Review Article　　　　　　　　　　　　　　　　　　　　　　　　　　　　　**Open Access**

Chemical Reaction Thermodynamics and Reaction Rate Theory

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Abstract

Chemical reactor modeling requires the formulation of Heat, Mass, and Chemical Species balances and depending on reactor configuration Computational Fluid Dynamic (CFD) to account for mixing effects. Thermochemical properties such as the species enthalpy have to be considered to account for heat of chemical reactions when conducting an overall or finite energy balance. To properly calculate the heat of reaction due to a reversible reaction, knowledge of the forward and reverse rate coefficients is required. Similarly, the species balance requires knowledge of the net rates of chemical reactions within the reactor to account for composition changes and the equilibrium constant is needed.

Keywords: Thermodynamics; Chemical kinetics

Reaction Thermodynamics

There are some fundamental thermochemical relations that are relevant in the mathematical treatment of the chemical reactor. For an ideal gas, if the natural elements are taken as reference, the specific enthalpy for the kth species can be written as follows

$$H_k^0(T) = \Delta H_{f,k}^0(25) + \int_{25}^{T} c_{p,k}^0 dT \qquad (1)$$

Where standard conditions are at 1.0 atmosphere of pressure, $\Delta H_{f,k}^0(25)$ is the species heat of formation at 25°C, and $C_{p,k}$ is the specific heat at constant pressure. The standard heat of reaction at temperature T can then be written as [1],

$$\Delta H_{rxn}^0(T) = \sum_k \nu_k H_{f,k}^0(25) + \sum_k \nu_k \int_{25}^{T} c_{p,k}^0 dT \qquad (2)$$

Where ν_k is the stoichiometric coefficient for the kth species participating in the reaction and it is negative for reactants.

Similarly, the standard entropy change for a chemical reaction is given by equation

$$\Delta S_{rxn}^0(T) = \sum_k \nu_k S_k^0(25) + \sum_k \nu_k \int_{25}^{T} \frac{c_{p,k}^0}{T} dT \qquad (3)$$

Where S_k^0 is the absolute entropy for the kth species in the chemical reaction at 25°C.

The properties given by equations (2) and (3) are important because from them the standard free energy for the reaction at temperature T can be obtained as follows

$$\Delta G_{rxn}^0(T) = \Delta H_{rxn}^0(T) - T\Delta S_{rxn}^0(T) \qquad (4)$$

and the equilibrium constant for the reaction can then be estimated by equation (5) [1]

$$\Delta G_{rxn}^0(T) = -RT \ln K_{activity} \qquad (5)$$

Furthermore, if the forward rate coefficient k_f of a chemical reaction is known, the reverse rate coefficient k_r is calculated as follows (by the principle of microscopic reversibility)

$$K_{activity} = K_c (RT)^{\Delta \nu} \qquad (6)$$

$$K_C = \frac{k_f}{k_r} \qquad (7)$$

Where K_c is the reaction equilibrium constant in concentration units.

To account for the change in species concentrations within the reactor, the net rate of formation for a given species has to be estimated. Consider I- elementary reversible (or irreversible) chemical reactions [2] involving K chemical species that can be represented in the following general form

$$\sum_{k=1}^{K} \gamma'_{ki} \chi_k \Leftrightarrow \sum_{k=1}^{K} \gamma''_{ki} \chi_k \qquad (i=1, 2, 3 \ldots. I) \qquad (8)$$
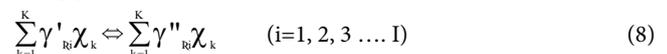
Where χ_k is the chemical symbol for the kth species. The production rate r_k of the kth species can be written in terms of the rate-of-progress variables q_i for all reactions involving the kth species

$$r_k = \sum_{i=1}^{I} \gamma_{ki} q_i \quad (k=1,2,....K) \qquad (9)$$

Where

$$\nu_{ki} = \nu''_{ki} - \nu'_{ki} \qquad (10)$$

and q_i for the ith reaction is given by the difference of the forward and reverse rates as

$$q_i = k_{fi} \prod [X_k]^{\nu^{ki}} - k_{fr} \prod [X_k]^{\nu^{ki}} \qquad (11)$$

Where $[X_k]$ is the molar concentration of the kth species and k_{fi}, and k_{ri}, are the forward and reverse rate constants of the ith reaction.

In summary, the mathematical treatment of chemical reactor design requires knowledge of thermodynamic properties such as species heat of formation, heat capacity, entropy, and kinetic coefficients for chemical reactions. If experimental or estimated values for these properties were not available in the literature, it becomes necessary to make sound estimates by methods described in the sections that follow this introduction.

Estimation of Thermochemical Properties

The emphasis on this section will be illustrating methods that

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can be used to estimate the thermochemistry of Polycyclic Aromatic Hydrocarbons (PAH) in order to be able to model mathematically experiments conducted dealing with toxic trace components in simple hydrocarbon fuels. The discussion is not meant to cover all of the theoretical aspects (only the main results are presented), but enough references are given to make it possible for the reader to find more extensive treatment of methods used for estimating thermochemistry.

Conventional methods: additivity

There are three important thermochemical properties of stable molecules that are required input in the mathematical models of reactors: heat of formation, absolute entropy, and specific heat. Conventional methods of estimating thermochemical properties include methods that are highly empirical in nature, such as those based on various forms of additivity principles, as well as those that are based on the use of statistical mechanical calculations [3]. Statistical mechanics Figure 1 however is of no use in estimating the heat of formation of molecules. The discussion that follows is expended on the works of Benson, Senkan and Golden [3-5].

