Reaction kinetics & Chemical Reaction Models

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The fundamentals of chemical reaction kinetics will be presented with the purpose of building, starting with elementary reactions, complex mechanisms. These mechanisms consisting of many elementary reactions can be used with existing software (discussed later) 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 (Gargurevich, 1997).

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 (Worstell, 2001; Arakawa et al., 1998). 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),

$$A + B \Rightarrow C \qquad (1)$$

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

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 (Senkan, 1992).

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 (Chang, 1994). The proposed mechanism is a two-step mechanism,

I2 < = = > 2I (3)
H2 + 2I < = = > 2HI (4)

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 (Dryer, 1991)

RH + O2 < = = > R +HO2 +M (5)

R + O2 <= = > RO2 (6)

in 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 (Seinfield, 1989). If the temperature is high enough, the decomposition of the reactant is initiated by a thermal decomposition such as reaction (7),

CH4 <= = => CH3 + H (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:

Initiation H2 + O2 < = = > 2OH (8)
Propagation H2 + OH < = = > H2O + H (9)

Branching $H + O_2$ < = = > $OH + O$ (10)
$H_2 + O$ < = = > $H + OH$ (11)
$H_2O + O$ < = = > $OH + OH$ (12)
Termination $+ OH + M$ < = = > $H_2O + M$ (13)

Plus Others…

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 (Miller et al., 1992) consideration is given to the following reactions:

$CH_4 + X$ < == > $HX + CH_3$ (14)
$CH_3 + O_2$ < = = > $CH_2O + H$ (15)
$CH_2O + X$ < = = > $CHO + HX$ (16)
$HCO + M$ < = = > $H + CO + M$ (17)
$HCO + O_2$ < = = > $CO + HO_2$ (18)
$HCO + OH$ < = = > $CO + H_2O$ (19)
$HCO + H$ < = = > $CO + H_2$ (20)
$CO + OH$ < = = > $CO_2 + H$ (21)

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,

$H + O_2$ < = = > $OH + O$ (10)

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,

$CH_4 + M$ < = = > $CH_3 +H + M$ (22)

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.

Estimation of Kinetic Coefficients

Elementary chemical reactions can be classified as either energy-transfer limited or chemical reaction rate limited (Senkan, 1992). In energy transfer-limited processes, the observed rate of reaction corresponds to the energy transfer to or from species either by intermolecular collisions or by radiation, or intramolecularly due to energy transfer between different degrees of freedom of a chemical species. All thermally activated unimolecular reactions become energy-transfer limited at low-density conditions because the reactant can receive the necessary activation energy only by intermolecular collisions. The reaction then becomes pressure dependent at a given temperature. An example of such reaction is the thermal decomposition of hydrogen,

$$\mathrm{H2} + \mathrm{M} <==> \mathrm{H} + \mathrm{H} + \mathrm{M} \qquad (23)$$

The energy for the reaction to occur is generated by collision with a second body M.

Chemical rate limited processes, in the other hand, correspond to chemical reactions occurring under conditions in which the statistical distribution of molecular energies obey the Maxwell-Boltzman form, i.e., the fraction of molecules that have an energy E or larger is proportional to $e^{-E/RT}$. The rates of intermolecular collisions are very rapid and all species are in equilibrium with the gas mixture.

Table 1 depicts several theories that can be applied to estimate rate coefficients in order of increasing complexity. In the simplest approach, the rate coefficient of a bimolecular reaction is simple the collision frequency between the molecules. To improve upon this approximation, the collision frequency needs to be corrected to account for the fact that only those collisions with energies above the activation energy of the reaction will result in a net reaction. Also, a steric factor has to be included, since only collisions taking place in a given spatial arrangement will lead to a net reaction.

The next level of complexity is Transition State Theory (TST) of both unimolecular and bimolecular reactions. In TST, the rate coefficients include an activation energy factor, and an entropy factor to account for steric factors. TST only applies to chemical rate limited processes. The Lindemann approach to unimolecular reactions would fall within this level of complexity.

Finally, the most complex theories involve the quantum mechanical treatment of energy transfer limited processes such as thermal activation and unimolecular/bimolecular chemical activation. By chemical activation, in the case of a bimolecular reaction for example, is meant that as the result of a bimolecular reaction an intermediate species is formed possessing excess energy over the ground state that can more easily lead to some final product by decomposition,

A + B < = = > Activated Molecule < = = > Products

These quantum theories account for the dependence of the overall rate coefficients on the excess vibrational energy of the molecular species.

