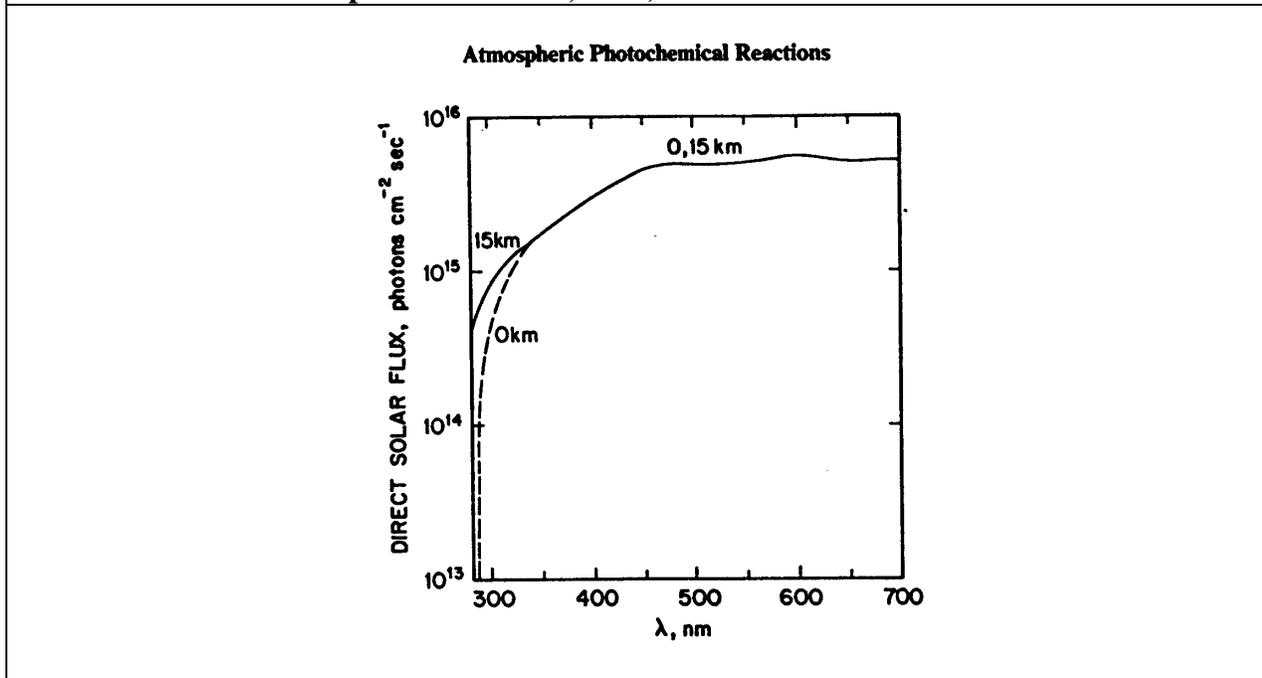

Atmospheric Photochemical Reactions

TABLE 1: Major photodissociating species in the lower atmosphere.

Species	Reactions	Comments
NO_2	$NO_2 + h\nu \rightarrow NO + O$	Because of the atmospheric importance of NO_2 photolysis, considerable research effort has been devoted to its understanding. The literature reviews of Baulch et al. (1982), DeMore et al. (1982), and Atkinson and Lloyd (1984) all recommend the use of the absorption cross-section data of Bass et al. (1976) for the range 290–400 nm and the quantum yield measurements of Harker et al. (1977) in the 375–420 nm region. For shorter wavelengths (295–365 nm) Baulch et al. (1982) and DeMore et al. (1982) suggest the use of the formula $$\phi(\lambda) = 1.0 - 0.0008(\lambda - 275)$$ Atkinson and Lloyd (1984) recommend a slightly different expression $$\phi(\lambda) = 1.0 - 0.0025(\lambda - 295)$$ and Demerjian et al. (1980) use a best fit to a range of different experimental measurements. Atkinson and Lloyd (1984) state that current determinations of $\phi(\lambda)$ and $\sigma(\lambda)$ are accurate to within ± 10–15 percent. The published photolysis rates of Demerjian et al. (1980) provide a suitable basis for establishing NO_2 photolysis rates.
$O_3{}^a$	$O_3 + h\nu \rightarrow O(^3P) + O_2$ $315 \leq \lambda \leq 1200$ nm $\rightarrow O(^1D) + O_2$ $\lambda \leq 315$ nm	Ozone has a bond energy of 26 kcal mole^{-1}. Solar photons having wavelengths between 315 and 1200 nm can dissociate O_3 and produce an oxygen atom in its ground electronic state $O(^3P)$. When O_3 absorbs a photon in the near ultraviolet with wavelengths shorter than 315 nm, an electronically excited oxygen atom, the singlet oxygen atom, $O(^1D)$, is formed. The $O(^1D) \rightarrow O(^3P)$ transition is forbidden, so $O(^1D)$ must react with other species. Information needed to calculate the diurnal variation of O_3 photolysis rate constants is available in Demerjian et al. (1980) and Baulch et al. (1982). Whereas the accuracy of O_3 absorption cross-section data is excellent, there are more uncertainties associated with the wavelength dependence of the O_3 quantum yields for the various photolysis paths, especially those leading to $O(^1D)$ (Atkinson and Lloyd, 1984).
HNO_2	$HNO_2 + h\nu \rightarrow NO + OH$	The photolysis of nitrous acid (HNO_2) is important in atmospheric chemistry because it is a source of hydroxyl (OH) radicals. On the basis of the work by Cox and Derwent (1977), Demerjian et al. (1980), Baulch et al. (1982), and DeMore et al. (1982) all recommend a value