There are empirical methods based on additivity principles. The first level in the hierarchy of additivity methods is the bond additivity. In this approach, the molecular properties can be considered as being made up of additive contributions from the individual bonds in the molecule. For example, the heat of formation of CH_3Cl [3] at 298 °K can be calculated as follows:

$$\Delta H_f(298) = 3\Delta H_f(C-H) + \Delta H_f(C-Cl) = 3(-3.8) + (-7.4) = -18.8 \text{ kcal/mol}$$

Where the bond contributions C-H and C-Cl can be found in Benson [4]. (A similar procedure would be used to estimate the heat capacity and absolute entropy). This estimate is within 5% of the experimentally measured value of -19.6 k cal/mol. It has been found that bond additivity rules reproduce experimental heat capacity and entropy values within ± 1 cal/mol-K on the average, but the error is greater for heavily branched compounds. Values of heat formation are generally estimated to be within ± 2 kcal/mol but again are subject to large errors in heavily branched compounds. Bond additivity methods cannot be employed to distinguish differences in properties of isomers such as n- butane and isobutene, for example.

The next level in additivity hierarchy is group additivity. Properties are associated with groups making up the molecule, a group consisting of a polyvalent atom in a molecule together with all its ligands. For example Benson [4], the molecule $CH_3CHOHCH_3$ contains four groups as follows:

2	$C-(C)(H)_3$
1	$C-(C)_2(O)(H)$
1	$O-(C)(H)$
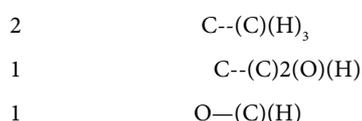
Values of heat capacity and entropy estimated by group additivity are on the average within ± 0.3 cal/mol-K of the measured values, whereas heat of formation estimates is within ± 0.5 kcal/mol. For heavily substituted species, deviations in heat capacity and entropy may go as high as ± 1.5 ca Umol-K, and the heat of formation may deviate by ± 3 kcal/mol.

Group additivity makes it possible to estimate the intrinsic entropy S_{int} of a chemical species. The absolute entropy is then given by

$$S_{abs} = S_{int} + R_{ln}(\eta) - R_{ln}(\sigma) + R_{ln}(g_e) \tag{12}$$

Where η, σ, and g_e ($g_e = 2s + 1$, where s is the total spin) are the

number of optical isomers, the total symmetry number, and electronic degeneracies, respectively. The symmetry number σ is the total number of independent permutations of identical atoms or groups in a molecule that can be arrived by simple rotations. Both the internal (σ_{int}) and external (σ_{ext}) symmetries must be considered in establishing the total symmetry number or

$$\sigma = (\sigma_{int}) \times (\sigma_{ext})$$

Group values of hydrocarbons and halogen-containing compounds for estimating heat capacity, intrinsic entropy, and heats of formation can be found in Benson [4]. Total symmetry number for common molecules can be found in Senkan [3]. The properties calculated by group additivity often need to be corrected for next-nearest-neighbor interactions such as cis, trans or gauche interactions, as well as nongroup interactions such as corrections due to ring-strain in cyclic molecules. Values for these corrections can be found in Benson [4].

Group Additivity and PAH

Group additivity has been used successfully to estimate the thermodynamic properties of PAH by Stein and Benson (Figure 2), Stein and Fahr and Wang [6-8]. More recently group additivity was used to estimate the properties of fullerene precursors by Pope et al. [9] who used groups developed by Moiseeva [10] to estimate the properties of PAH containing 5-carbon rings such as fluoranthene. Figure 2 shows the various groups existing in a PAH and the group additivity values taken from Stein and Benson. Stein and Benson [6] show that the average difference between predicted and measured heats of formation for eleven PAH including pyrene, for example is <2 kcal/mol, with the only exception being perylene for which the error was 6.7 kcal/mol and may be due to the inability of group additivity to account for "destabilization" of aromatic systems due to the presence of rings that contain only exo-type bonds. The average error for estimates of entropy and heat capacity was less than 1 cal/mol-K.

They also found that the average error in the estimated values for the heats of formation of substituted naphthalenes was about 1.2 k cal/mol.

The procedure for estimating properties can be demonstrated in reference to ; the heat of formation of benzo (a) pyrene would be

Figure 1: Statistical Mechanics of Molecular Properties.

A = $[C_B-(H)]$
B = $[C_{BF}-(C_B)_2(C_{BF})]$
C = $[C_{BF}-(C_B)(C_{BF})_2]$
D = $[C_{BF}-(C_{BF})_3]$

Benzo[a]pyrene consists of 12 $[C_B-(H)]$, 4 $[C_{BF}-(C_B)_2(C_{BF})]$, 2 $[C_{BF}-(C_B)(C_{BF})_2]$, and 2 $[C_{BF}-(C_{BF})_3]$ groups.