In reaction modeling rate coefficients are normally expressed in the modified Arrhenius form,

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \qquad (24)$$

A is the collision frequency factor, T is the temperature (the exponent n accounts for non-Arrhenius behavior to fit experimental data) and E_a is the activation energy. Non-Arrhenius behavior is most obvious in reactions that have little activation energies with the pre-exponential factor determining the temperature dependence.

The discussion above has established an approach for building more complex reaction mechanisms, and the theoretical foundations for the estimation of reaction rate coefficients. The most important consideration always is the chemistry included in the mechanism. Assembling the elementary reactions composing the mechanism is followed then by the best assessment for the mathematical expression giving the rate coefficients of each reaction. The procedure to follow based on the author’s experience is discussed below.

1. Literature Data & Order-of-Magnitude Estimates.

Very often, the best value to use for the rate coefficient of the reaction is the literature value, i.e. experimentally determined coefficient, if available. Consideration must be given to the temperature and pressure conditions since as the discussion above has illustrated, they have an effect on the rate coefficient. This is true, for example, in the case of unimolecular reactions, and chemically activated reactions.

There several sources of chemical kinetic data, some of which are as follows:

(a) High Temperature Reactions- (for example, Methane Combustion) in chronological order:
Baulch et al. (1992), Wang (1992), Miller & Bowman (1989), Warnatz (1984), Westbrook & Dryer (1984).

(b) Chlorinated Hydrocarbons- High Temperature Reactions:
Qun & Senkan (1994), Senkan (1993).

(c) For lower temperatures and reactions occurring in the ambient air:
DeMore et al. (1990).

An extensive data base for chemical reaction kinetics can be found in the National Institute of Standards Chemical Kinetics Database (1994). The reference can be found at the end of the manuscript.

Sometimes, a rough-order-of magnitude value for the rate constant is needed for two reasons: either no other value is available or the aim is to scan the mechanism for reactions that have small impact on the consumption of the reactant, product formation, or formation of any other species of interest. One way to make such an estimate is by the method of analogous reactions as depicted in Table 2 taken form Senkan (1992). On inspection of Table 2, there are several issues that are of importance in estimating rate coefficients. Unimolecular fission reactions are endothermic, and the heat of reaction corresponds to the minimum activation energy that could be expected for the reaction.

Simple kinetic theory of bimolecular reactions gives the following expression for the rate coefficient of the reaction between molecules A and B (Laidler, 1987),

$$k = Z_{AB} = N_A \pi \sigma_{AB}^{\ 2} \left(\frac{8kT}{\pi \mu^2} \right)^{1/2} \quad \text{cm}^3\text{/mol-sec} \qquad (25)$$

Z_{AB} is the molar collision frequency, σ_{AB} is the mean collision diameter or rigid sphere collision cross-section, μ_{AB} is the reduced mass, N_A is Avogadro’s number, and k is Boltzmann’s constant. The estimate of the molar collision frequency at 300 ^oK turns out to be 1.0 x 10^{13} cm^3/mol-sec, and it represents the upper limit for the bimolecular rate coefficient without accounting for the activation energy or steric factor. As stated above, a lower limit for the activation energy for endothermic reactions is the heat of reaction.

Another method that can be used to estimate the activation energy of metathesis reactions such as,

H + CH4 < = = > CH3 + H2

is the Evans-Polanyi relationship for similar reactions or,

$$E = \alpha\left(-\Delta H_{rn}\right) + \beta \qquad (26)$$

where $-\Delta H_{rn}$ is the heat of reaction, which is defined as positive for an exothermic reaction, and α and β are the Evans-Polanyi empirical constants for the family of reactions. Polanyi relationships often fail when there is charge separation involved in the transition state, such is the case when atoms or groups involved in the reaction differ in electronegativities.

2. Transition State Theory of Unimolecular/Bimolecular Reactions.

A chemical reaction is presumably a continuous process involving a gradual transition from reactants to products. It has been found extremely helpful, however, to consider the arrangement of atoms at an intermediate stage of reaction as though it were an actual molecule. This intermediate structure is the transition state, and its energy content corresponds to the top of the reaction energy barrier along the reaction coordinate. The rate coefficients according to TST will be given here without proof, they correspond to a thermodynamic approach where the reaction rate is given in terms of thermodynamic functions. One of the main assumptions of TST is that the process is chemical rate limited (Laidler, 1987).

a. Bimolecular Reactions.

