

## Construction of Detailed Chemical Reaction Models

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### Abstract

Additional principles of chemical reaction kinetics will also be presented with the purpose of building, starting with elementary reactions, complex mechanisms. These mechanisms consisting of hundreds of elementary reactions can be used with existing software to make predictions on the performance of chemical reactors with special consideration to the formation of trace species. The focus will be on homogeneous processes taking place in the gas phase. The majority of the material presented in this manuscript is based on the author's own research.

**Keywords:** Chemical reaction; Chemical kinetics

### Introduction

The most important steps during the assembly of complex chemical reaction models are illustrated in Figure 1 and Ref. [1]. In this section the discussion of each of the steps will be expanded to gain a deeper understanding with emphasis on the chemistry for the model or the main the foundation for any reactor modeling.

Both in past and present literature dealing with the design of

chemical reactors, there is an oversimplification of the chemical reaction models, with the use of global mechanisms consisting of a few reactions with empirically determined reaction rates [2,3]. For example, the rate of consumption of reactant A by B to form product C, represented by the overall reaction (1) below, is presented in the form of equation (2),



$$d[A]/dt = A_e \exp(-E/RT) [A]^a [B]^b \quad (2)$$

Where  $A_e$  is the pre-exponential factor, E an empirically determined activation energy, and a and b, the exponents of the reactant concentrations that are able to represent the concentration dependence over a range of conditions also empirically determined.

Unfortunately, these oversimplified mechanisms, to give an example, may not be able to accurately predict the formation of toxic products present in very small concentrations because depending on conditions their formation is dependent on complex chemistry involving stable and radical species, as well as reaction temperature. There is a need then to arrive at more complex mechanisms consisting of elementary reactions that are relevant to the consumption of the reactants, formation of intermediate species and products, and any other chemical species of interest [4].

### General features of reaction mechanisms

There are fundamental features in most reaction mechanisms occurring in the gas phase that can be used to assemble such mechanisms. The most important one is the role played by free radicals in the decomposition of any reactant. A very simple example found in freshman chemistry books is the formation of hydrogen iodide starting from hydrogen and iodine [5]. The proposed mechanism is a two-step mechanism,

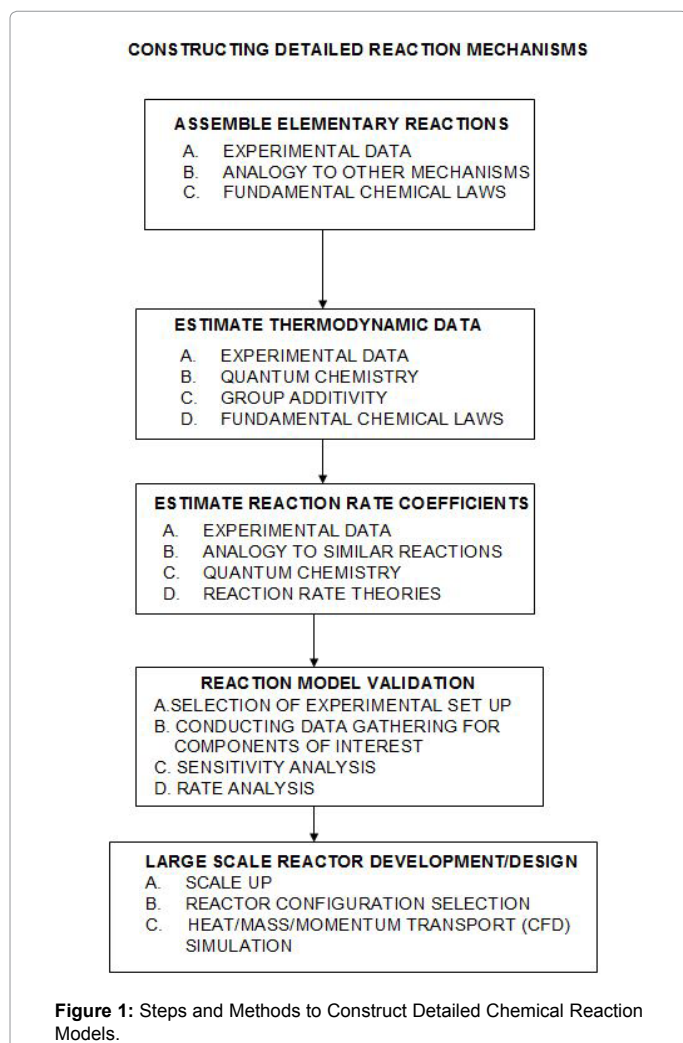


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The first step involves the formation of iodine radicals in reaction (3), and it is followed by the formation of hydrogen iodide. Another example is the oxidation of hydrocarbons at low temperatures initiated by the following reactions [6]