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TABLE 1 CONTINUED:

		of unity for the quantum yield of the reaction over the wavelength range 300–400 nm. The recommended absorption cross-section measurements are those of Stockwell and Calvert (1978).
H_2O_2	$H_2O_2 + h\nu \rightarrow 2OH$	The absorption cross sections used by Demerjian et al. (1980) for calculating the H_2O_2 photolysis rates over the range 200–350 nm are based on Molina et al. (1977). These values are slightly higher (5%) than the current recommendations of DeMore et al. (1982). For the purposes of atmospheric calculations the published photolysis rates of Demerjian et al. (1980) are sufficiently accurate.
NO_3	$NO_3 + h\nu \rightarrow NO + O_2$ $\rightarrow NO_2 + O$	Recommended values (DeMore et al., 1982): Quantum yield—Magnotta and Johnston (1980); Absorption cross-section—Graham and Johnston (1978).
HCHO	$HCHO + h\nu \overset{a}{\underset{b}{\rightarrow}} HCO + H$ $\rightarrow CO + H_2$	Formaldehyde photolysis is a significant source of free radicals in the urban atmosphere. The current recommendations of Baulch et al. (1982) for HCHO absorption cross sections are to use an average of the results from Bass et al. (1980) and Moortgat et al. (1980). The relative quantum yields for the production of radicals (H and HCO) and molecular products (H_2 and CO) exhibit a complex variation as a function of wavelength. The peak radical production occurs at 300 nm and path (b) becomes the dominant pathway above 320 nm. Despite these complexities there are only minor variations among the quantum yields recommended by DeMore et al. (1982), Baulch et al. (1982), and Atkinson and Lloyd (1984).
CH_3CHO	$CH_3CHO + h\nu \rightarrow CH_3 + HCO$	Like HCHO, the photolysis of acetaldehyde is a significant source of free radicals in the urban atmosphere. Recommended Values (Baulch et al., 1982): Quantum Yield—Horowitz and Calvert (1982); Absorption Cross-Section—Calvert and Pitts (1967) and Weaver et al. (1977).
$CH_3C(O)CH_3$	$CH_3C(O)CH_3 + h\nu \rightarrow CH_3 + CH_3CO$	
$CH_3CH_2C(O)CH_3$	$CH_3CH_2C(O)CH_3 + h\nu \rightarrow C_2H_5 + CH_3CO$ $\rightarrow CH_3 + C_2H_5CO$	Recommended values (Atkinson and Lloyd, 1984): Quantum yield—$\phi(\lambda) = 0.33$ for acetone $\phi(\lambda) = 1.00$ for methylethylketone; Absorption Cross-section— Calvert and Pitts (1967).

[a] Two electronic states of the oxygen atom are important in atmospheric chemistry: the unexcited and first-excited electronic states, triplet-P oxygen atoms $O(^3P)$, and singlet-D oxygen atoms $O(^1D)$, respectively. The dissociation of NO_2 upon light absorption in the wavelength range 290–430 nm yields an oxygen atom in the triplet-P state. It is this form to which our attention will be mainly focused. The singlet-D oxygen atom, which is much more reactive than the ground-state triplet-P oxygen atom, can be formed by ozone photolysis in the wavelength range < 315 nm.