In a successful bimolecular collision, part of the kinetic energy of the fast-moving reactant molecules is used to provide the energy of activation and thus to produce the high-energy molecular arrangement of the transition state. TST applied to the reaction,

$$A + B <==> AB^{\Upsilon} ==> R + S \qquad (27)$$

in which AB^{Υ} is the transition state structure, leads to the following expression,

$$k = 1.25x10^{13} T^{2} \left(\Delta S^{\gamma} \big/ R \right) \exp\left(-E_a \big/ RT \right) \qquad (28)$$

the units are cm^3/mol-sec. TST shows a T^2 dependence on temperature, and the change in entropy leading to the transition state is needed. There is now quantum chemistry software available that make it possible to estimate the properties of the transition state, this will be discussed more fully later. Unfortunately, properties of the transition state cannot yet be tested experimentally, thus the uncertainty in the calculations for the transition state would not be well known. The best approach is to be most familiar with the particular quantum chemistry package that is to be used and its limitations in general.

b. Unimolecular Reactions

In unimolecular reactions, the necessary energy for the reaction may accumulate in the molecule as the result of intermolecular collisions, photon activation, or as the result of unimolecular chemical activation. Once energy is imparted to the molecule, it is rapidly distributed amongst its vibrational and rotational energy levels with the energized molecule taking many configurations. If one of these configurations corresponds to the localization of enough energy along the reaction coordinate, then the reaction occurs.

The application of TST theory to the process below,

$$A \ <= = > A^{\Upsilon} \ <= = > P \qquad (29)$$

leads to the following expression (the units are sec^{-1})

$$k = 4.60x10^{10} T \exp\left(\Delta S^{\gamma} / R\right) \exp\left(-E_a / RT\right) \qquad (30)$$

TST predicts a first order temperature dependence for the rate coefficient. As with bimolecular reactions, the entropy change leading to the transition state will be required, and quantum chemistry methods may be used for this.

c. Lindemann's Approach to Unimolecular Reactions

No discussion on chemical kinetic theory would be complete without Lindemann's theory of unimolecular reactions which attempts to explain the pressure dependence of unimolecular reactions.The overall unimolecular reaction is given below,

$$A \ \overset{k_{uni}}{= =>} \ B \qquad (31)$$

At a given temperature, and for high pressure conditions, the rate of decomposition of A is first order in its concentration, but a low enough pressures, the rate becomes pressure dependent, i.e., the process is energy transfer limited. The dependence of k_{uni} on pressure is shown in Figure 1.

In the mechanism developed by Lindemann (Laidler, 1987), the decomposition of reactant A occurs according to the following two step scheme,

$$A + M \ \underset{k_{-1}}{\overset{k_1}{< = = >}} \ A^* + M \qquad (32)$$

$$A^* \ \overset{k_2}{= = \ >} \ P \qquad (33)$$

In reaction (32), molecules of A are energized by collision with a second body M. Reaction (33) describes the process by which the energized molecules of A* turns into the final product. The results of this approach will be given below without a proof, Laidler (1987), Garginer (1972) present a full discussion of Lindemann's Theory.

In the high pressure limit the unimolecular rate coefficient takes the form,

$$k_{uni}^{\infty} = \lim_{[M] \xrightarrow{\infty}} k_{uni} = k_2 \frac{k_1}{k_{-1}} \qquad (34)$$

whereas at low pressure,

$$k_{uni}^{o} = \lim_{[M] \xrightarrow{0}} k_{uni} = k_1[M] \qquad (35)$$

The high pressure limit does not show a dependence on pressure, in the other hand, the low pressure coefficient is dependent on pressure through the term [M], as it is found experimentally. Estimates of the high pressure limit rate coefficient k_{uni}^{∞} can be made using TST, quantum chemistry can be used to estimate the properties of the transition state. In equation (35), in order to calculate the low-pressure coefficient, k_1 is expressed as follows,

$$k_1 = Z_{A^*M} \bullet f(E_0) \bullet \beta \qquad (36)$$

Z_{A^*M} is the molar collisional frequency between energized A* molecules and M (see Equation (25)), $f(E_o)$ is the fraction of molecules with energies higher than E_o and can be activated according to reaction (32), this term may be given in terms of the Boltzmann distribution function P(E) or

$$f(E_o) = \int_{E_o}^{\infty} P(E) dE \qquad (37)$$

β is a collisional efficiency that accounts for the fact that not every collision between an activated A* molecule and M results in deactivation of A* back to A.