Figure 2: PAH Group Additivity (Stein and Benson) [6].
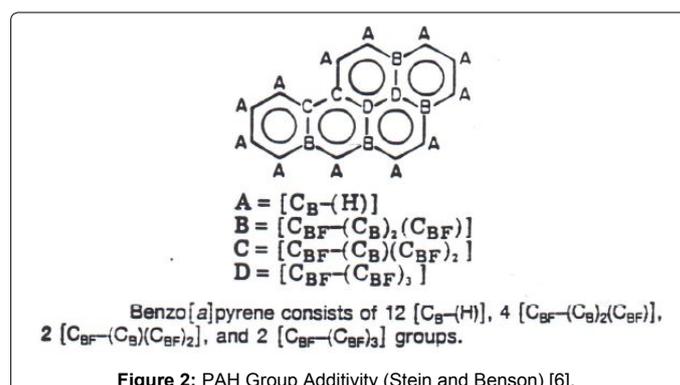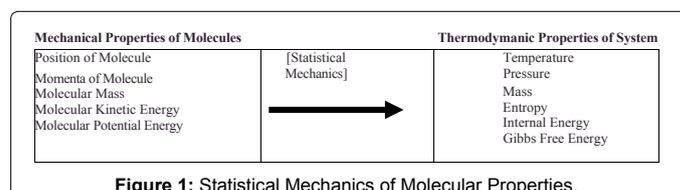
estimated as follows:

$$\Delta H^o_{f,298} = 12[C_B-(H)] + 4[C_{BF}-(C_B)_2(C_{BF})] + 2[C_{BF}-(C_B)(C_{BF})_2] + 2[C_{BF}-(C_{BF})_3]$$

$$= 12(3.30) + 4(4.8) + 2(3.7) + 2(1.45) = 69.1 \text{ kcal/mol} \qquad (13)$$

which compares well with the experimentally determined value of 69.0 kcal/mol from the NIST DATABASE 25.

Wang [8] found that although the group additivity method is adequate for estimating the heat of formation of small PAH, it generally does not perform well for larger PAH having highly fused ring structures. Table 1A taken from Wang [8] shows that group additivity predicts higher heats of formation for large PAH. Table 1B depicts the molecular structure for most of these PAH. As Wang points out, Stein and Benson [6] assumed that the heat of formation value for the group CBF (CBF)³ equals the heat of sublimation of graphite per carbon atom (1.45-1.5 kcal/mol) so that the enthalpy of formation of an infinitely large PAH molecule would converge to that of a graphite monolayer, nevertheless the calculated enthalpies for highly fused aromatics are too high if group values derived from relatively small PAH are used in the estimates.

Finally, Moiseeva [9] estimated group values for PAH containing five- membered rings based on experimental data and statistical mechanical calculations. The reader is directed to this work for further discussion.

Statistical Mechanics

As stated above, statistical mechanics methods can be employed to estimate the entropy and heat capacity of a molecule if the vibrational frequencies and moments of inertia of the molecule are known either experimentally or via computational quantum chemistry (Figures 3 and 4). Statistical mechanics is the discipline that makes the connection between the microscopic mechanical properties of a large collection of molecules (the larger the collection, the more reliable the results) and macroscopic thermodynamic properties as demonstrates.

The actual values of the molecular mechanical variables are not known. What are known as the possible values that these mechanical variables may take for any single molecule. Statistical mechanical methods are designed to consider the typical or average behavior to be expected from a large collection of particles. The entropy and heat capacity are expressed in terms of the total molar partition function Q as follows [10].

$$S = R \ln Q + R [\delta \ln Q / \delta_{\ln} T]_V \qquad (14)$$

$$c_v = R/T^2 [\delta^2 \ln Q / \delta (1/T^2)]_V \qquad (15)$$

where $c_p = c_v + R$, and Q can be expressed as the product of partition functions for each of the degree of freedom of the system as shown below:

$$Q = Qtrans * Qrot * Qvib * Qelec \qquad (16)$$

Expressions for each of the partitioned functions of equation (16) will not be shown here since they can be found in most standard books on statistical mechanics [11]. To be able to calculate the vibrational contribution to Q, the normal vibrational frequencies of the molecule must be known, similarly, the rotational contribution requires knowledge of molecular geometry in order to calculate the moments of inertia.

The thermodynamic properties of radical species can also be estimated using group additivity methods, some group values are available [4]. For the most part, the entropy and heat capacity of free

radical are estimated using the model compound approach and bond dissociation energy (BDE) or computational quantum chemistry for estimates of heats of formation. For example, the heat of formation of methyl radical can be determined from the reaction

$$CH_3CL <==> CH_3 + Cl \qquad (17)$$

Where the C-Cl BDE is known to be +84 k cal/mol [3]. The heat of formation is determined from the following expression

$$\Delta H_f(CH_3) = BDE + \Delta H_f(CH_3Cl) - \Delta H_f(Cl)(3.21) = 84 - 18.8 - 29.0 = 36 \text{ kcal/mol}$$

This value compares well with the experimental value of 35 k cal/mol.

Computational Quantum Chemistry: An Illustration of Applications and Concepts

The origin of the branch of physics called Quantum Mechanics dates back to the search for explaining several phenomena:

- Black Body radiation
- Photo-electric effect
- Dual nature of the electron
- The existence of the atom, even as simple as the Hydrogen atom

Molecule	ΔH$_{f,298}$ (kcal/mol)		
	Experimental	Ab initio-GE	Group Additivity
Benzene (C_6H_6)	19.81	20.8	19.8
Pyrene ($C_{16}H_{10}$)	51.59	51.3	55.1
Coronene ($C_{24}H_{12}$)		61.5	77.1
Circumcoronene ($C_{54}H_{18}$)		126	152
2-Circumcoronene ($C_{96}H_{24}$)		212	244
3-Circumcoronene ($C_{150}H_{30}$)		320	354

Table 1A: Enthalpy of Formation of Benzene and Highly Fused Aromatics [8].