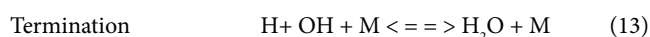
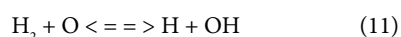
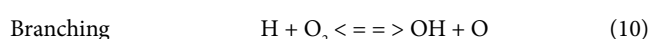
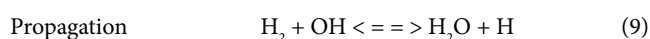
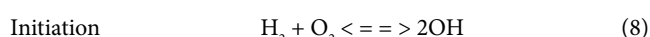
which the hydrocarbon radical R plays a role in reaction (6) forming a species that can lead to the formation of oxygenated species such as alcohols and aldehydes. These types of reaction seem to take place in the urban atmosphere [7]. If the temperature is high enough, the decomposition of the reactant is initiated by a thermal decomposition such as reaction (7),



Reaction (7) is endothermic and its extent would depend on temperature, and results in the formation of methyl radical. This type of reaction would occur in shock tubes, for example, where the decomposition of the fuel is initiated by a traveling shock wave causing temperature and pressure to rise considerably in a very short time.

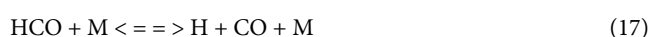
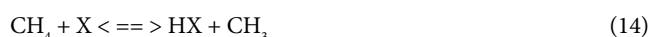
The above examples then illustrate a very important point to remember when examining reaction mechanisms: the decomposition of the reactant is initiated by formation of radical species that can later participate in the reactions leading to the product. The concentration of the radicals formed increase as the reaction time or temperature increase.

Another important consideration is the formation of chain reactions. The basic premise of chain reaction mechanisms is also that free radicals play a leading role in the destruction of reactant molecules. The chain reaction mechanism itself consists of several steps: initiation, propagation, branching (not always present), and termination. This can be illustrated, for certain range of temperature and pressure, by some of the reactions in the following Hydrogen oxidation mechanism:

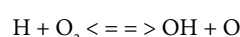


The initiation step is responsible for the initial decomposition of the reactants. Propagation steps involve a radical-molecule reaction with generation of a radical in the product, while branching reactions produce two radicals per single radical in the reactants. For example, the generation of a flame in combustion is due to branching reactions predominating over termination, with a large generation of radicals resulting in the fast decomposition of the fuel.

To illustrate what has been discussed above, in assembling the main reaction paths for the combustion of methane [8] consideration is given to the following reactions:



where X represents the free radicals H, OH, or O. The relative concentration of the radicals depend on the stoichiometry of combustion for example, in fuel rich flames, the chemistry of H radicals gains much importance. To the above reactions one must add the very important chain branching reaction,



In examining this simplified mechanism, the main conclusions are that at the high temperature of combustion the decomposition of methane is initiated by radical attack such as in reaction (14) since the concentration of free radicals is relatively abundant. Reactions (15), (16), (18), (21) propagate the decomposition of methane. Reactions (17), (10) are chain branching reactions. Reactions (19), (20) lead to stable molecules and would be considered as termination reactions. Obviously, the radical pool is initiated by the thermal decomposition of methane in the hot region of the flame or reaction (22) below,



with the very important branching reaction (10) adding to the radical pool.

To summarize, reaction mechanisms can be assembled from elementary reactions using free radicals as the means for decomposition of the reactant, and intermediate products. Chain branching reactions, if they occur, take a very important role in the mechanism as they lead to the formation of increasing concentrations of radicals. Reaction time and temperature have a bearing on radical concentration, and the type of reaction initiating the consumption of the reactant.

### Hierarchical nature of hydrocarbon combustion chemical models

The combustion mechanisms for hydrocarbons of small or large molecules are known to follow a hierarchical structure as depicted in Figure 2. This is of great aid in the assembly of oxidation mechanisms for hydrocarbons starting with methane.