From J. Seinfeld. Air Pollution

5.5.2 Ozone Formation - NO$_x$ Route

When nitrogen oxides (NO or NO$_2$) are present in sunlight, ozone formation occurs as the result of NO$_2$ photolysis. The mechanism is as follows:

$$NO_2 + h\nu \xrightarrow{\quad k_1 \quad} NO + O \tag{1}$$

$$O + O_2 + M \xrightarrow{\quad k_2 \quad} O_3 + M \tag{2}$$

$$O_3 + NO \xrightarrow{\quad k_3 \quad} NO_2 + O_2 \tag{3}$$

This is an entirely closed cycle in which the energy is ultimately absorbed by the third body, M , and no overall change occurs. However, the dynamics of the system are of interest in determining if one starts with a certain concentration of $[NO]_o$ and $[NO_2]_o$ what would the peak concentration of ozone $[O_3]_{max}$ be. Clearly PSSA implies

$$R_O = k_1 [NO_2] - k_2 [O_2][M][O] = 0$$

$$[O] = \frac{k_1 [NO_2]}{k_2 [O_2][M]}$$

Since $[O_2]$, $[M]$ are large and approximately constant we see that $[O]$ adjusts itself rapidly by following $[NO_2]$.

A species balance for ozone in a closed system (i.e system of constant volume with no exchange with surroundings) yields

$$\frac{d[O_3]}{dt} = R_{O_3} = k_2 [O][O_2][M] - k_3 [O_3][NO]$$

Upon substitution of $[O]$ in the above we get

$$\frac{d[O_3]}{dt} = R_{O_3} = k_1 [NO_2] - k_3 [O_3][NO]$$

Similarly making a balance on NO and NO_2 we get

$$\frac{d[NO]}{dt} = R_{NO} = k_1 [NO_2] - k_3 [O_3][NO]$$

$$\frac{d[NO_2]}{dt} = R_{NO_2} = - k_1 [NO_2] + k_3 [O_3][NO]$$

From the above it is evident that

$$\frac{d}{dt}\{[O_3] - [NO]\} = 0$$

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so that

$$[O_3] - [O_3]_o = [NO] - [NO]_o$$

It is also evident that

$$\frac{d}{dt}\{[NO] + [NO_2]\} = 0$$

so that

$$[NO] - [NO]_o = [NO_2]_o - [NO_2]$$

Using these relations we eliminate both concentrations of NO and NO_2 in terms of the concentration of ozone and of the initial concentrations indicated by subscript o

$$[NO] = [NO]_o - [O_3]_o + [O_3]$$
$$[NO_2] = [NO_2]_o + [O_3]_o - [O_3]$$

which yields the following rate of change of ozone concentration for any starting mixture

$$\frac{d[O_3]}{dt} = k_1\{[NO_2]_o + [O_3]_o - [O_3]\} - k_3[O_3]([NO]_o - [O_3]_o + [O_3])$$

At $t = 0$ $[O_3] = [O_3]_o$

We are at the moment only interested in the maximum ozone concentration which occurs at the pseudostationary state i.e when $\frac{d[O_3]}{dt} = 0$. We can also look at it as the PSSA solution to the problem if we assume O_3 also to be an active intermediate. This is justified since its concentration is always much smaller than that of oxides of nitrogen. Now we get:

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]} = \frac{k_1([NO_2]_o + [O_3]_o - [O_3])}{k_3([NO]_o - [O_3]_o + [O_3])}$$

Solving the resulting quadratic equation for $[O_3]$ results in:

$$[O_3] = \frac{1}{2}\sqrt{\left([NO]_o - [O_3]_o + \frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}([NO_2]_o + [O_3]_o)}$$
$$- \frac{1}{2}\left([NO]_o - [O_3]_o + \frac{k_1}{k_3}\right)$$

If $[NO]_0 = [O_3]_0 = 0$ then the above simplifies to the following:

$$[O_3] = \frac{1}{2}\left(\sqrt{\left(\frac{k_1}{k_3}\right)^2 + \frac{4k_1}{k_3}[NO_2]_o} - \frac{k_1}{k_3}\right)$$ (*)

Since $k_1 / k_3 = 0.01$ ppm we get from equation (x)

$$
\begin{array}{llccc}
[NO_2]_o & ppm & 0.1 & 1.0 & 10 \\
[O_3]_{max} & ppm & 0.027 & 0.095 & 0.311
\end{array}
$$

If we take $[NO_2]_o = [O_3]_o = 0$ then $[O_3] = 0$ since ozone formation cannot get started.