Benzene

Pyrene

Coronene

Circumcoronene
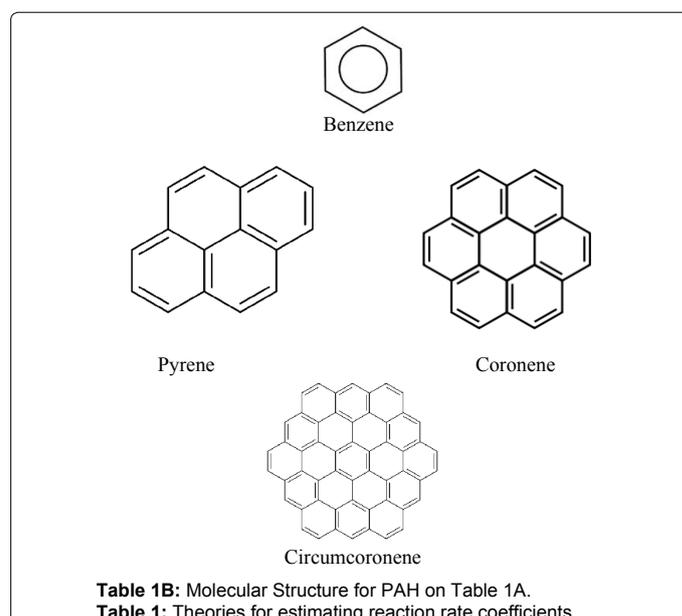
Table 1B: Molecular Structure for PAH on Table 1A.
Table 1: Theories for estimating reaction rate coefficients .

Computational Quantum Chemistry Objectives

Molecular Geometries (Stable molecules, Transition States, Conformers)

Molecular Properties (Heat of Formation, Enthalpy, Entropy)

Electron Density

Electrostatic Potentials

Dipole Moments

Solvent Effects

Figure 3: Computational Objectives with Quantum Chemistry (Chemistry, Chemical Engineering).

The discussion is not part of this work but a complete discussion of the above can be found in Physics, 8th edition by Cutnell and Johnson.

Figures 3 and 4 is a brief summary and introduction to the objectives of using Computational Quantum Chemistry in the area of Chemistry and Chemical Engineering. From the perspective of the chemical reactor engineer, thermochemical properties and transition state energy and geometry are most important. The effect of solvents in the rate of chemical reactions is also of great interest. Figure 4 provides an overview of the use of Computational Quantum Chemistry to obtain Molecular Properties.

In summary, the conventional methods applied to estimate the thermochemical properties of large molecules as PAH when lacking
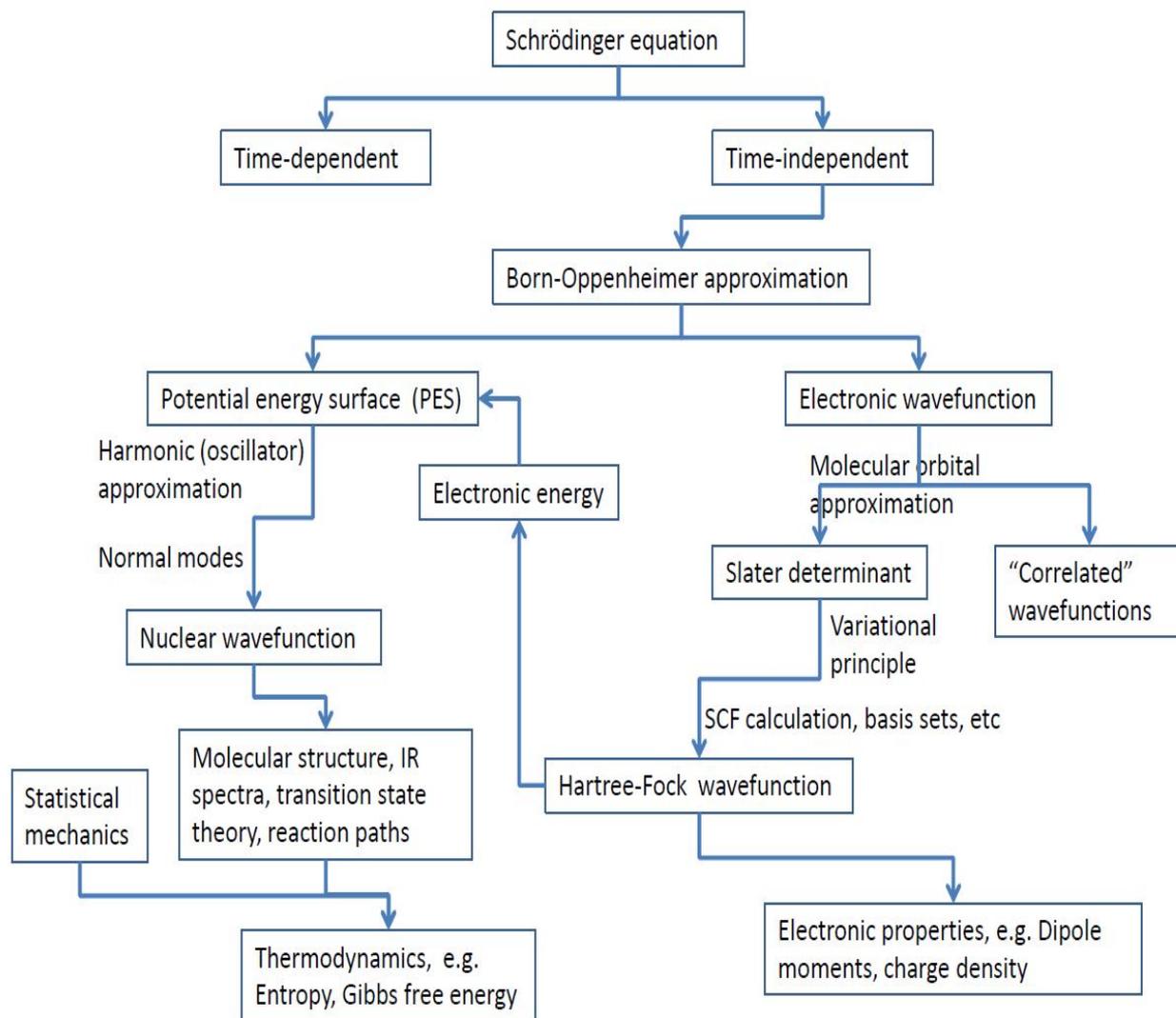
Figure 4: Molecular Properties form Computational Quantum Chemsitry (Skylaris CK, Chem 3023, University of South Hampton, Chemistry Department).