Using the combustion of methane as an example, the mechanism

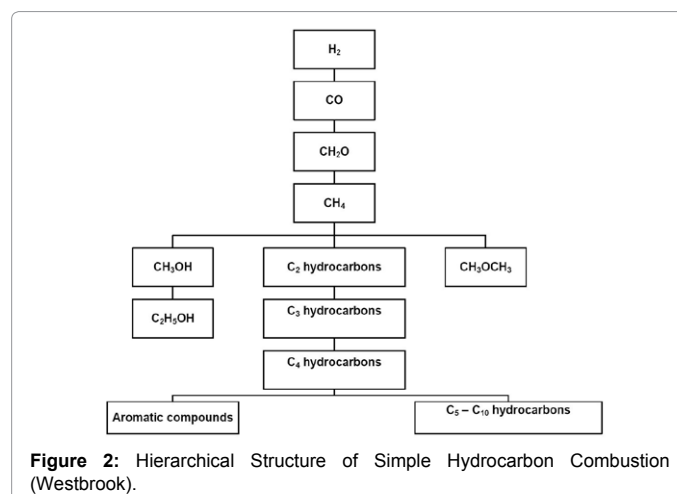
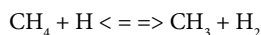
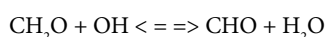
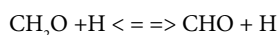
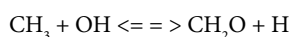


Figure 2: Hierarchical Structure of Simple Hydrocarbon Combustion (Westbrook).

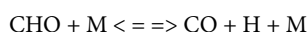
must include chemical steps for the formation of formaldehyde, hydrogen and carbon monoxide. These species are common not only to methane combustion but for the combustion of larger hydrocarbon molecules. The formation of hydrogen in methane combustion is explained by the Hydrogen abstraction reaction



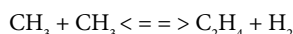
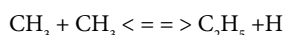
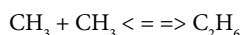
Carbon monoxide is formed via the formation of formaldehyde,



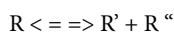
Followed by,



The formation of  $\text{C}_2$  hydrocarbons is explained a the sequence of reactions involving  $\text{CH}_3$  radicals or,



The combustion of large hydrocarbon molecules can be explained by reactions similar to those in the oxidation of heptane as illustrated by the work of Ref. [9]. At high temperatures the long hydrocarbon chains will break up into smaller fragments or,



Where  $\text{R}'$  and  $\text{R}''$  are two distinct smaller alkyl radical fragments. Another pathway involves Hydrogen abstraction to produce an alkyl radical which can further decompose,

$\text{R} + \text{H} \rightleftharpoons \text{R}' + \text{H}_2 \rightleftharpoons$  Decomposition of Radical products by fission.

A summary of the High temperature oxidation of Hydrocarbons is depicted in Figure 3 below from Ref. [10].

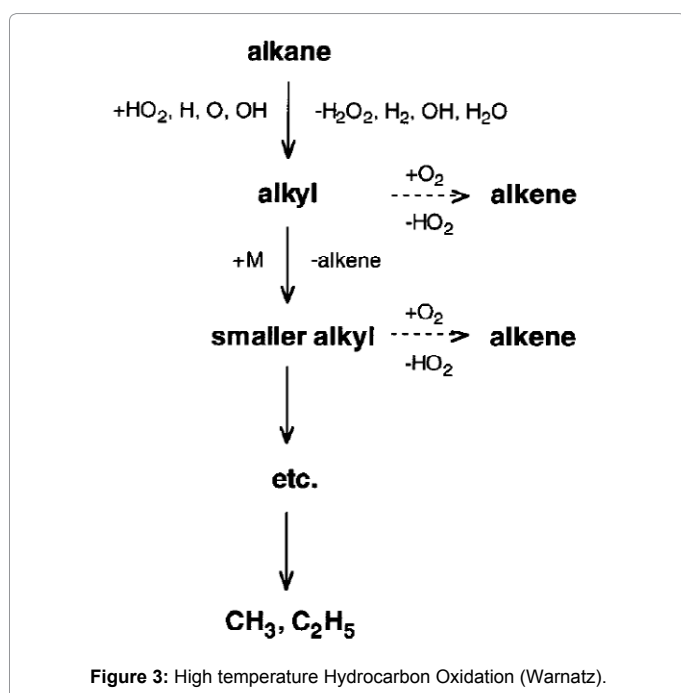


Figure 3: High temperature Hydrocarbon Oxidation (Warnatz).

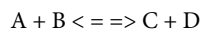
Again, the main feature is the break up of the large hydrocarbons into smaller fragments leading to smaller molecules such as  $\text{CH}_3$ , and  $\text{C}_2\text{H}_5$ . The fragmentation is initiated either by small radical attack such as with H or thermal fission.

### Chemical reactions of catalysis

Transition state theory shows that the rate of reaction is determined by the free energy of formation of the transition state complex existing between reactant and product on the reaction coordinates. Catalysis is the process in which a catalytic agent causes a reduction of the free energy of the transition state complex and the result is for the rate of reaction relative to the uncatalyzed reaction increases.

