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Chapter 1 Understanding chemical reactions at the molecular level

"chem·i·stry (kem' i strë), *n., pl.* -tries. The science that deals with or investigates the composition, properties, and transformations of substances and various elementary forms of matter." The dictionary definition emphasizes chemical transformation as a central theme of chemistry.

By the end of the nineteenth century, the young science of physical chemistry had characterized the dependence of the rate of the chemical transformation on the concentrations of the reactants. This provided the concept of a chemical reaction rate constant k and by 1889 Arrhenius showed¹ that the temperature dependence of the rate constant often took on the simple form $k = A \exp(-E_a/RT)$, where A is referred to as the pre-exponential factor and E_a as the activation energy. Arrhenius introduced the interpretation of E_a as the energetic barrier to the chemical rearrangement. Only later did we understand that reactions also have steric requirements and that the Arrhenius A factor is the carrier of this information.

It was next realized that the net transformation often proceeds by a series of elementary steps. A key progress was the identification of the reaction mechanism, which is a collection of elementary processes (also called elementary steps or elementary reactions) that leads to the observed stoichiometry and explains how the overall reaction proceeds. A mechanism is a proposal from which you can work out a rate law that agrees with how the observed rate of the reaction depends on the concentrations. The fact that a mechanism "explains" the experimental results, however, is not a proof that the mechanism is correct. Bulk kinetic studies are carried out at a controlled temperature, that is, under conditions of thermal equilibrium. The measured thermal rate constants refer to an average over all accessible reactant states weighted by the populations of those states at that temperature. As might be expected, such averages hide detailed information about what factors really cause the reaction to proceed. What we need is the ability to examine the individual processes and preferably to do so with selection of the energetic (and orientation) states of the reactants.

One of the greatest challenges in chemistry is to devise experiments that can reveal how chemical transformations occur that are otherwise hidden behind thermal averages and multi-step mechanisms **and** to develop the theoretical framework for describing and understanding these chemical changes. With this book

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you are invited to a dance of molecules. With an appreciation of the dance steps comes the power to understand and predict chemical behavior, if not become a molecular choreographer.

1.1 What is molecular reaction dynamics?

Reaction dynamics is the study of the molecular level mechanism of elementary chemical and physical processes. It seeks to understand what actually takes place at that level when a change, chemical or physical, occurs. As an example, when molecular chlorine gas is introduced into a vessel containing bromine vapor, a chemical reaction does take place, and it can be monitored in time by a change in the color. The net chemical change in the vessel is $Cl_2 + Br_2 \rightarrow 2BrCl$. The reaction rate is observed to be of second order, that is, the rate of disappearance of Cl_2 or Br_2 is first order in the concentration of each reactant. Yet on the molecular level the elementary reaction

$$Cl_2 + Br_2 \rightarrow 2BrCl$$

does not take place. In other words, when a single chlorine molecule strikes a single bromine molecule, the two molecules bounce off each other without exchanging atomic partners, and this fact has been demonstrated experimentally.²

Molecular reaction dynamics is the study of elementary processes and the means of probing them, understanding them, and controlling them. We will also apply molecular reaction dynamics to reactions in solution and to reactions on surfaces, exploring the elementary steps in catalysis. As a bridge between the gas and condensed phase we discuss clusters of molecules. Molecular reaction dynamics is not limited to neutral reagents and products but also includes positively and negatively charged species (cations and anions), either in their bare state or solvated in solution. Biochemical reactions provide important examples of processes where electrostatic effects are central. Current rational drug design includes the consideration of the approach of the intended drug to its receptor and how both are modified as a result of their interaction. Molecular reaction dynamics has applications in all branches of chemistry because chemists are not content just to prepare a desired product. Nor is it sufficient to optimize conditions such as temperature or solvent or catalyst so as to get high reaction rate and purity. Chemists nowadays require a molecular-level **understanding** of reactivity.

Molecular reaction dynamics is becoming relevant well outside the traditional boundaries of chemistry and increasingly addresses technological issues. The reason is that from modern genetics to size-reducing nanoscience the molecular point of view provides a unified framework. First we needed to understand the structural aspects. But these are now well in hand and we are increasingly trying to unravel the time-history of the event. The need to understand change on the molecular scale is now common throughout the natural sciences.

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1.1 What is molecular reaction dynamics?