For thermodynamic conditions where unimolecular reactions fall in a regime that is between high and low pressure or the fall-off regime, software is available that can make estimates of the coefficient based on the constants given in equations (34) and (35): Kee et al. (1993), Stewart et al (1989). The reader is referred to these references for more details.

3. Quantum-Rice-Ramsperger-Kassel (QRRK) Treatment of Energy Transfer Limited Reactions.

Only a brief introduction will be given here to the QRRK treatment of unimolecular and bimolecular reactions. References will be provided for the reader to become more acquainted with this theory as well as software available to carry out the computations needed under the theory.

The Lindemann Theory deviates somehow form the experimentally determined behavior of unimolecular reaction (see Figure 1). The reason for this can be explained by discussing what is presented illustrated in Figure 2. The molecule A is activated to A* but in the QRRK treatment, the rate coefficient $k_{rxn}(E)$ depends on the excess energy of the activated molecule over the ground state. As the figure shows, QRRK treats the molecular energy as being quantized. A full discussion of this problem can be found in Westmoreland et al. (1986).

In a similar manner, for bimolecular reactions (Westmoreland,et al., 1986), the process is depicted in Figure 3. As with unimolecular reactions, the reaction leads to an activated molecule A*. The fate of this molecule depends on its excess energy. The rate coefficient $k_2(E)$ for the decomposition to products P + P' depends on excess energy over the ground state. The energy is considered as being quantized. More complex schemes involving izomerization of the activated molecule can be found in Kazakov et al. (1994).

Software for the mathematical treatment of chemically activated reactions can be found, see for example Dean, Bozzelli, and Ritter (1991) for an introduction to the CHEMACT program and Dean and Westmoreland (1987) for additional information. The reader is referred to these references for a more thorough discussion of chemical activation.

4. Computer Software for Chemical Reactor Engineering.

(a) Chemical Kinetics.

References were given above for programs that are available to estimate chemically activated reaction. However, very often no information is available for the activation energy of chemical reactions, or properties of the transition state to be able to estimate rate coefficients according to TST. Computer software is now available that can be used to make estimates of such parameters. The software uses the methods of quantum chemistry, a discussion of these methods is beyond the scope of this manuscript, and the reader is referred to Gargurevich (1997), Pople (1970), and Murrell (1972) for a thorough discussion of the theory upon which these programs are based.

The software that the author is most familiar with is the Molecular Orbital Package (MOPAC) developed through the Quantum Chemistry Program Exchange at Indiana University. MOPAC is based on semi-empirical methods that use experimental data to arrive at solutions of the equations derived from quantum chemistry. Other properties can be calculated using MOPAC such as the heat of formation of chemical species if needed.

Computer software is also available that use ab initio methods, i.e., the equations derived from quantum chemistry are solved using strict theoretical calculations. These require more computer memory and speed than the semi-empirical methods.

A list of computer software can be found in www.chemistry-software.com/software_guide/modeling_index.htm.

As it was stated above, a major problem in studying reactions by any current theoretical models is the lack of experimental data for properties of the transition state. Calculations of these properties then have not been tested, and the performance of the method used for such calculations is safer, the better the performance of the method in question in all areas where it can be tested.

(b) Chemical Reactor Design.

The reactor simulator that the author is most familiar with is the CHEMKIN package developed by Sandia National Laboratories (R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia National Laboratories Report, SAND89-8003, 1989). CHEMKIN uses different modules in order to carry out the necessary simulation of plug flow reactors, or combustion phenomena for example. These modules are as follows: (1) chemical species and their thermodynamic properties, (2) the elementary reactions composing the complex mechanism, and the reaction rate constants for each reaction, (3) transport properties of each chemical species (this is necessary for the treatment of combustion phenomena). The modules interface with each other to numerically solve the problem at hand. This software was used extensively by the author to simulate combustion phenomena (Gargurevich, 1997).