Catalysis may be realized both homogeneously and heterogeneously. The most important application is the heterogeneous catalysis by a solid in contact with the reactant-bearing fluid, usually a gas. The catalyzed reactions take place on active sites of the solid.

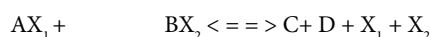
Catalytic surfaces on solids are complex beasts. If one considers the surface of a crystalline substance such as silicon dioxide, the surface silicon will have an unfulfilled bond or dangling bond. This of course is a high energy configuration, and the surface will reduce its energy by either adsorption of atoms or molecules from the surrounding environment or by reconstructing: changing the geometry of the surface to allow additional bonding of the surface atoms, in this case Silicon Dioxide [11]. In semiconductor manufacturing, the clean surfaces are annealed with hydrogen to eliminate dangling bonds as Si-H [12], describes the general chemistry of a catalyzed reaction on a solid surface with reactants in the gas phase. For the overall reaction,



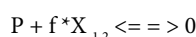
Reacting on active sites  $\text{X}_1$  and  $\text{X}_2$ , catalyst sites poisoned by P and deactivated thermally, the mechanism is as follows,



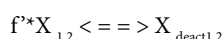
Surface reaction and desorption,



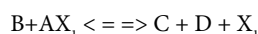
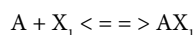
Poisoning,



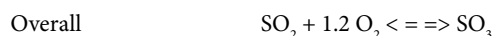
Thermal deactivation



where  $f$  is the fraction of poisoned sites, and  $f'$  the fraction thermally deactivated. Note that if only one reactant is chemisorbed, the mechanism takes the form,



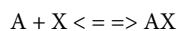
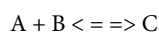
An illustration of a catalytic process is the sulfuric acid process with  $\text{V}_2\text{O}_5$  catalytor.



Where  $\text{X} = \text{V}_2\text{O}_5$  and  $\text{V}_2\text{O}_4 = \text{AX}$   $\text{X} = \text{active site}$

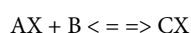
An example of the reaction rate analysis for the simple catalyzed

reaction, can be found in Ref. [13]. The rate of chemisorption of reactant A is, assuming no dissociative adsorption,



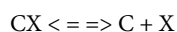
$$R_{ads} = k_{ads}(C_A)(C_v) - k'_{ads}(C_{A,ads})$$

Where  $C_v$  is the concentration of vacant sites and  $C_A$  is the gas concentration of reactant A, and  $C_{A,ads}$  is the adsorbed concentration of A. The rate of surface reaction, Finally, the reaction rate of desorption expression is,



$$R_{surf} = k_{surf}(C_{A,ads})(C_B) - k'_{surf}(C_{C,ads})$$

ads= adsorbed species



$$R_{des} = k_{des}'(C_{C,ads}) - k_{des}(C_C)(C_v)$$

### Validation of chemical reaction models

After the assembly of the chemistry for the chemical reactor by guidelines presented in this Chapter and the method of Analogous reactions shown, it will be necessary to validate the chemical kinetic model with the use of an experimental apparatus and compare model predictions with actual experiments.

Shock tubes can be used to study the kinetics of reactions at very high temperatures, however because of the speed of the reactions in the shock tube due to extreme conditions available diagnostic techniques often can not resolve many details of the combustion or reaction process. For this reason, shock tubes are useful in studying the thermal decomposition or initiation reactions for fuels at high temperatures, but often not useful in the validation of detailed chemical kinetic models (DCKM).

Plug Flow Reactor experiments provide very valuable information for the oxidation of fuels in the medium temperature regime. The characteristic time for fuel decomposition is such that concentration profiles can easily be generated for a large number of species making it possible to validate DCKM.

Finally, flames are also a valuable technique for validating DCKM. More specifically, premix laminar flames can be modeled more easily than say turbulent diffusion flames (by diffusion is meant that fuel and oxidizer are not premixed) and still present features that are in common

to many real combustion devices such as furnaces and gas engines (Westbrook) [14]. A premix laminar flame experimental apparatus is fully described in Gargurevich [1].

Fristrom RM in "Flame Structure and Processes" provides a very complete description of various experimental techniques for validation of DCKM in combustion processes. His work includes description of burner systems, flame temperature measurements, composition measurement techniques in flames, flame sampling, laser diagnostics, and analysis of flame data.

"Applied Combustion Diagnostics" by Kohse-Hoinghaus and Jeffries [15] is also a comprehensive guide to experimental techniques for validation of DCKM in combustion processes.

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