The maximum ozone concentration is achieved when the initial charge contains only NO_2 in air. Nevertheless, the mechanism consisting solely of eqs (1-3) does not explain the level of ozone concentrations encountered (i.e it underpredicts them) and needs to be modified.

5.5.3 Photolysis Rate of NO₂

We want to find the photolysis rate constant k_1 from experimental measurement in a closed system. To understand the dynamics of NO_2 photolysis let us add the following 6 mechanistic steps to the previously considered three step mechanism:

$$O + NO_2 \xrightarrow{k_4} NO + O_2$$ (4)
$$O + NO_2 + M \xrightarrow{k_5} NO_3 + M$$ (5)
$$NO + NO_3 \xrightarrow{k_6} 2NO_2$$ (6)
$$O + NO + M \xrightarrow{k_7} NO_2 + M$$ (7)
$$NO_2 + NO_3 + M \xrightarrow{k_8} N_2O_5 + M$$ (8)
$$N_2O_5 \xrightarrow{k_9} NO_2 + NO_3$$ (9)

Inclusion of a third body M indicates a third order reaction.

Our experience and measurements in this system indicates that O, O_3, NO_3 and N_2O_5 can be treated as active intermediates since their concentrations are much smaller than those of the other species. Applying PSSA to these 4 species we get

$$R_O = r_1 - r_2 - r_4 - r_5 - r_7 =$$
$$\qquad k_1[NO_2] - k_2[O][O_2][M] - k_4[O][NO_2] - k_5[O][NO_2][M] - k_7[O][NO][M] = 0$$
$$R_{O_3} = r_2 - r_3 = k_2[O][O_2][M] - k_3[O_3][NO] = 0$$
$$R_{NO_3} = r_5 - r_6 - r_8 + r_9 = k_5[O][NO_2][M] - k_6[NO][NO_3]$$
$$\qquad - k_8[NO_2][NO_3][M] + k_9[N_2O_5] = 0$$
$$R_{N_2O_5} = r_8 - r_9 = k_8[NO_2][NO_3][M] - k_9[N_2O_5] = 0$$

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From $R_{N_2O_5} = 0$ we get

$$[N_2O_5] = \frac{k_8}{k_9}[NO_2][NO_3][M]$$

From $R_{NO_3} = 0$ we get

$$[NO_3] = \frac{k_5[O][NO_2][M]}{k_6[NO]}$$

which substituting in the above yields

$$[N_2O_5] = \frac{k_5 k_8 [O][NO_2]^2[M]^2}{k_6 k_9 [NO]}$$

From before we knew that

$$[O_3] = \frac{k_2[O][O_2][M]}{k_3[NO]}$$

and we get the active oxygen concentration from $R_O = 0$ as:

$$[O] = \frac{k_1[NO_2]}{k_2[O_2][M] + k_4[NO_2] + k_5[NO_2][M] + k_7[NO][M]}$$

Substitution of the expression for $[O]$ into the equation for $[O_3]$ completes the problem of determining the concentrations of active intermediates in terms of concentrations of stable species.

Let us now consider our goal, which is to monitor the rate of change of $[NO_2]$ in a closed system. The governing equation is:

$$\frac{d[NO_2]}{dt} = -r_1 + r_3 - r_4 - r_5 + 2r_6 + r_7 - r_8 + r_9$$

Using the above PSSA relations for the rates we get

$$\frac{d[NO_2]}{dt} = -r_2 - 2r_4 - 2r_5 + r_3 + 2r_6 = -2r_4$$

So that

$$\frac{d[NO_2]}{dt} = -2k_4[O][NO_2]$$

$$t = 0 \qquad [NO_2] = [NO_2]_o$$

The above can be rearranged as

$$\frac{1}{[NO_2]}\frac{d[NO_2]}{dt} = \frac{d\,\ell n[NO_2]}{dt} = -2k_4[O]$$

Substituting in the expression for $[O]$ and rearranging yields

$$\frac{-2k_1}{\dfrac{d\,\ell n[NO_2]}{dt}} = 1 + \frac{k_5[M]}{k_4} + \frac{k_7[M][NO]}{k_4[NO_2]} + \frac{k_2[M][O_2]}{k_4[NO_2]} \qquad (**)$$

In the absence of any reactions but 1 and 4 (i.e $k_2 = k_5 = k_6 = k_7 = k_8 = k_9 = 0$) all oxygen atoms would end up as molecular oxygen giving an <u>overall</u> quantum yield of 2, <u>i.e.</u> two molecules of NO_2 disappear for each photon absorbed. In that case

$$\frac{-d\,\ell n[NO_2]}{dt} = 2k_1$$

which is observed at very low pressure experiments when $[M] \approx 0$. However, that is not the case at atmospheric pressure when other interactions indicated by the mechanism above occur.