There are other process simulators available that also can be used for the simulation of chemical reactors. The most commonly used are software from Aspen Technology Inc.(Cambridge, Mass.), Simulation Sciences Inc. (Brea, Calif.), Hyprotech (Calgary, Alberta) , and Chemstations Inc. (Houston, Texas) ("Simulators seek a broader community of users", Chemical & Engineering News, March 27, 1995). The author is not familiar with the use of these simulators in the design of chemical reactors except for PRO II 5.5 (Simulations Science) for other applications. PRO II has a plug flow reactor unit operation plus others which allow the user to specify the reactions and the rate coefficients for each reaction.

LEAST COMPLEX

CHEMICAL RATE LIMITED

(1) Simple Kinetic Theory of bimolecular reactions: reaction rate coefficient equals the collision frequency.

(2) Modified Kinetic Theory: reaction rate coefficient equals, collision frequency x activation energy factor x steric factor

(3) a. Transition State Theory (TST): unimolecular/bimolecular reactions. Rate coefficient includes an activation energy factor, and an entropy factor to account for steric effect.
    b. Lindemann theory of unimolecular reactions.

ENERGY TRANSFER LIMITED.

(4) Quantum mechanical treatment of thermal activation, and unimolecular/bimolecular chemical activation. Rate coefficients depend on the internal energy of molecular species.

MOST COMPLEX

Table 1. Theories for estimating reaction rate coefficients.

Reaction Type	**$Log_{10}A$**	**E_a (Kcal/mole)**	**ΔH_r (Kcal/mole) @298 K**
I.Unimolecular Reactions, k= A exp($-E_a/RT$), s^{-1}			
a. Simple Fission Reactions			
CH4 < = = > CH3 +H	16.0	105	105
Recommendation	15.5	ΔH_r	
b. Complex Fission Reactions			
b1. Radical Fissions			
C2H5 < = => C2H4 +H	13.6	40.9	38.7
Recommendation	13.0	ΔH_r	
CH3CO <= = > CH3 + CO	12.4	16.7	14.2
Recommendation	13.0	ΔH_r +5	
b2. Molecular Fissions			
Three and Four Center Eliminations			
C2H5Cl < = = > C2H4 + HCl	13.5	56.6	20.2
Recommendation	13.5	1/3(sum of bond energies broken) or ΔH_r + 25	
b3. Isomerization Reactions			
b3.1 Cis- Trans Isomerization			
CHCl=CHCl cis < = = > trans	13.8	63.0	0.0
Recommendation	13.0	Pi-bond energy + 4.0	
b3.2 Atom Migrations			
1-C3H7 <= = > 2-C3H7	12.4	34.0	0.0
Recommendation	13.0	35 for 1,2 shift 25 for 1,3 shift	
b3.3 Cyclizations & Decyclizations	15.2	65.0	-27.6
Recommendation	15.0	60.0	

Table 2. High Pressure Rate Coefficients for Analogous Reactions (Senkan, 1992

Reaction Type	**$Log_{10}A$**	**E_a (Kcal/mole)**	**ΔH_r (Kcal/mole) @298 K**
II Bimolecular Reactions $K= AT^2exp(E_a/RT)$ cm^3/mol-sec			
a. Atom Metathesis Reactions			
H + CH4 < = = > CH3 + H2	8.85	11.6	0.0
Recommendation	8.50	F_A x F_C see below	
CH3 + C2H6 < = = > CH4 + C2H5	6.55	10.8	-4.7
Recommendation	7.00	F_A x F_C see below	
Reaction A + BC , = = > AB + C			
Group or Atom	F		
H	3.00		
Cl	0.57		
O	2.15		
OH	1.30		
NH2	1.30		
HO2	1.70		
CHO	1.55		
CH3	3.50		
C2H5	2.85		
b. Radical-radical Metathesis			
C2H3 + H < = = > C2H2 +H2	8.35	0.0	-66.3
Recommendation	8.00	0.0	
c. Molecule-Molecule Metathesis			
C2H4 + C2H4 < = = > C2H3 + C2H5	9.15	72.0	70.0
Recommendation: Use microscopic reversibility.			
III.Complex Bimolecular Reactions $k= Aexp(E_a/RT)$ cm^3/mol-sec			
CH3 + O2 <= = > CH2O + OH	13.7	34.6	-53.0
Recommendation: None.			

Table 2. High Pressure Rate Coefficients for Analogous Reactions (Senkan, 1992).

