

Application of Ab initio Principles for Prediction of Chemical Reactivity

S.R. Saraf, W.J. Rogers and M.S. Mannan
Mary Kay O'Connor Process Safety Center
Chemical Engineering Department
Texas A&M University
College Station, Texas 77843-3122.

Abstract

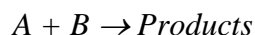
To simulate the behavior of a chemical reaction or unit operation, thermodynamic, kinetic or mechanistic information is necessary. Such data are usually obtained from direct experimental measurements, empirical correlations, or by estimation. Data can also be obtained from molecular simulation. Prediction of reaction rates from first principles allows comparisons between theory and experiment and hence determination of reaction mechanisms on the molecular level. This paper combines developments of quantum chemistry and computer algorithms to predict reaction rate constants based on transition state theory (TST).

Introduction:

In the development of a manufacturing process - raw materials, intermediates, process streams, and final products must be evaluated to determine the potential for hazardous chemical reactivity. The desired chemical reactions that make up the synthetic pathway must be evaluated as well as undesired reactions that may occur in any of the process streams¹. The undesired reactions include thermal degradation or polymerization initiated at higher temperatures as well as reactions that result from mischarging, reactions with contaminants, catalysis by contaminants, etc. Reactivity information can be obtained from experimental measurements and also from theoretical considerations. The high cost of obtaining laboratory data for all possible combinations makes computational techniques attractive. The normal approach to determine kinetics is mostly experimental and provides no satisfactory explanation for the reaction mechanism. The prediction of reaction kinetics is important for reactor design and for estimating the runaway potential of a reaction system. Quantum mechanical calculations can be combined with Transition State Theory (TST) to predict dynamics of a chemical reaction. This article focuses on the use of available software to obtain information about chemical reactions.

Kinetic information from experiments:

Consider the reaction,



The mass balance equation used for the reactor design can be represented as²:

$$\text{Batch time or residence time} = C_{A0} \int_0^x \frac{dx}{(-r_A)} \quad (1)$$

where,

C_{A0} – initial concentration of reactant A

r_A – rate of reaction

The energy balance equation similarly involves the rate of reaction term, r_A . For many reactions the rate can be written as the product of the rate constant (k) and the concentration of reacting species. The experimental approach to determine the rate law is to obtain an algebraic expression of the form:

$$r_A = [k(T)][f_n(C_A, C_B)] \quad (2)$$

The rate constant (k) is a strong function of temperature and can be correlated by an expression of the type,

$$k(T) = Ae^{-E/RT} \quad (3)$$

where,

A – frequency factor

E – energy of activation

Though there are different interpretations of activation energy (E) as an empirical parameter, the proposal of Arrhenius equation remains as an important steps in chemical kinetics and retains its usefulness today, nearly a century later after it was introduced. The parameters of the Arrhenius equation are determined by carrying out the reaction over a range of temperatures.

Why do we need to predict reactivity?

Such an experimental approach has been successfully employed but it is more of a curve fitting exercise and it provides no real insight into the mechanism of reaction; or quoting the famous Benson's Rule – 'It is impossible to prove a chemical reaction mechanism from kinetic rate data, only disprove one'.

Thus the kinetic data obtained from experiments cannot be extrapolated to conditions that are not achieved experimentally but possible during a runaway reaction. The computational approach to predict kinetics or properties of a material is advantageous because

- It can provide information about the structure, properties or performance of a system in a more rapid, more detailed or more cost-effective way than is possible by experiment.

- It gives insight into the mechanism of reaction and also enables the prediction of a potential runaway reaction.

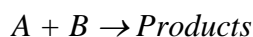
Theories of Chemical Reactions:

Classical theories for calculating the rate constant can be divided into three groups: transition state theory (TST), unimolecular rate theory in gases, and theory of diffusion controlled reactions³.

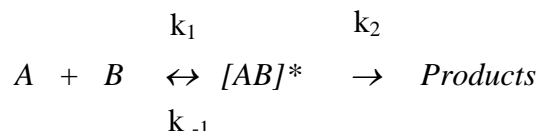
A. Transition State Theory (TST)

Our understanding of reactions on microscopic scale is largely based on TST, which has been effectively applied to gas phase reactions. The appealing feature of TST is the simple picture it provides for understanding the nature of reactive barrier passage: an activated complex, in quasi-equilibrium with reactants, which proceeds to form products.

Again, consider the reaction,



The above reaction can be modeled by the following scheme⁴,



Under the steady state assumption, rate of reaction can be written as,

$$r_A = k_2 \frac{q_{AB}^*}{q_A q_B} \exp(-\varepsilon / k_B T) [A][B] \quad (4)$$

where,

q – partition function per unit volume.