Now, by assuming that the measurable stable nitrogen species are $[NO]$ and $[NO_2]$ only, the mass balance on nitrogen requires that

$$[NO] = [NO]_o + [NO_2]_o - [NO_2]$$

Substitution into eq (**) and integration yields

$$-2k_1\int_o^t dt = \int_{[NO_2]_0}^{[NO_2]}\left(1 + \frac{k_5[M]}{k_4} + \frac{k_7[M]([NO_2]_0 + [NO]_0 - [NO_2])}{k_4[NO_2]} + \frac{k_2[M][O_2]}{k_4[NO_2]}\right)\frac{d[NO_2]}{[NO_2]}$$

$$-2k_1\int_o^t dt = \int_{[NO_2]_o}^{NO_2}\left(1 + \frac{k_5[M]}{k_4} + \frac{k_7[M][NO_2]_o + [NO]_o - [NO_2]}{k_4[NO_2]} + \frac{k_2[M][O_2]}{k_4[NO_2]}\right)\frac{1}{[NO_2]}d[NO_2]$$

The result of this integration can be presented as:

$$2k_1 t = (1 + a_1 - a_2) \ln \frac{[NO_2]_0}{(NO_2)} + a_2 \left(\frac{[NO_2]_0}{(NO_2)} - 1 \right)$$

$$+ \left((a_2 [NO]_0 + a_3 [O_2]_0) \frac{[NO_2]_0 - [NO_2]}{[NO_2]_0 [NO_2]} \right)$$

where $a_1 = \dfrac{k_5 [M]}{k_4}$; $a_2 = \dfrac{k_7 [M]}{k_4}$; $a_3 = \dfrac{k_2 [M]}{k_4}$

Further simplification is possible by conducting the experiment with $[NO]_o = [O_2]_o = 0$ i.e. in a closed system containing only N_2 and NO_2 initially. Then

$$2k_1 t = (1 + a_1 - a_2) \ell n \frac{[NO_2]_o}{[NO_2]} + a_2 \left(\frac{[NO_2]_o}{[NO_2]} - 1 \right)$$

Monitoring the concentration $[NO_2]$ as a function of time and plotting the right hand side as the ordinate versus time, t, as abscissa allows the determination of k_1. Agreement between data and experiment is indicated in Figure 4 for two different light intensities.

FIGURE 4:   Nitrogen dioxide concentration as a function of time in a system initially comprising 5 ppm NO₂ in N₂. Experimental data and the predictions of the mechanism in the text are shown for two light intensities (Holmes et al, 1973).
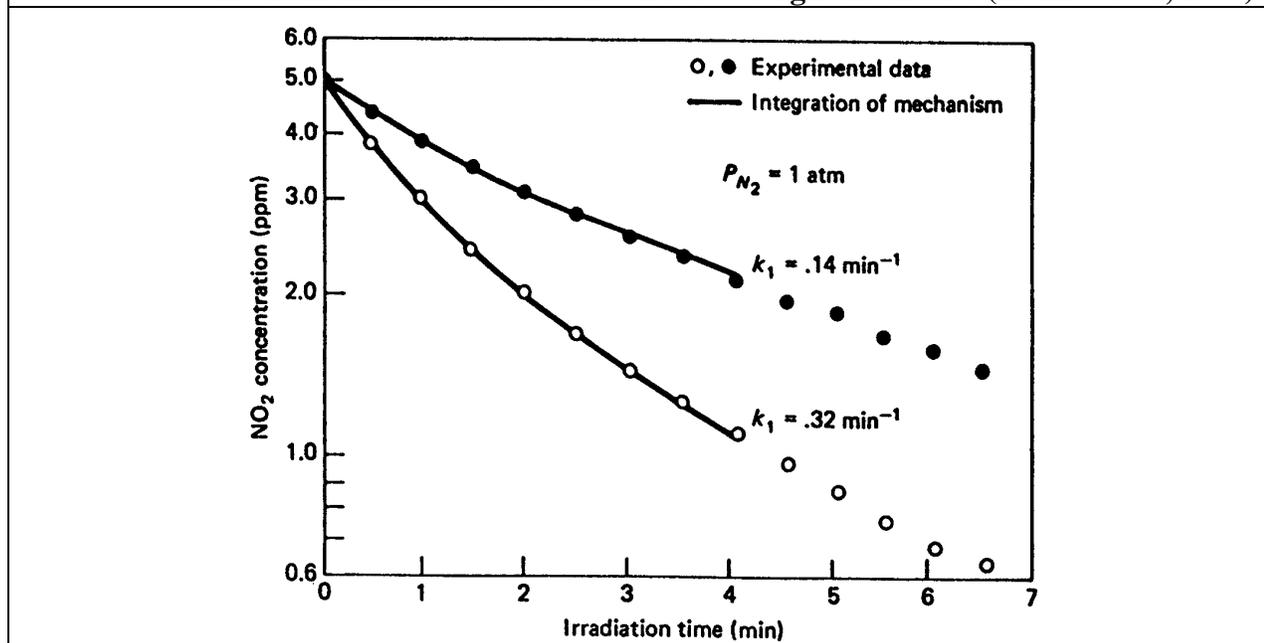
5.5.4 Ozone Formation - CO Role