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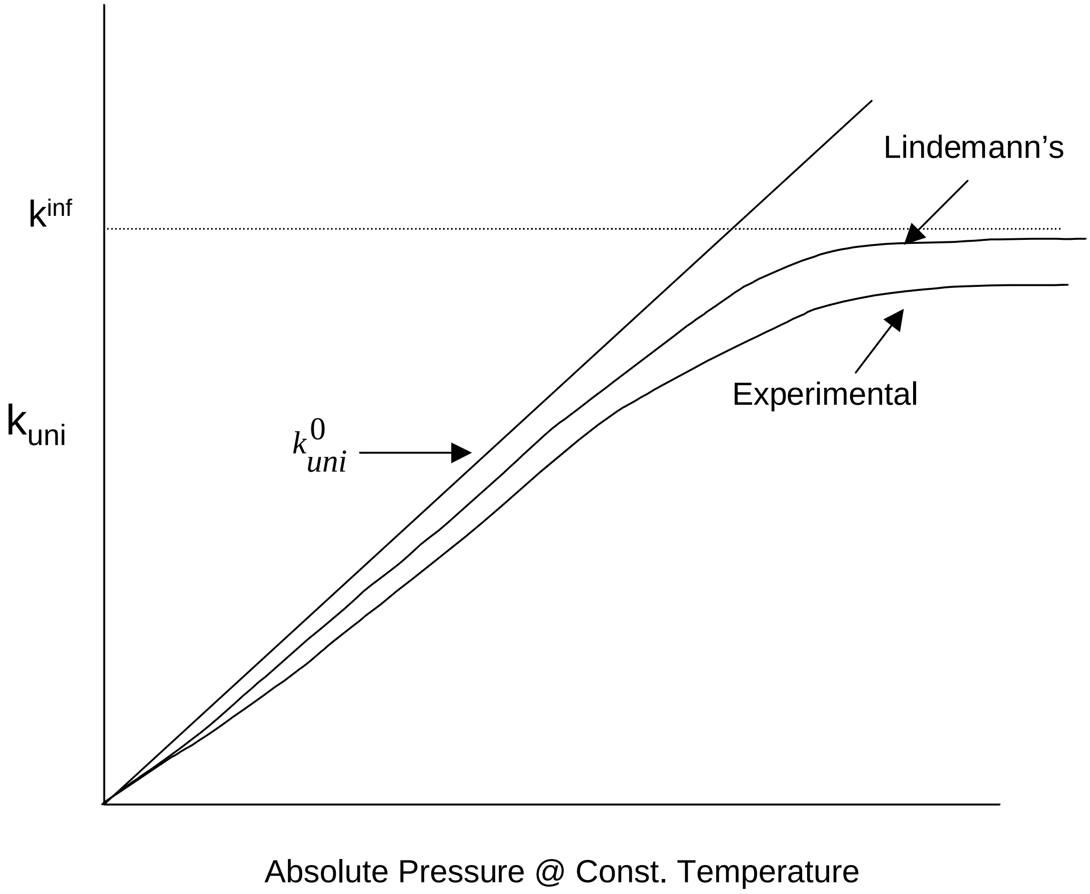