The partition function is a number that describes the number of states available to the system at a given temperature. For independent degrees of freedom the partition function for a single particle is simply the product of the partition functions for each type of motion namely, translational, rotational, vibrational, and electronic.

$$\therefore q = q_t q_r q_v q_e \quad (5)$$

The partition functions and their order of magnitude values are given in Table 1. An excellent explanation of partition functions and ensembles can be found in reference 5.

Table 1. Partition Functions for Molecular Degrees of Freedom

Type of motion	Partition Function	Order of Magnitude
Translational 3D per unit volume	$q_t / V = (2\pi mk_B T)^{3/2} / h^3$	10^{24} cm^{-3}
Rotational, linear molecule	$q_r = 8\pi^2 I k_B T / h^2 \sigma$	10^2
Rotational non-linear molecule	$q_r = \frac{\pi^{1/2}}{h^3 \sigma} (8\pi^2 k_B T)^{3/2} (I_A I_B I_C)^{1/2}$	10^3
Vibrational, each degree of freedom	$q_v = (1 - e^{-h\nu/k_B T})^{-1}$	1 (high ν) 10 (low ν)
Electronic	$q_e = \sum g_i \exp(-\varepsilon_i / k_B T)$	1

The rate constant, k_2 , describes the unimolecular decomposition rate of $[AB]^*$ going to products. Assuming the rate of $[AB]^*$ decomposition is simply equal to the frequency of vibration of the complex along the path of reaction coordinate denoted by ν^* , equation (4) simplifies to

$$r_A = \nu^* \frac{q_{AB}^*}{q_A q_B} \exp(-\varepsilon / k_B T) [A][B] \quad (5)$$

If we separate the partition function for the vibration along the reaction coordinates into two factors, a partition function for the vibration along the reaction coordinate and a partition function for the remaining degrees of freedom (q^*) equation (5) simplifies to

$$r_A = \frac{k_B T}{h} \frac{q^*_{AB}}{q_A q_B} \exp(-\varepsilon / k_B T) [A][B] \quad (6)$$

The prime notation indicates that the partition function for the transition state is missing one degree of freedom (the vibration along the reaction coordinate).

Interpretation of above equation:

The factor $k_B T / h$ equal to $6.25 \times 10^{12} \text{ s}^{-1}$ at room temperature (300 K), is the frequency with which reactants attempt to get to the activated complex.

The term,

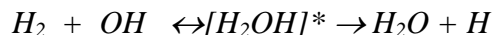
$$\frac{q^*_{AB}}{q_A q_B} \exp(-\varepsilon / k_B T)$$

determines the number of states available to the activated complex divided by the number of states available to the reactants. The rate constant is frequency times this ratio.

Example:

Order of estimate of frequency factor(A):

Consider the reaction,



With the help of values in Table 1 and equation (4), frequency factor (A) can be calculated. The transition state has 4 atoms. Thus the total number of vibrational modes excluding the vibration along the reaction coordinate is 5.

$$A = \frac{k_B T}{h} \frac{q_{TS}}{q_{H_2} q_{OH}}$$

$$\therefore A = 6 \times 10^{12} \frac{10^{24} 10^5 10^3}{(10^{24} 10^2 10)(10^{24})} = 6 \times 10^{-10} \text{ cm}^3 / \text{s}$$

Temperature dependence of frequency factor (A):

According to TST, $A \propto T^n$ and 'n' can be determined by using the formulas in Table 1 and knowing the reaction.



The transition state has 4 atoms and hence the total number of vibrational modes excluding the vibration along the reaction coordinate is 5. The temperature dependence follows from the formulas in Table1.

	Translational	Vibrational	Rotational
Cl	$T^{3/2}$	-	
O ₃	$T^{3/2}$	$T^3(n=3)$	$T^{3/2}$
ClO ₃	$T^{3/2}$	$T^5(n=5)$	$T^{3/2}$

$$A = \frac{k_B T}{h} \frac{q_{TS}}{q_{Cl} q_{O_3}}$$

$$\therefore A \propto T \frac{T^{3/2} T^5 T^{3/2}}{(T^{3/2})(T^{3/2} T^{3/2} T^3)} \propto T T^{1/2} \propto T^{3/2}$$

Use of software for predicting reaction dynamics

Rate constant:

From the earlier discussion the rate constant,

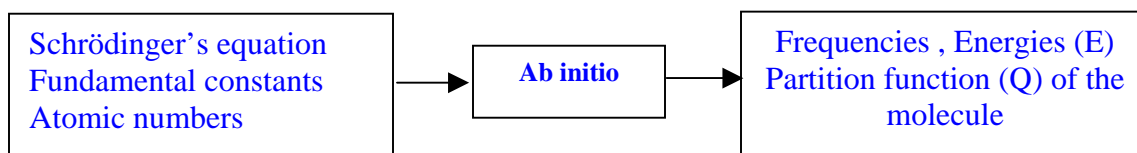
$$k = \frac{k_B T}{h} \frac{q_{AB}^*}{q_A q_B} \exp(-\varepsilon/k_B T) \quad (7)$$

To calculate the rate constant, k at a given temperature we need to determine partition functions of the reactant species, transition state and products.

