

# Chemical Kinetics: Including Investigation of Experimental Conditions

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**ABSTRACT:** Chemical kinetics, also known as reaction kinetics, is the branch of physical chemistry that is concerned with understanding the rates of chemical reactions. It is to be contrasted with chemical thermodynamics, which deals with the direction in which a reaction occurs but in itself tells nothing about its rate. Chemical kinetics includes investigations of how experimental conditions influence the speed of a chemical reaction and yield information about the reaction's mechanism and transition states, as well as the construction of mathematical models that also can describe the characteristics of a chemical reaction. In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances. Van 't Hoff studied chemical dynamics and in 1884 published his famous "Études de dynamique chimique". In 1901 he was awarded by the first Nobel Prize in Chemistry "in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions". After van 't Hoff, chemical kinetics deals with the experimental determination of reaction rates from which rate laws and rate constants are derived. Relatively simple rate laws exist for zero order reactions (for which reaction rates are independent of concentration), first order reactions, and second order reactions, and can be derived for others. Elementary reactions follow the law of mass action, but the rate law of stepwise reactions has to be derived by combining the rate laws of the various elementary steps, and can become rather complex. In consecutive reactions, the rate-determining step often determines the kinetics. In consecutive first order reactions, a steady state approximation can simplify the rate law. The activation energy for a reaction is experimentally determined through the Arrhenius equation and the Eyring equation. The main factors that influence the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction. Gorban and Yablonsky have suggested that the history of chemical dynamics can be divided into three eras. The first is the van 't Hoff wave searching for the general laws of chemical reactions and relating kinetics to thermodynamics. The second may be called the Semenov--Hinshelwood wave with emphasis on reaction mechanisms, especially for chain reactions. The third is associated with Aris and the detailed mathematical description of chemical reaction networks.

**KEYWORDS:** chemical kinetics, mechanism, rate constant, Arrhenius equation, dynamics, complex

## I. INTRODUCTION

### Factors affecting reaction rate

#### Nature of the reactants

The reaction rate varies depending upon what substances are reacting. Acid/base reactions, the formation of salts, and ion exchange are usually fast reactions. When covalent bond formation takes place between the molecules and when large molecules are formed, the reactions tend to be slower.

The nature and strength of bonds in reactant molecules greatly influence the rate of their transformation into products.<sup>1</sup>

#### Physical state

The physical state (solid, liquid, or gas) of a reactant is also an important factor of the rate of change. When reactants are in the same phase, as in aqueous solution, thermal motion brings them into contact. However, when they are in

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(An ISO 3297: 2007 Certified Organization)

Vol. 4, Issue 7, July 2015

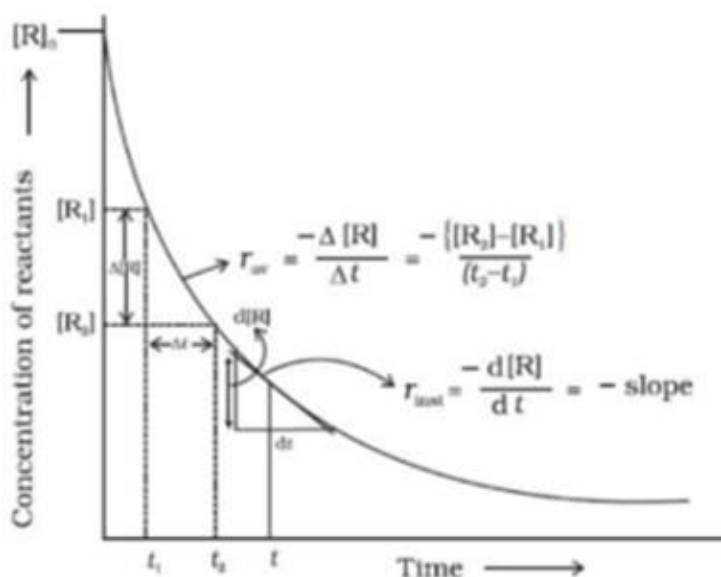
separate phases, the reaction is limited to the interface between the reactants. Reaction can occur only at their area of contact; in the case of a liquid and a gas, at the surface of the liquid. Vigorous shaking and stirring may be needed to bring the reaction to completion. This means that the more finely divided a solid or liquid reactant the greater its surface area per unit volume and the more contact it with the other reactant, thus the faster the reaction. To make an analogy, for example, when one starts a fire, one uses wood chips and small branches — one does not start with large logs right away. In organic chemistry, on water reactions are the exception to the rule that homogeneous reactions take place faster than heterogeneous reactions (are those reactions in which solute and solvent not mix properly)<sup>2</sup>