Figure 1. Pressure Dependence of k_{uni}

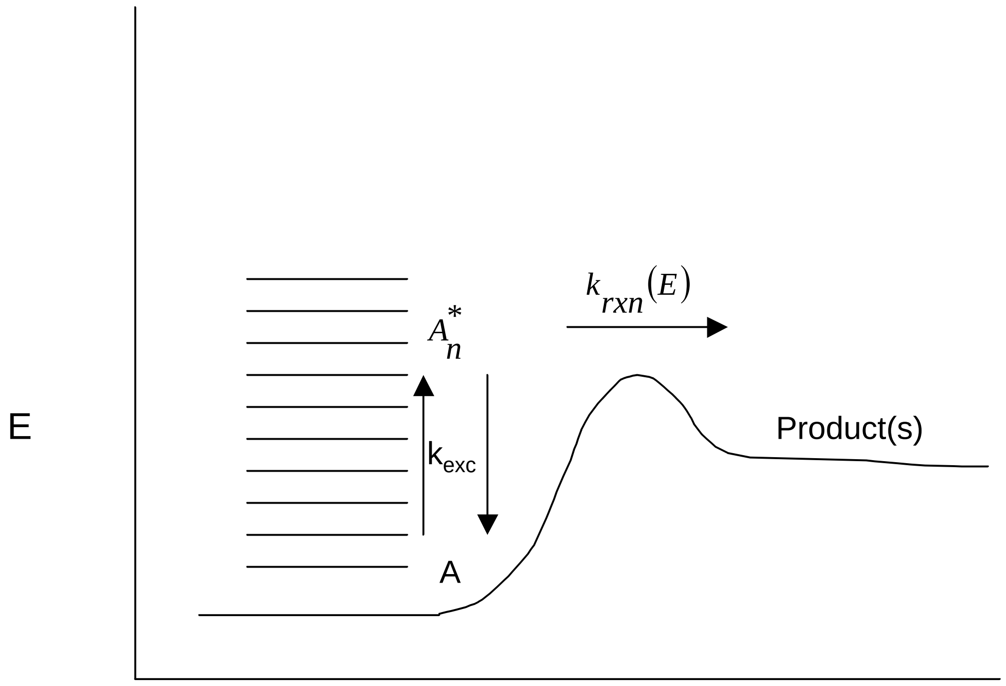

Figure 2. Energy Dependence of k_{uni} (Westmoreland (1986).

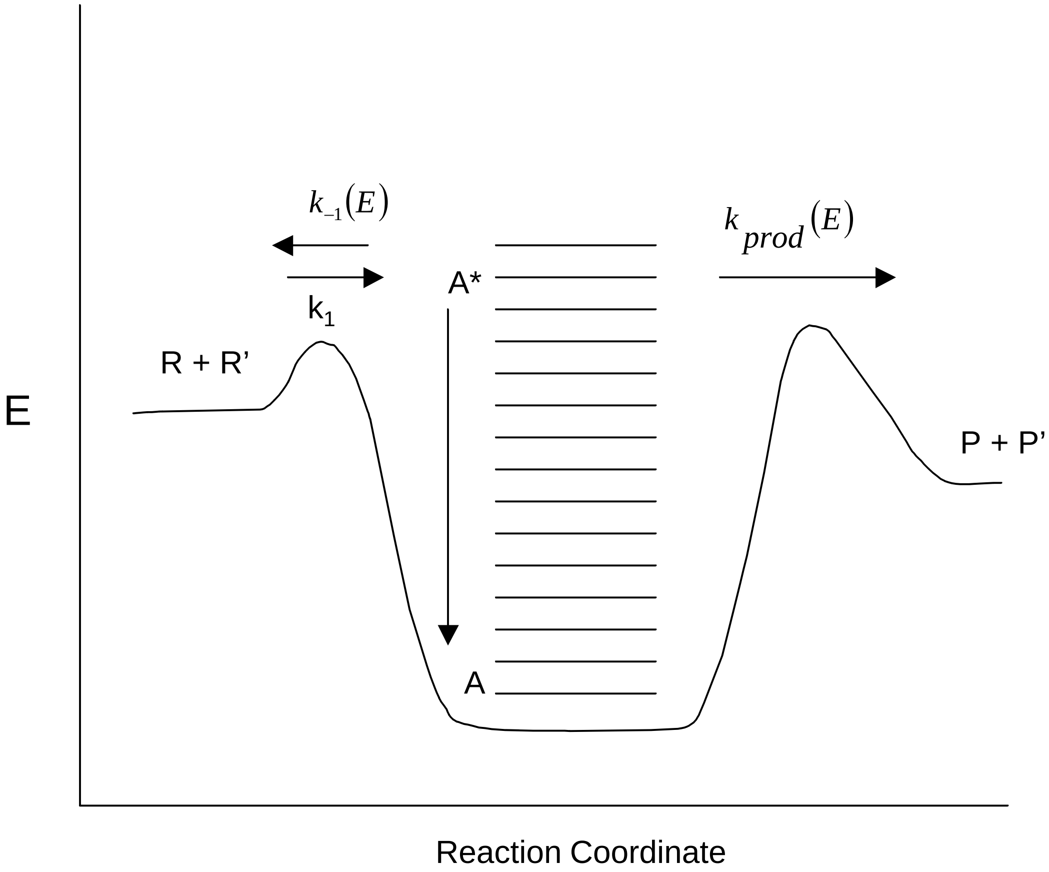

Figure 3. Bimolecular Chemical Activation (Westmoreland (1986).