Heats of reaction:

Heats of reaction can be calculated by determining the energies or heats of formation of reactants and products.

Software is used for optimization of geometry for a given chemical formula. The accuracy of calculation depends on the sophistication of theory used for calculations. From the optimized structure, the energy and partition function can be calculated.



NOTE :

- To calculate the properties associated with transition state the highest possible energy state has to be determined along the minimum energy path. Significant user input and understanding of basic chemistry is required for this step.
- In the above calculation we take only one representative of a reaction species, i.e. we are neglecting the effect of environment on the reaction path or in other words gas phase reaction kinetics can be predicted in the above manner but not liquid phase or solid catalyzed reactions.

GAUSSIANXY is an ab initio package used for calculations, where XY indicates the year of release of the software. A review of the techniques involved and the theory can be found in reference 6.

B. Extending TST to reactions in solutions

Solvent influences the reaction pathway and thereby the rate constant of reactions in the liquid phase. To extend TST to liquid phase reactions the effect of solvent on reaction pathway must be accounted for. The primary assumption of TST that all the reactants achieving activation would cross the reaction barrier is in question when the solvent interacts in a manner so as to impede successful barrier crossing.

Kramer's theory is a popularly applied to model liquid phase reactions. Kramer suggested the introduction of a dynamic correction factor called the transmission coefficient to modify the rate constant (k) obtained from TST to account for solvent effects⁷.

C. Heterogeneous catalysis

The rate of reaction is given by the following equations:

$$rate(gmol / m^2 s) = \frac{k_B T}{h} \frac{[S_2]}{q_A q_B} \exp(-E_s / RT) \quad (8)$$

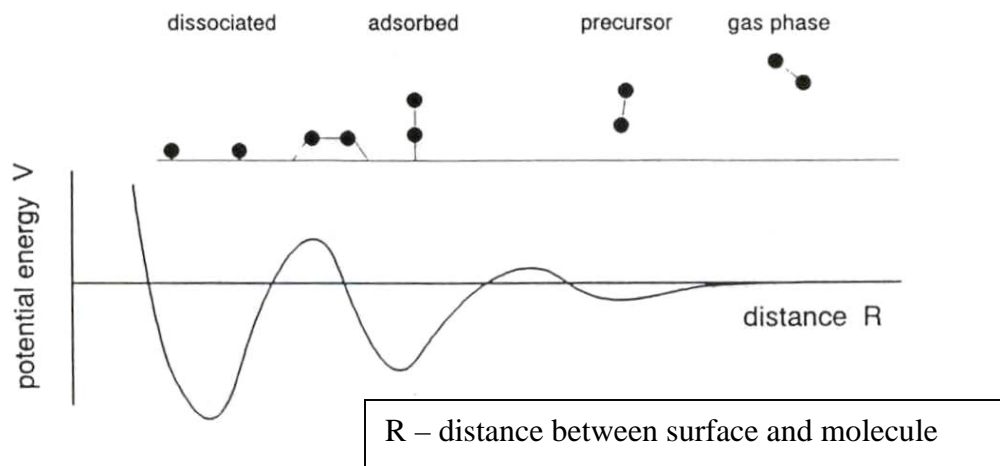
where,

S_2 - number of active sites per unit area

E_s - activation energy for the modified process

Monte Carlo simulation has been employed for modeling catalytic surface reactions⁸.

Our calorimetric studies on 50 wt.% hydroxylamine - water system demonstrate that the decomposition of hydroxylamine is enhanced by metal surfaces. The catalytic behavior can be explained based on interaction energies between the molecules and the metal surface⁹.



The above figure shows that the dissociated state of adsorbed molecule is energetically favored as compared to the undissociated molecule.

Conclusion:

TST can thus be effectively combined with quantum mechanical calculations to determine the kinetics of a reaction. The thermochemistry information can be obtained if the stoichiometry of a reaction is known. However to obtain the kinetics the elementary steps involved in the reaction must be known. By calculating the rate constant for every proposed elementary step, an overall rate constant can be determined. Comparing the results with experimental data validates the proposed reaction mechanism. The rapid growth in computing power has resulted in development of powerful algorithms, but this must be supplemented with development in ab initio theory to predict rate constants more accurately.

Symbols

A	Frequency factor
C_A	Concentration of specie A
C_{A0}	Initial concentration of reactant A.
E_A	Activation energy
h	Plank's constant
I	Moment of Inertia
k	Reaction rate constant
k_B	Boltzmann constant
T	Temperature
x	Conversion
q	Partition function
ε	Activation energy (molecular basis)
ν	Frquency of vibration

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