The study of dynamics allows us to raise additional questions, questions that do not quite make sense when we study the net change, at or near equilibrium, in the bulk. For example, we can wonder if exciting vibrational motion in either or both reactant diatomic molecules will make the $Cl_2 + Br_2$ four-center reaction proceed more rapidly. In bulk chemical kinetics, when the reactants are intentionally arranged to be in thermal equilibrium, a particular mode cannot be energized preferentially. To learn about a selective role of internal energy in promoting a reaction it is necessary to work under non-equilibrium conditions.³

Section 1.2 provides a case study of the kind of new questions raised by dynamics. In doing so, it also points to where we are going to go in the following chapters. We will, for example, discuss how lasers can act so as to prepare the reactants or, better yet, to access directly the transition region from reactants to products.⁴ When the laser is intense enough it can even alter completely the dynamical course. As an example, an intense laser field can be tailored to alter the ratio of products in two dissociation pathways of acetophenone:⁵



Different options for control using lasers feature throughout our road ahead.

Spectroscopy provides essential information about the structure of molecules through radiation-matter interactions. The application of spectroscopy, technically made possible using lasers, to molecular dynamics has allowed us to extend the asking of structural questions into the time domain, even for times comparable to or shorter than the periods of molecular vibrations. We will seek to understand how the reactants evolve over time into products. In so doing we must recognize that during a chemical transformation molecules must become less rigid and more floppy. It is the electrons, which are fast moving compared to the slower nuclei, that set up the energy landscape for the motion of the nuclei. Sometimes the electrons may not move quite as fast as we assume.

The technical details of the experimental and theoretical methods of molecular dynamics can be intricate but the concepts are simple. An understanding of these concepts – the ability to read the language – is all that is necessary to be able to view the very process of chemical change. This book is a primer of the language for expressing chemical transformations as dynamical events, proceeding in space and time.

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1.1.1 Much of chemistry is local: from the elementary act to complex systems

We begin our journey with elementary events. Our first example will be a simple chemical transformation, a hydrogen atom transfer between two atoms, in the gas phase. There are numerous systems that are chemically more exciting; say, the mechanism of C—H bond activation⁶ by metal complexes, in solution, or how does an enzyme transfer chemical energy liberated at a localized site to a functionally relevant receptor site?⁷ We adopt a bottom-up approach that almost all of chemistry is local in character; even a complex process is a sequence of elementary steps, each involving only a few atoms. Just as organic chemists break a complete synthesis into its essential steps (Corey, 1991), so we want to chart what are the possibly few atom events that, played in rapid succession, make up a complex reaction.

Chemistry is local because chemical forces are short range. An atom sees only its immediate surroundings. It is therefore possible to break the evolution from reactants to products into simpler steps. Our first task is to examine and understand the elementary dynamical events; only then can we build up to more complex processes.

A key factor in our ability to understand complex systems is the coming of age of modern computational chemistry.⁸ It is the fast motion of the electrons that determines the forces that act on the nuclei. Quantum chemistry provides the methods for analyzing electronic structure and thereby allows the determination of the equilibrium configuration for the nuclei and the energy of the electrons at that point.* In the same computation we can also determine the forces at that point and not only the potential. This allows the computation of the frequencies for the vibrations about the stable equilibrium. Next, methods have been introduced that enable us to follow the line of steepest descent from reactants to products and, in particular, to determine the stationary points along that route, and the forces at those points.⁹ Our ability to do so provides us with the means for quantitative understanding of the dynamics.

1.2 An example: energy disposal in an exoergic chemical reaction

Typical of the kind of information that is available from the experimental techniques of molecular dynamics is the determination of the *energy disposal* in exoergic atom–molecule exchange reactions. One example of such a system is the H-atom transfer reaction

$$Cl + HI \rightarrow ClH + I$$

In the course of this reaction the relatively weak HI bond is broken and replaced by the stronger HCl bond. The reaction liberates chemical energy, as shown

^{*} The electronic energy is the potential energy for the nuclei. The change in the electronic energy when the nuclei are displaced is the force. See also Sections 5.0.1 and 7.0.2.