The key reactions in O_3 formation via NO_2 are reactions 1-3 of the above proposed mechanism in section. In addition we will now consider 6 more mechanistic steps that can contribute to ozone formation. They are (for values of the rate constants at room temperature see Table 2):

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$$O_3 + h\nu \xrightarrow{\ k_4\ } O^* + O_2 \tag{4}$$

$$O^* + M \xrightarrow{\ k_5\ } O + M \tag{5}$$

$$O^* + H_2O \xrightarrow{\ k_6\ } 2OH^* \tag{6}$$

$$CO + OH^* \xrightarrow{\ k_{7a}\ } CO_2 + H^* \tag{7a}$$

$$H^* + O_2 + M \xrightarrow{\ k_{7b}\ } HO_2^* + M \tag{7b}$$

$$HO_2^* + NO \xrightarrow{\ k_8\ } NO_2 + OH^* \tag{8}$$

$$OH^* + NO_2 \xrightarrow{\ k_9\ } HNO_3 \tag{9}$$
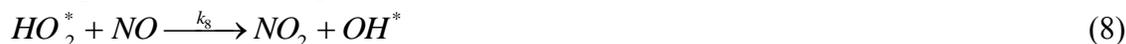
TABLE 2:   Atmospheric chemistry of CO and NO$_x$

Reaction	Rate Constant[a]
1. $NO_2 + h\nu \rightarrow NO + O$	Depends on light intensity
2. $O + O_2 + M \rightarrow O_3 + M$	$6.0 \times 10^{-34}(T/300)^{-2.3}$ cm^6 molecule^{-2} sec^{-1}
3. $O_3 + NO \rightarrow NO_2 + O_2$	$2.2 \times 10^{-12}\exp(-1430/T)$ cm^3 molecule^{-1} sec^{-1}
4. $O_3 + h\nu \rightarrow O(^1D) + O_2$	$0.0028k_1$
5. $O(^1D) + M \rightarrow O + M$	2.9×10^{-11} cm^3 molecule^{-1} sec^{-1}
6. $O(^1D) + H_2O \rightarrow 2OH\cdot$	2.2×10^{-10} cm^3 molecule^{-1} sec^{-1}
7. $CO + OH\cdot \xrightarrow{O_2} CO_2 + HO_2\cdot$	2.2×10^{-13} cm^3 molecule^{-1} sec^{-1b}
8. $HO_2\cdot + NO \rightarrow NO_2 + OH\cdot$	$3.7 \times 10^{-12}\exp(240/T)$ cm^3 molecule^{-1} sec^{-1}
9. $OH\cdot + NO_2 \rightarrow HNO_3$	1.1×10^{-11} cm^3 molecule^{-1} sec^{-1}

Note that O^* is $O(^1D)$ is the excited singlet oxygen atom for which direct transition to O ground state oxygen atom is forbidden . Hence, O^* must react with another species present. The proposed mechanism clearly indicates the importance of the hydroxyl radical OH^* and of the hydroperoxyl radical HO_2^*.

The excited hydrogen atom $H^{*,}$ formed by (7a), is so short lived and disappears by (7b) that the two steps must be combined by PSSA to yield:

$$\left[H^*\right] = \frac{k_{7a}\left[CO\right]\left[OH^*\right]}{k_{7b}\left[O_2\right]\left[M\right]}$$

Now we can combine steps (7a) and (7b) into step (7)

$$CO + OH^* \xrightarrow[(O_2)]{\ k_7\ } HO_2^* + CO_2 \tag{7}$$

where O_2 is indicated as being incorporated to satisfy the mass balance but does not affect the rate of step 7 which is second order overall, i.e first order w.r.t. CO and OH^* each. The value of k_1 is indicated in Figure 5.