### Surface area of solid state

In a solid, only those particles that are at the surface can be involved in a reaction. Crushing a solid into smaller parts means that more particles are present at the surface, and the frequency of collisions between these and reactant particles increases, and so reaction occurs more rapidly. For example, Sherbet (powder) is a mixture of very fine powder of malic acid (a weak organic acid) and sodium hydrogen carbonate. On contact with the saliva in the mouth, these chemicals quickly dissolve and react, releasing carbon dioxide and providing for the fizzy sensation. Also, fireworks manufacturers modify the surface area of solid reactants to control the rate at which the fuels in fireworks are oxidised, using this to create diverse effects. For example, finely divided aluminium confined in a shell explodes violently. If larger pieces of aluminium are used, the reaction is slower and sparks are seen as pieces of burning metal are ejected.<sup>3</sup>

### Concentration

The reactions are due to collisions of reactant species. The frequency with which the molecules or ions collide depends upon their concentrations. The more crowded the molecules are, the more likely they are to collide and react with one another. Thus, an increase in the concentrations of the reactants will usually result in the corresponding increase in the reaction rate, while a decrease in the concentrations will usually have a reverse effect. For example, combustion will occur more rapidly in pure oxygen than in air (21% oxygen).<sup>4</sup>



The rate equation shows the detailed dependence of the reaction rate on the concentrations of reactants and other species present. The mathematical forms depend on the reaction mechanism. The actual rate equation for a given reaction is determined experimentally and provides information about the reaction mechanism.<sup>5</sup>

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### Temperature

Temperature usually has a major effect on the rate of a chemical reaction. Molecules at a higher temperature have more thermal energy. Although collision frequency is greater at higher temperatures, this alone contributes only a very small proportion to the increase in rate of reaction. Much more important is the fact that the proportion of reactant molecules with sufficient energy to react (energy greater than activation energy:  $E > E_a$ ) is significantly higher and is explained in detail by the Maxwell–Boltzmann distribution of molecular energies. At a given temperature, the chemical rate of a reaction depends on the value of the A-factor, the magnitude of the activation energy, and the concentrations of the reactants. Usually, rapid reactions require relatively small activation energies.

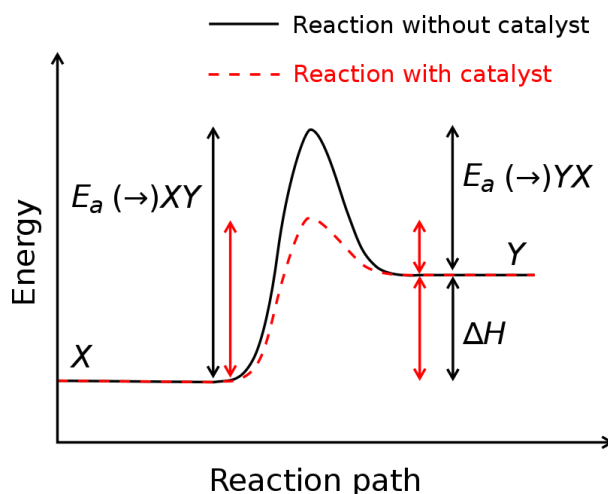
The 'rule of thumb' that the rate of chemical reactions doubles for every 10 °C temperature rise is a common misconception. This may have been generalized from the special case of biological systems, where the  $Q_{10}$  (temperature coefficient) is often between 1.5 and 2.5.