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(Ă) HI HCl 1 3 Ε 2 ΔE_{c} 1 40000

Figure 1.1 The energetics of the reaction $CI + HI \rightarrow CIH + I$. The plot is drawn so as to have a zero of energy common to the reactants and products. This is achieved by taking the zero of energy when all three atoms are at rest and far apart from each other. The reactants or products, where two atoms are bound, are then below the zero. The exoergicity, ΔE_0 , of the reaction is the difference in the bond dissociation energies. Here ΔE_0 is negative because the new bond is stronger. The figure further shows the vibrational levels for the old, HI, or the new, HCI, bonds. For this purpose the potential energies of the HI and HCI bonds are plotted as a function of the bond stretch coordinate, $1 \text{ Å} = 10^{-10} \text{ m} = 0.1 \text{ nm}$. If the molecular reactant is cold, i.e., an HI molecule in its ground state, then the energy of the reactants is just the translational energy $E_{\rm T}$ of the relative motion of CI and HI. As shown in the figure, this energy is sufficient to form the products up to and including the fourth vibrational state of HCl.

graphically in Figure 1.1. The *exoergicity* is about 134 kJ mol⁻¹ or, equivalently, see Appendix, 32 kcal mol⁻¹, or about 1.39 eV. This amount of energy is large by chemical standards when we recall that the H-H bond energy is about 435 kJ mol⁻¹. Do not confuse the exoergicity of the reaction with the *exother*micity (or heat) of a **bulk** chemical process. In the bulk there are subsequent collisions where the nascent products collide with other molecules. We focus attention on the elementary chemical event. We are dealing with the nascent products of an isolated triatomic system, ClHI. We ask: when this system of three atoms evolves into the products HCl + I, where is the liberated energy to be found?

In a short while we discuss how to obtain an experimental answer to our question. What is important is the idea that we center attention on the isolated system and ask to probe the products prior to their engaging in any further action. The question is: immediately after the reactive collision of Cl + HI is over, how is the energy distributed among the reaction products? Even if both products are formed in their electronic ground states, we need to determine the partitioning of the excess energy of the chemical reaction into the three remaining modes of energy disposal. They are: vibration of HCl; rotation of HCl; and relative



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Figure 1.2 Two distributions, P(v), of vibrational states of HCl, drawn on a log scale vs. the vibrational quantum number v. Left: the distribution measured for the nascent HCl product of the Cl + Hl reaction (adapted from the observed chemiluminescence (in the infrared) of the vibrationally excited HCl(v) by D. H. Maylotte, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1547 (1972). See also Polanyi (1987)). The observed distribution of HCl(v) immediately after the reaction is **qualitatively** different from the distribution at thermal equilibrium, which is shown on the right. The distribution at thermal equilibrium is exponentially decreasing with the excess vibrational energy of HCl. Not so for the distribution on the left, which is loosely described as showing a *population inversion*.

translation of I and HCl recoiling from one another.¹⁰ But what is the distribution of energy among these three modes?

When a reaction is studied in the "bulk" gas phase, the nascent products soon collide with other molecules, energy is transferred upon collision (thus becoming effectively partitioned among all molecules), and the overall reaction exoergicity is finally liberated in its most degraded form, i.e., heat. In macroscopic terms, the reaction is exothermic, i.e., $\Delta H^0 < 0$. The microscopic approach of molecular dynamics, however, is concerned with the outcome of the **individual** reactive collisions. The experimental challenge, as discussed in Section 1.2.5, is to arrest the *collisional relaxation* of the nascent reaction products and to probe them as they exit from the reactive collision. In this sense, it is customary to speak about the nascent or newborn reaction products.

1.2.1 Distribution of products' energy states

Figure 1.2 shows on the left a typical experimental result, illustrating the distribution of energy among the vibrational states of nascent HCl. A vibrational quantum of HCl is about 35.5 kJ mol⁻¹, so that a large fraction of the available energy (134 kJ mol⁻¹ + the thermal energy of the reactants) goes into vibrational excitation of HCl, and thus, by difference, only a small fraction into translational recoil of HCl and I or into the rotation of HCl.

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1.2 Energy disposal in an exoergic chemical reaction

The vibrational distribution on the left of Figure 1.2 can be compared with that on the right, which is expected when a reaction is run under "bulk" conditions and the system has run to equilibrium. Then a Boltzmann equilibrium distribution would be produced: the most probable state is v = 0 and the relative populations decline exponentially with the vibrational quantum number. Of course, the bulk population does not arise from a single elementary process but rather from a succession of energy-degrading collisions of the vibrationally energy-rich HCl molecules with various other molecules.