experimental or literature data have been presented.

Group additivity was used to estimate the entropy and heat capacity of stable PAH as recommended by Wang [8] using the group values recommended by Stein and Benson and Moiseeva [6,9].

The heats of formation of stable PAH were estimated by computational quantum chemistry with group equivalent corrections based on the group additivity approach. The heats of formation of radical PAH species were estimated using the BDE approach. The entropy and heat capacity of PAH radicals were estimated using the group values of Benson [4] when applicable, otherwise the model compound approach was applied.

The objectives of computational chemistry methods were presented as well, the calculation of heats of formation and transition state energy and geometry are also most important to the reaction engineer.

Chemical Kinetics and Theories of Reaction Rate Coefficients

Chemical kinetics

Kinetics from the perspective of the Chemical engineer has some principal functions:

• Determine the mechanism of the reaction consisting of elementary reactions

• Collecting experimental rate data

• Establishing the mathematical equation correlating with chemical rate data, including rate coefficients

• Designing chemical reactors

• Specifying operating conditions, methods of control, and auxiliary equipment

Reactions can be classified in accordance to several criteria.

Mechanism

• Irreversible

• Reversible

• Simultaneous

• Consecutive

For example, the decomposition of N_2O_5 is given by the overall reversible reaction,

$2N_2O_5 <==> 4NO_2 + O_2$ (overall reaction)
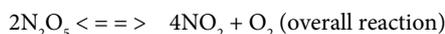
However, the decomposition takes place in several steps or elementary reactions (or molecular events) such as,

$N_2O_5 <==> NO_2 + NO_3$

$NO_2 + NO_3 <==> NO + O_2 + NO_2$ (slow)

$NO + NO_3 <==> 2NO_2$
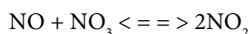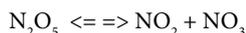
Molecularity: It depends on the number of molecules involved in the reaction,

• **Unimolecular**

• **Bimolecular**

Order: In general, the rate of the overall irreversible chemical reaction,

$A + B ==> C + D$
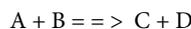
can be expressed by the following mathematical expression,

Rate = $kC_A^p * C_B^q$

Where C_A and C_B are the concentrations of species A and B in the overall reaction, k is the rate coefficient, and p and q are exponents such that the order of the reaction is given by,

Reaction Order=p+q, or sum of the exponents.

Order and molecularity are the same for elementary reactions describing a molecular event.

Operating conditions

• Isothermal at constant volume

• Isothermal at constant pressure

• Adiabatic

• Nonadiabatic, nonisothermal

Reactions can also be classified according to the phase involved as well as catalyzed or uncatalyzed, i.e.,

• Homogenous: gas, liquid, or solid

• Heterogeneous

• Catalyzed

• Uncatalyzed

The rate of a chemical reaction at constant volume conditions is given in general by the following mathematical expression,

R=(-1/V) dn/dt

Or if at constant volume only,

R=-(d(n/V)/dt=-dC/dt

Where, V is the reaction volume, n is the amount of material at time t, C is the material concentration, and t is the reaction time.

Law of mass action: The law of mass action states that the rate of a reaction is proportional to the mass of the participant chemical species.

Considering a reaction of general form,
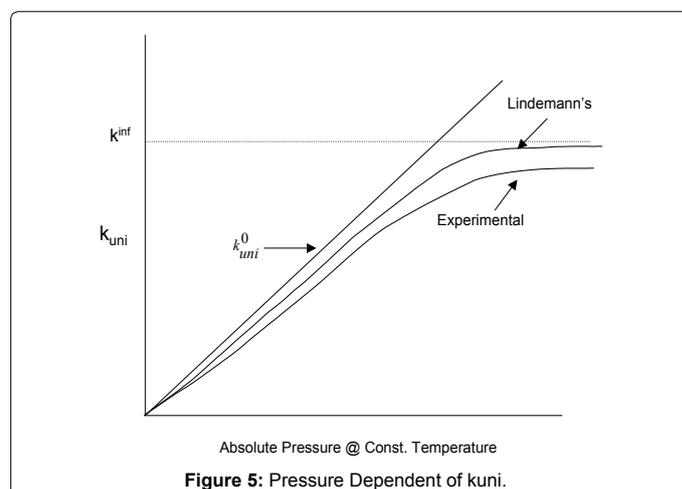
Figure 5: Pressure Dependent of kuni.