FIGURE 5:   Comparison of calculated diurnal variation of NO2, photolysis rate with experimental measurements of Zafonte et al. (1977) in Los Angeles. Reprinted with permission from Environmental Science and Technology. Copyright (1977). American Chemical Society.
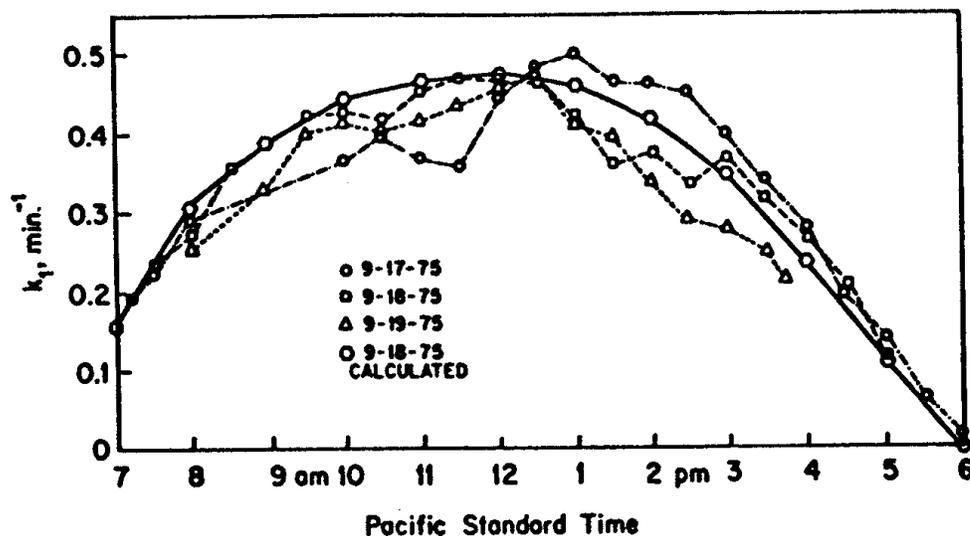
The application of PSSA to the 4 intermediates O, O^*, OH^*, HO_2^* yields

$$R_O = r_1 - r_2 + r_5 = k_1[NO_2] - k_2[O][O_2][M] + k_5[M][O^*] = 0$$

$$R_{O*} = r_4 - r_5 - r_6 = k_4[O_3] - k_5[M][O^*] - k_6[H_2O][O^*] = 0$$

$$R_{OH^*} = 2r_6 - r_7 + r_8 - r_9 = 0$$

$$R_{HO_2^*} = r_7 - r_8 = 0$$

Summing the last two rates yields:

$$R_{OH^*} + R_{HO_2^*} = 2r_6 - r_9 = 2k_6[H_2O][O^*] - k_9[OH^*][NO_2] = 0$$

In addition, ozone can be treated as an active intermediate:

$$R_{O_3} = r_2 - r_3 - r_4 = k_2[O][O_2][M] - k_3[O_3][NO] - k_4[O_3] = 0$$

We solve now for the concentrations of all the active intermediates

$$[O_3] = \frac{k_2[O][O_2][M]}{k_3[NO] + k_4}$$

$$[OH^*] = \frac{2k_6[H_2O][O^*]}{k_9[NO_2]}$$

$$[O^*] = \frac{k_4[O_3]}{k_5[M] + k_6[H_2O]}$$

$$[O] = \frac{k_1[NO_2] + k_5[M][O^*]}{k_2[O_2][M]}$$

Hence by substituting $[O^*]$ into the expression for $[O]$ we get

$$[O] = \left\{ k_1[NO_2] + \frac{k_4 k_5[M]}{k_5[M] + k_6[H_2O]}[O_3] \right\} / k_2[O_2][M]$$

Substitution of $[O]$ into the expression for $[O_3]$ yields

$$[O_3] = \frac{k_1[NO_2] + \dfrac{k_4 k_5[M][O_3]}{k_5[M] + k_6[H_2O]}}{k_3[NO] + k_4}$$

Solving for $[O_3]$ we get

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO] + k_4 a}$$

where $a = \dfrac{1}{1 + \dfrac{k_5[M]}{k_6[H_2O]}}$

which is constant at constant relative humidity.