The kinetics of rapid reactions can be studied with the temperature jump method. This involves using a sharp rise in temperature and observing the relaxation time of the return to equilibrium. A particularly useful form of temperature jump apparatus is a shock tube, which can rapidly increase a gas's temperature by more than 1000 degrees.<sup>6</sup>

### Catalysts

A catalyst is a substance that alters the rate of a chemical reaction but it remains chemically unchanged afterwards. The catalyst increases the rate of the reaction by providing a new reaction mechanism to occur with in a lower activation energy. In autocatalysis a reaction product is itself a catalyst for that reaction leading to positive feedback. Proteins that act as catalysts in biochemical reactions are called enzymes. Michaelis–Menten kinetics describe the rate of enzyme mediated reactions. A catalyst does not affect the position of the equilibrium, as the catalyst speeds up the backward and forward reactions equally.

In certain organic molecules, specific substituents can have an influence on reaction rate in neighbouring group participation<sup>7</sup>



Generic potential energy diagram showing the effect of a catalyst in a hypothetical endothermic chemical reaction. The presence of the catalyst opens a new reaction pathway (shown in red) with a lower activation energy. The final result and the overall thermodynamics are the same.<sup>8</sup>

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(i) **Average rate of reaction,**

$$r_{av} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

The units of rate of a reaction are mol L<sup>-1</sup> s<sup>-1</sup> or mol L<sup>-1</sup> min<sup>-1</sup>.

(ii) **Instantaneous rate of reaction** ( $r_{inst}$ ) can be calculated from  $r_{av}$  in the limit  $\Delta t \rightarrow 0$  and is represented as

$$r_{inst} = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

In general for a reaction,  $aA + bB \rightarrow cC + dD$

$$\begin{aligned} \text{Rate} &= -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} \\ &= +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt} \end{aligned}$$

## 1) Pressure

Increasing the pressure in a gaseous reaction will increase the number of collisions between reactants, increasing the rate of reaction. This is because the activity of a gas is directly proportional to the partial pressure of the gas. This is similar to the effect of increasing the concentration of a solution.<sup>9</sup>

In addition to this straightforward mass-action effect, the rate coefficients themselves can change due to pressure. The rate coefficients and products of many high-temperature gas-phase reactions change if an inert gas is added to the mixture; variations on this effect are called **fall-off** and **chemical activation**. These phenomena are due to exothermic or endothermic reactions occurring faster than heat transfer, causing the reacting molecules to have non-thermal energy distributions (**non-Boltzmann distribution**). Increasing the pressure increases the heat transfer rate between the reacting molecules and the rest of the system, reducing this effect.

Condensed-phase rate coefficients can also be affected by pressure, although rather high pressures are required for a measurable effect because ions and molecules are not very compressible. This effect is often studied using diamond anvils.<sup>10</sup>

A reaction's kinetics can also be studied with a pressure jump approach. This involves making fast changes in pressure and observing the relaxation time of the return to equilibrium.

## 2) Absorption of light

The activation energy for a chemical reaction can be provided when one reactant molecule absorbs light of suitable wavelength and is promoted to an excited state. The study of reactions initiated by light is photochemistry, one prominent example being photosynthesis.<sup>11</sup>

## Experimental methods

The experimental determination of reaction rates involves measuring how the concentrations of reactants or products change over time. For example, the concentration of a reactant can be measured by spectrophotometry at a wavelength where no other reactant or product in the system absorbs light.

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**NOTE:**

Let us consider a general reaction:

$$A + B \longrightarrow C + D$$

Rate of this reaction can be expressed as:

$$\text{Reaction rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$


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For example,  $N_2 + 3H_2 \longrightarrow 2NH_3$

Rate of this reaction can be expressed as,

$$-\frac{d[N_2]}{dt} = -\frac{1}{3} \frac{d[H_2]}{dt} = \frac{1}{2} \frac{d[NH_3]}{dt}$$


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In general, for a reaction,

$${}_aA + {}_bB \longrightarrow {}_cC + {}_dD$$

Rate of this reaction can be expressed as,

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

For reactions which take at least several minutes, it is possible to start the observations after the reactants have been mixed at the temperature of interest.