aA + bB +cC = = > lL + mM + ...
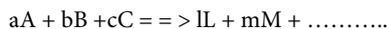
Mathematically, the law of mass action for the disappearance of reactant A at time t is given as,

$$R_A = -dC_A/dt = k\,(C_A)^p\,(C_B)^q\,(C_C)^r$$

Where C stands for concentration of species, k is the rate coefficient, t is reaction time, and a, b, c are the stoichiometric coefficients. Also note that,

$$R_A/a = R_B/b = R_C/c = -R_L/l = -R_M/m = ...$$

Or the rates of transformation or formation of other participants in the reaction are related by the stoichiometric coefficients.

If the reaction is an elementary reaction then,

Order = p + q + r =......= a +b +c + ...

And, p = a, q = b, r = c, ... etc.

Reaction Rate Upper-Limits

It helps to have an understanding of upper limits of reaction rates or coefficients depending on the nature of the system. These can be used as preliminary estimates for the reaction at hand depending on conditions or as a check of the validity of more complex theoretical estimates.

Bimolecular reactions in the gas phase

An upper limit to the rate of bimolecular reaction is the collision frequency between the molecules at hand. No consideration is given to steric factors or energy barriers. The collision frequency Z_{AB} for a bimolecular reaction is given by the expression [11]:

$$z_{AB} = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N^2}{10^6} \sqrt{8\pi kT\left(\frac{1}{M_A} + \frac{1}{M_B}\right)} C_A C_B \qquad (1)$$

Z_{AB}=number of collisions of A with B/sec-cm^3

σ=molecular diameter, cm

M=(Molecular weight/N), mass of molecule gm

N=6.023 × 10^{23} molecules/mol, Avogadro's number

C=molecular concentration of A or B, mol/liter

k=R/N=1.30 × 10^{-16} erg/°K, Boltzman Constant

Heterogeneous reactions at interfaces: gas, solid or liquid

Since an interface is involved the mechanism consists of five steps (as in a catalytic reaction involving two different molecules in the gas phase):

- Transport to surface (convective or diffusion)

- Adsorption (chemical or physical) of reactant molecules onto surface

- Elementary steps involving surface molecules, either entirely on the surface or between adsorbed and gas phase molecules.

- Desorption of product molecules form surface

- Removal of product molecules away from surface (convection or diffusion).

If transport phenomena are not a consideration, for a reaction involving a gas molecule A at the solid surface, the upper limit corresponds to the collision frequency between the gas molecule and the solid "wall" or impingement rate, Z_w

$$Z_w = \frac{P}{(2\pi kTM_A)^{1/2}}\ \text{molecules/cm}^2\text{-sec} \qquad (2)$$

Reactions within a solvent

The reaction of molecules in solution involves several steps:

- Transport of molecules in the bulk of the solvent

- Encounter of the reacting molecules within a the solvent "cage"

- Transport of products out of the cage into the bulk of the solvent

The presence of a solvent can cause diffusion effects to predominate as well as to impact the activation energy for the chemical reaction between the molecules. In very viscous fluids, the rate of reaction is diffusion controlled and the effective activation energy for the rate coefficient is fairly low. On the other hand, activation control is the most common, the rate of reaction depends on the rate of collision within the solvent cage and much higher activation energies are common. The simple treatment of this problem presented here comes mostly from the book "Reaction Kinetics by Michael J Pilling and Paul W Seakins. Consider a reaction between molecules A and B in solution which approach by diffusion to form an encounter pair {AB} and forming a so called solvent cage (the AB species are surrounded by solvent molecules within a cage). The kinetic scheme is as follows:

$$A + B \underset{R_{-d}}{\overset{R_{-d}}{\longleftrightarrow}} \{AB\} \xrightarrow{R_i} \text{Products} \qquad (3)$$
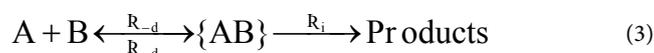
Where {AB} is the encounter pair, and k_d, k_d, and k_r, are the rate coefficients for diffusion approach, separation, and chemically activated reaction (within the solvent cage). Applying the steady state approximation to the encounter pair (or rate of formation of {AB} is equal to its rate of destruction):

$$d\,[\{AB\}]/dt = k_d\,[A][B] - (k_{-d} + k_r)[\{AB\}] = 0 \qquad (4)$$

The overall rate of reaction R_s (second order) is given by,

$$R_s = k_r[\{AB\}] = k_d k_r\,[A][B]/(k_{-d} + k_r) \qquad (5)$$

The approach has been similar to that used to pressure dependent reactions with collisions with the solvent (bath gas) are not explicitly involved in the kinetic scheme. We recognize two limiting conditions depending on the relative contributions of the terms in the denominator.

$k_r \gg k_{-d}$. If separation of {AB} is relatively difficult as in a viscous fluid, or if the reaction has small activation energy, the kinetics becomes diffusion-controlled.

If $k_r \ll k_{-d}$. For reactions with large activation energies (E> 20 kJ/mol) such as reactions in water solvent, the kinetics is activation-controlled. The reaction rate is now determined by the rate of passage over the activation energy barrier and the equilibrium concentration of encounter pairs {AB}.