Now we also get

$$[O^*] = \frac{k_4[O_3]}{k_6[H_2O]} a = \frac{k_1 k_4[NO_2] a}{k_6[H_2O](k_3[NO] + k_4 a)}$$

$$[OH^*] = \frac{2 a k_4[O_3]}{k_9[NO_2]} = \frac{2 a k_1 k_4}{k_9(k_3[NO] + k_4 a)}$$

etc.

The dynamics of the system is now described by:

$$\frac{d[NO_2]}{dt} = -r_1 + r_3 + r_8 - r_9$$

$$\frac{d[NO]}{dt} = r_1 - r_3 - r_8$$

$$\frac{d[CO]}{dt} = -r_7$$

Upon substitution of the rate forms, and elimination of the concentrations of the intermediates, we get:

$$\frac{d[NO_2]}{dt} = \frac{k_1 k_4 a \left(2 k_7 [CO]/k_9 - 3[NO_2]\right)}{k_3[NO] + k_4 a}$$

$$\frac{d[NO]}{dt} = \frac{k_1 k_4 a \left([NO_2] - 2 k_7 [CO]/k_9\right)}{k_3[NO] + k_4 a}$$

$$\frac{d[CO]}{dt} = -\frac{2 k_1 k_4 k_7 a [CO]/k_9}{k_3[NO] + k_4 a}$$

with initial conditions at

$$t = 0 \qquad [NO_2] = [NO_2]_o$$
$$[NO] = [NO]_o$$
$$[CO] = [CO]_o$$

The above equations certainly can be integrated on any computer. Before doing so an approximate analysis is in order.

Examination of Table 2 reveals $k_3[NO] \gg k_4 a$ for all levels of $[NO]$ concentrations of interest. Then

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO] + k_4 a} = \frac{k_1[NO_2]}{k_3[NO]}$$

as found before for the simple mechanism consisting of only 3 steps.

This part of the cycle can be represented as follows:

$$NO_2 \; \underset{\longleftarrow}{\overset{hv, O_2}{\longrightarrow}} \; NO + O_3$$
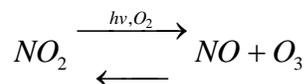
Photolysis generates O and NO which with O_2 results immediately in $NO + O_3$. Ozone reacts with NO to regenerate NO_2.

When CO is present the above cycle is modified as NO can be converted back to NO_2 via the hydroperoxyl radical i.e. step 8

$$NO_2 \xrightarrow{hv,O_2} NO+O_3$$

$$HO_2^*$$
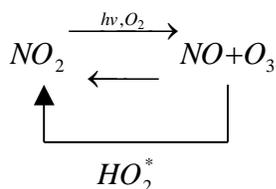
But the HO_2^* radical gets converted to OH^*, which with CO regenerates the HO_2^* radical. Hence, one has two cycles - the fast NO_2, NO, O_3 cycle and a slower CO, OH^*, HO_2^* cycle

$$NO_2 \xrightarrow[-O_2]{hv,O_2} NO+O_3$$
$$CO+OH^* \longrightarrow HO_2^*$$
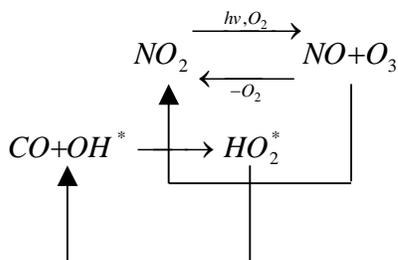
The CO/NO_x reaction mechanism is a <u>chain reaction</u> with OH^* as the chain carrier. The <u>chain length</u> L_c of such a reaction is defined as the number of propagation steps occurring for each termination step. In our mechanism

$$L_c = \frac{r_8}{r_9} = \frac{r_7}{r_9} = \frac{k_7[CO]}{k_9[NO_2]}$$

The role of the CO slow cycle is to slowly change (<u>i.e.</u> increase) the $[NO_2]$ concentration and hence increase $[O_3]$ concentration which is still given by its pseudo steady state value. Because of the extreme rapidity of NO_2/O_3 cycle it is the external independent paths that affect $[NO_2]$ which determine maximum $[O_3]$ levels.

For completion of the ozone story one would need to include reactions of organic compounds and the effect of particulate matter (aerosol) as potential catalyst. This is beyond the scope of illustration of the PSSA assumption. The same rules as illustrated here can be applied.