### Fast reactions

For faster reactions, the time required to mix the reactants and bring them to a specified temperature may be comparable or longer than the half-life of the reaction. Special methods to start fast reactions without slow mixing step include

- Stopped flow methods, which can reduce the mixing time to the order of a millisecond. The stopped flow methods have limitation, for example, we need to consider the time it takes to mix gases or solutions and are not suitable if the half-life is less than about a hundredth of a second.
- Chemical relaxation methods such as temperature jump and pressure jump, in which a pre-mixed system initially at equilibrium is perturbed by rapid heating or depressurization so that it is no longer at equilibrium, and the relaxation back to equilibrium is observed. For example, this method has been used to study the neutralization  $H_3O^+ + OH^-$  with a half-life of  $1 \mu s$  or less under ordinary conditions.
- Flash photolysis, in which a laser pulse produces highly excited species such as free radicals, whose reactions are then studied<sup>12</sup>

## II.DISCUSSION

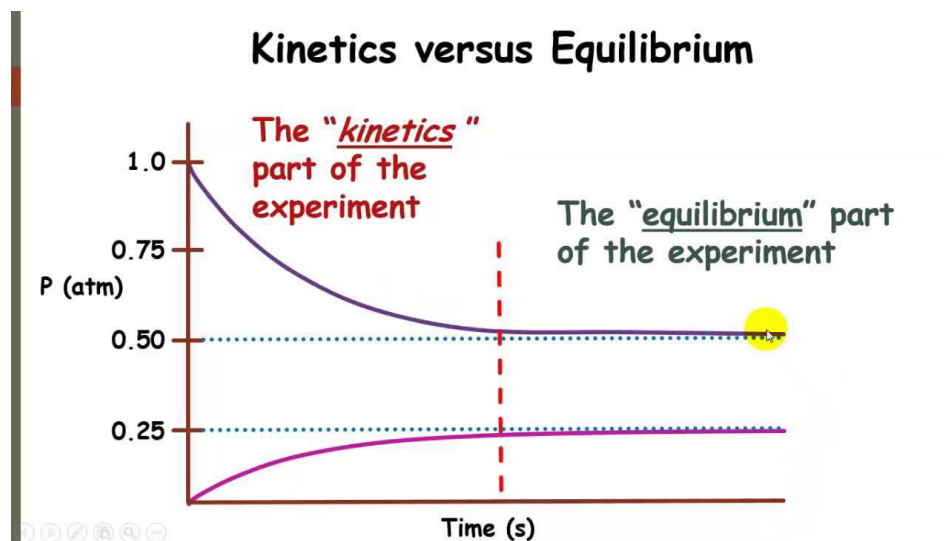
### Equilibrium

While chemical kinetics is concerned with the rate of a chemical reaction, thermodynamics determines the extent to which reactions occur.

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In a reversible reaction, chemical equilibrium is reached when the rates of the forward and reverse reactions are equal (the principle of dynamic equilibrium) and the concentrations of the reactants and products no longer change. This is demonstrated by, for example, the Haber–Bosch process for combining nitrogen and hydrogen to produce ammonia. Chemical clock reactions such as the Belousov–Zhabotinsky reaction demonstrate that component concentrations can oscillate for a long time before finally attaining the equilibrium.<sup>13</sup>