Estimation of kinetic (reaction rate) coefficients

Elementary chemical reactions can be classified as either energy-transfer limited or chemical reaction rate limited (Tables 2 and 3). 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 intramolecular 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,

$$H_2 + M <==> H + H + M \qquad (6)$$

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 2 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 as 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,

$$A + B <==> Activated\ Molecule <==> Products \qquad (7)$$
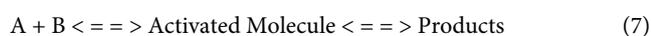
These quantum theories account for the dependence of the overall rate coefficients on the excess vibrational energy of the molecular species.

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

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \qquad (8)$$

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 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.

Literature data and 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 [13-16].

(b) Chlorinated Hydrocarbons- High Temperature Reactions [17,18].

(c) For lower temperatures and reactions occurring in the ambient air [19].

An extensive data base for chemical reaction kinetics can be found in the National Institute of Standards Chemical Kinetics Database. 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 3 taken from Senkan [3]. On inspection of Table 3, 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.

= =>**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 2: Theories for estimating reaction rate coefficients.

Reaction Type	$Log_{10}A$	E_a (Kcal/mole)	ΔH_r (Kcal/mole) @298 K
II Bimolecular Reactions $K= AT_2 exp(E_a/RT)$ cm_3/mol-sec			
a. Atom Metathesis Reactions			
$H + CH_4 <==> CH_3 + H_2$	8.85	11.6	0.0
Recommendation	8.50	F_A x F_C see below	
$CH_3 + C_2H_6 <==> CH_4 + C_2H_5$	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		
NH_2	1.30		
HO_2	1.70		
CHO	1.55		
CH_3	3.50		
C_2H_5	2.85		
b. Radical-radical Metathesis			
$C_2H_3 + H <==> C_2H_2 + H_2$	8.35	0.0	-66.3
Recommendation	8.00	0.0	
c. Molecule-Molecule Metathesis			
$C_2H_4 + C_2H_4 <==> C_2H_3 + C_2H_5$	9.15	72.0	70.0
Recommendation: Use microscopic reversibility.			
III. Complex Bimolecular Reactions $k= Aexp(E_a/RT)$ cm_3/mol-sec			
$CH_3 + O_2 <==> CH_2O + OH$	13.7	34.6	-53.0
Recommendation: None.			

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			
$CH_4 <==> CH_3 + H$	16.0	105	105
Recommendation	15.5	ΔH_r	
b. Complex Fission Reactions			
b1. Radical Fissions			
$C_2H_5 <==> C_2H_4 + H$	13.6	40.9	38.7
Recommendation	13.0	ΔH_r	
$CH_3CO <==> CH_3 + CO$	12.4	16.7	14.2
Recommendation	13.0	ΔH_r +5	
b2. Molecular Fissions			
Three and Four Center Eliminations			
$C_2H_5Cl <==> C_2H_4 + HCl$	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			
$1-C_3H_7 <==> 2-C_3H_7$	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 3: High Pressure Rate Coefficients for Analogous Reactions [3].

As already explained, simple kinetic theory of bimolecular reactions gives the following expression for the rate coefficient of the reaction between molecules A and B [20],

$$k = Z_{AB} = N_A \pi \sigma_{AB} \left(\frac{8kT}{\pi\mu} \right) \text{ cm}^3/\text{mol-sec} \quad (9)$$

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 K turns out to be 1.0×10^{13} cm³/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,

$$H + CH_4 <==> CH_3 + H_2$$
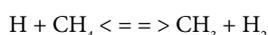
is the Evans-Polanyi relationship for similar reactions or,

$$E = \alpha\left(-\Delta H_{rn}\right) + \beta \quad (10)$$

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.

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 [20].

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,

$$A + B <==> AB^\gamma ==> R + S \quad (11)$$

in which AB^γ is the transition state structure, leads to the following expression,

$$k = 1.25 \times 10^{13} T^2 \left(\Delta S^\gamma / R \right) \exp\left(-E_a / RT \right) \quad (12)$$

The units are cm³/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.

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,

$$A <==> A^\gamma <==> P \quad (13)$$

Leads to the following expression (the units are sec⁻¹)

$$k = 4.60 \times 10^{10} T \exp\left(\Delta S^\gamma / R \right) \exp\left(-E_a / RT \right) \quad (14)$$

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.

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,

$$A \xrightarrow{k_{uni}} B \quad (15)$$

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 5.

In the mechanism developed by Lindemann Laidler [20], the decomposition of reactant A occurs according to the following two step scheme,

$$A + M \xrightarrow[k_1]{k_1} A^* + M \quad (16)$$

$$A^* \xrightarrow{k_2} P \quad (17)$$

In reaction (16), molecules of A are energized by collision with a second body M. Reaction (17) 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 and Gardiner [20,21] present a full discussion of Lindemann's Theory.