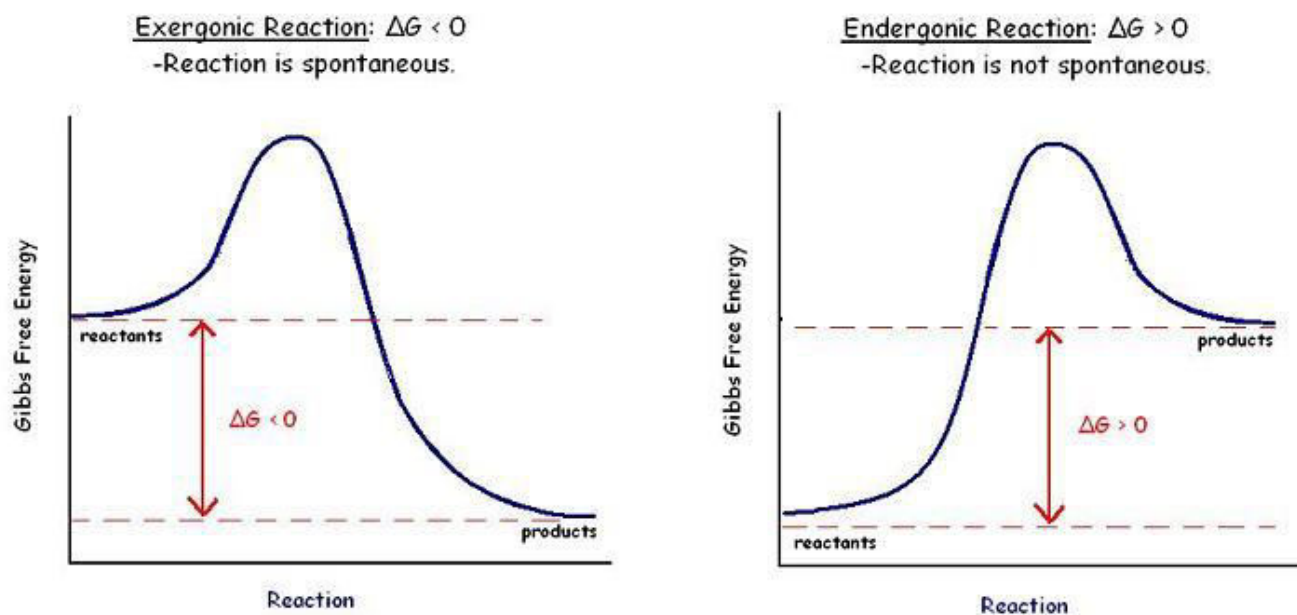
### Free energy

In general terms, the free energy change ( $\Delta G$ ) of a reaction determines whether a chemical change will take place, but kinetics describes how fast the reaction is. A reaction can be very exothermic and have a very positive entropy change but will not happen in practice if the reaction is too slow. If a reactant can produce two products, the thermodynamically most stable one will form in general, except in special circumstances when the reaction is said to be under kinetic reaction control. The Curtin–Hammett principle applies when determining the product ratio for two reactants interconverting rapidly, each going to a distinct product. It is possible to make predictions about reaction rate constants for a reaction from free-energy relationships. The kinetic isotope effect is the difference in the rate of a chemical reaction when an atom in one of the reactants is replaced by one of its isotopes.<sup>14</sup>

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Chemical kinetics provides information on residence time and heat transfer in a chemical reactor in chemical engineering and the molar mass distribution in polymer chemistry. It also provides information in corrosion engineering.

### Applications and models

The mathematical models that describe chemical reaction kinetics provide chemists and chemical engineers with tools to better understand and describe chemical processes such as food decomposition, microorganism growth, stratospheric ozone decomposition, and the chemistry of biological systems. These models can also be used in the design or modification of chemical reactors to optimize product yield, more efficiently separate products, and eliminate environmentally harmful by-products.<sup>15</sup> When performing catalytic cracking of heavy hydrocarbons into gasoline and light gas, for example, kinetic models can be used to find the temperature and pressure at which the highest yield of heavy hydrocarbons into gasoline will occur. Chemical Kinetics is frequently validated and explored through modeling in specialized packages as a function of ordinary differential equation-solving (ODE-solving) and curve-fitting.

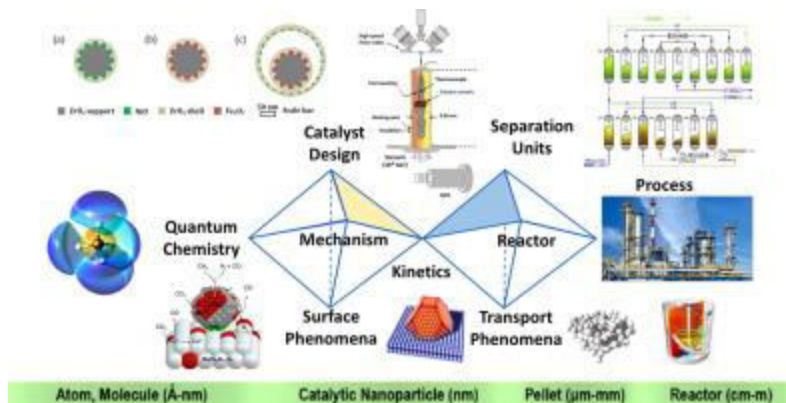
### Numerical methods

In some cases, equations are unsolvable analytically, but can be solved using numerical methods if data values are given. There are two different ways to do this, by either using software programmes or mathematical methods such as the Euler method. Examples of software for chemical kinetics are i) Tenua, a Java app which simulates chemical reactions numerically and allows comparison of the simulation to real data, ii) Python coding for calculations and estimates and iii) the Kintecus software compiler to model, regress, fit and optimize reactions.<sup>16</sup>