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

$$k_{uni}^\infty = \lim_{[M] \longrightarrow \infty} k_{uni} = k_2 \frac{k_1}{k_{-1}} \quad (18)$$

Whereas at low pressure,

$$k_{uni}^o = \lim_{[M] \longrightarrow 0} k_{uni} = k_1 [M] \quad (19)$$

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 (19), in order to calculate the low-pressure coefficient, k_1 is expressed as follows,

$$k_1 = Z_{A^*M} \bullet f(E_0) \bullet \beta \qquad (20)$$

Z_{A^*M} is the molar collisional frequency between energized A* molecules and M (see Equation (9)), $f(E_o)$ is the fraction of molecules with energies higher than E_o and can be activated according to reaction (16), this term may be given in terms of the Boltzmann distribution function P(E) or

$$f(E_o) = \int_{E_o}^{\infty} P(E)dE \qquad (21)$$

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 (18) and (19): [2,22]. The reader is referred to these references for more details.

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 (Figure 5). The reason for this can be explained by discussing what is presented illustrated in Figure 6. 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 Ref. [23].

In a similar manner, for bimolecular reactions Westmoreland et al. [23], the process is depicted in Figure 7. 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 isomerization of the activated molecule can be found in Kazakov et al. [24].

Software for the mathematical treatment of chemically activated reactions can be found, see for example Dean, Bozzelli, and Ritter [25] for an introduction to the CHEMACT program Dean and Westmoreland [26] for additional information. The reader is referred to these references for a more thorough discussion of chemical activation.

Solvent Effects on Reaction Rates in Solution

The following discussion is taken mostly from Mortimer and Taylor [27]. In the gas phase at relatively low pressure, molecules can be considered to move independently of each other. However, in a solution composed of solvent and solute molecules, the distances between molecules is relatively small and the particles are in continuous contact with each other.

The description of a bimolecular reaction in solution must take into account that reactant molecules are surrounded closely by solvent molecules within a solvent cage. The cage is not static since it is possible for molecules to enter and leave, see Figure 8.

A reactant molecule is envisioned as diffusing through the solution in a series of discontinuous jumps as it squeezes between the particles in the wall of one solvent cage and breaks through into a neighboring cage. If the solution viscosity is very high the reaction as discussed above is said to be diffusion controlled.

These jumps will be relatively infrequent so reactant molecules collide much less often than in the gas phase. However, when reactant molecules find themselves in the same cage, they remain there for a relatively long time.

This period is known as an encounter. During this period of time, the encounter pair of molecules, undergo a large number of collisions (with each other as well as the cage walls) until eventually they either react or escape to separate cages.

Solvent effects and organic reactions: transition state solvation

Organic reactions are mostly heterolytic (bonding electrons are taken away or provided in pairs), and carried out in solvents e.g.,

A +: B < = =>   A: B
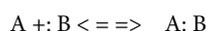
Thus, the effect of solvents on the rate of organic reactions is of significant importance due to the stabilization of reactants, products and transition state by the solvation effect of the chemical solvent on such species. The effect of solvents on organic reactions can speed up or slow down a reaction by a factor of 10^{20}, a change of solvent can bring about a million fold change in the reaction rate [28].

Figure 9 illustrates the effect of the solvent on the rate of heterolysis of an alkyl halide [28]. An example of such reaction or a S_N1 reaction (substitution nucleophilic unimolecular) is the following,

C $(CH_3)_3$-Br + OH$^-$ <= => C $(CH_3)_3$-OH + Br$^-$
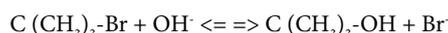
Where the nucleophile OH$^-$ substitutes Br$^-$ in the tert-butyl bromide molecule (a polar molecule). The rate of reaction is independent of OH$^-$ concentration.

As Figure 9 demonstrates [28], the presence of a polar solvent greatly stabilizes by solvation the structure of the transition state with the result of reducing the chemical activation energy for the S_N1 reaction by a great factor. Obviously since the transition state of the
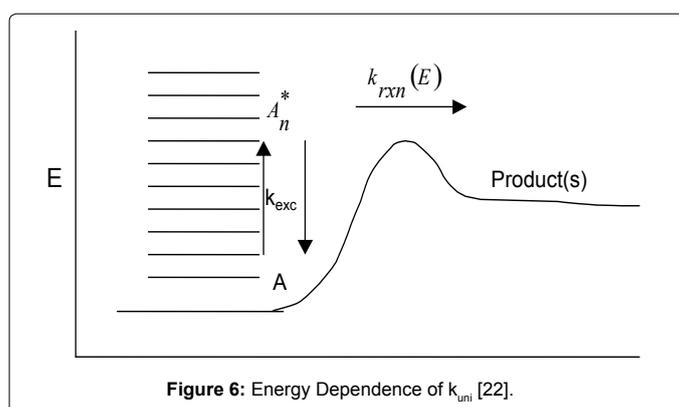
Figure 6: Energy Dependence of k_{uni} [22].

Figure 7: Bimolecular Chemical Activation [23].

Figure 8: Separate cages around two different reactant species in a dilute solution; **b)** Diffusion of the reactant species into the same cage at the beginning of an encounter; **c)** A reactant-reactant collision during the encounter; **d)** Reactant-solvent collisions during the encounter; **e)** Break-up of the encounter pair with no reaction having occurred [27].

Figure 9: Solvent Effect on Heterolysis of Alkyl halide. Transition State is more polar than reactant, and is more stabilized by solvent with dipole-dipole bonds [28].

tert-butyl Bromide is more polar than the reactant in this example, the effect is more pronounced the more polar are the solvents.

This serves as an introduction to the importance of salvation in Organic Chemical reactions. For a more comprehensive discussion of the subject (including bimolecular substitution or S_N2) the reader is referred to Organic Chemistry [28].

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