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Kinetics of chemical processes: From molecular to industrial scale

## III.RESULTS

The idea of a potential-energy surface sprang from the ideas of Dutch physical chemist Jacobus Henricus van 't Hoff and Swedish physicist Svante August Arrhenius that were put forward to explain the effect of temperature on reaction rates. An important advance was made in 1931 by American chemist Henry Eyring and British chemist Michael Polanyi, who constructed, on the basis of quantum mechanics, a potential-energy surface for the simple reaction  $H^{\alpha} + H^{\beta}-H^{\gamma} \rightarrow H^{\alpha}-H^{\beta}-H^{\gamma} \rightarrow H^{\alpha}-H^{\beta} + H^{\gamma}$ . For convenience the labels  $\alpha$ ,  $\beta$ , and  $\gamma$  are added as superscripts. When this reaction occurs, an atom  $H^{\alpha}$  attacks a hydrogen molecule  $H^{\beta}-H^{\gamma}$  and abstracts one of the hydrogen atoms from it. As the bond begins to form, the  $H^{\beta}-H^{\gamma}$  bond becomes more and more extended and finally breaks. Somewhere along the reaction path, there is a particular intermediate state corresponding to the maximum value of the potential energy.<sup>17</sup>

This particular intermediate state is usually designated by the superscript  $\ddagger$  (used above in the discussion of the Arrhenius equation). It is known as an activated complex and plays an important role in what has come to be called transition-state theory, developed independently in 1935 by Eyring, Polanyi, and English physical chemist M.G. Evans. The essential feature of the theory is that the activated complexes are considered to be formed from the reactants in a state in which they are in equilibrium with the reactants. Thus, the above reaction can be written as  $H^{\alpha} + H^{\beta}-H^{\gamma} \rightarrow H^{\alpha}-H^{\beta}-H^{\gamma}\ddagger$  (at equilibrium with  $H^{\alpha} + H^{\beta}-H^{\gamma}$ )  $\rightarrow H^{\alpha}-H^{\beta} + H^{\gamma}$ .

Since the activated complexes are in equilibrium, their concentration can be expressed in terms of the concentrations of the reactants. The reaction rate is this concentration multiplied by the frequency with which they form products, which is known from kinetic theory. Despite the approximations involved in transition-state theory, it has been successful in providing an insight into how chemical reactions occur and how their rates depend on various factors.<sup>16</sup>

## IV.CONCLUSIONS

### Molecular dynamics

The second theoretical approach to chemical kinetics is referred to as molecular dynamics, or reaction dynamics. It is a more detailed treatment of reactions and is designed to investigate the atomic motions that occur during a chemical reaction and the quantum states of the reactant and product molecules. Such studies are important in testing the validity of transition-state theory and similar treatments. Also, there are important practical applications of kinetics, such as reactions occurring in lasers, for which information about the energy states of the products of a chemical reaction is needed; this information is not provided by transition-state theory but is an important outcome of molecular dynamics. Consider a simple reaction of the type  $A + B-C \rightarrow Y + Z$ , where A is an atom and B-C is a diatomic molecule. A dynamical calculation would first involve calculating, using quantum mechanics, a potential-energy surface that



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gives the potential energy corresponding to a set of initial configurations. One can make dynamical calculations for a variety of vibrational states of the reactant B—C and for a variety of translational energies. Ideally the calculations would be based on quantum mechanics, but this proves difficult, and often classical mechanics is used. Except for certain types of reactions where quantum effects are important, it appears that for many reaction systems the error involved in neglecting quantum effects is not great. In principle the dynamical calculations should give more-reliable results than any other treatment; however, for any but the simplest reactions, the computer calculations are time-consuming, and, since many approximations must be made to save computer time, there is often some uncertainty about the results.<sup>17</sup>

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