Molecular dynamics in its "purist" approach tries to seek out (and understand) the truly elementary events. Thus it is more interested in the left than in the right panels of Figure 1.2. It is, however, concerned not only with the primary reactive collision process but also with the subsequent non-reactive, inelastic energy-transfer steps that take the system from the nascent distribution of products to the fully relaxed one. The Cl + HI system is not exceptional. Many exoergic reactions release a substantial part of their energy into internal modes of product excitation.¹¹ A key problem facing us is to understand this observation in terms of the forces that act during the collision. In this introductory case study we use a model.

1.2.2 Simple view of products' energy disposal: the spectator

We need a model, oversimplified of course, which will at least provide a simple interpretation of the observed energy disposal in the $Cl + HI \rightarrow HCl + I$ reaction. Let us try to take advantage of any "handle" that may help us approximate the dynamics of the problem.

One aspect of the collision is that it involves the transfer of a light atom (H) between two much heavier atoms. Recall that the I atom is about three times heavier than the Cl atom, which in turn is more than 30 times heavier than the H atom. The ClHI triatomic system is similar in that respect to the H_2^+ moleculeion, where it is the light electron that "mediates" between the two heavy protons. When a molecule undergoes an electronic transition we obtain insight into the distribution of the final vibrational states from the Franck–Condon principle, discussed in detail in Chapter 7. The principle says that during the very fast electronic transition the heavy nuclei do not change their momentum, the nuclei merely act as spectators during the rapid electronic rearrangement. A *spectator* is someone who is not involved, i.e., does not feel any impulse. From Newton's second law we expect that a spectator is likely to be "heavy," because its momentum is resilient to change, the mass being the measure of the inertia to change. It thus follows that a spectator has a constant momentum.

To apply similar ideas to the present problem we must assume that the H transfer reaction is over in a time short compared to the time required for the heavy nuclei to move substantially. The model is then that the heavy iodine

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atom acts as a spectator during the (rapid) transfer of the light hydrogen atom to the heavy chlorine atom. This means that the final momentum of the I atom after the collision (\mathbf{p}'_1) is essentially the same as the initial momentum of the I atom:

$$\mathbf{p}_{\mathrm{I}}' = \mathbf{p}_{\mathrm{I}} \tag{1.1}$$

It is easy to realize that this spectator model can account for the observation that very little of the reaction exoergicity is released as translational energy of the products. The Cl atom approaches the HI molecule with a particular momentum and "captures" the H. But the H atom is so light that the momentum of the I atom is left nearly unchanged, and so too is that of the Cl atom, which is part of the HCl product. But if energy is to be conserved without altering the translational motion, it follows that the exoergicity of the reaction must be "deposited" in the internal motion of the HCl. The quantitative version of our conclusion is the subject of Problem B. Here we proceed to look for additional experimental evidence that can lend support to the model.

1.2.3 Products' angular distribution

The spectator model makes a statement about vectors, namely that not only the magnitude but also the **direction** of the momentum of the iodine atom is unchanged in the collision (Newton's second law requires a force to change the direction of the momentum). Hence, the product iodine atom should appear in the same direction as that of the incident HI while the product HCl will appear in the direction of the incident chlorine atom. Leaving the details for later, it is sufficient to say that this description, which we colorfully call the *spectator stripping* picture, is qualitatively the behavior found experimentally. The product HCl appears mainly in the "forward" direction (i.e., in the direction of the incident chlorine atom). Note again that such a statement is only possible because we are focusing our attention on the isolated collision.¹² In the bulk, the products would soon collide with other molecules and very rapidly lose all memory of their nascent direction of motion.

The observation that the angular distribution of products is rather anisotropic implies that no long-lived CIHI intermediate "complex" is formed. If the reaction duration were long compared to the period of rotation of such an intermediate, almost all memory of the initial directions of the reactants would be erased and the products' angular distribution would not distinguish between the forward and backward directions. An insertion reaction for which this is the case is shown later in Figure 1.4. If there were a long-lived intermediate we would also not expect a very specific energy disposal because then there would be time for the energy to become approximately "equipartitioned" among the different modes of this intermediate.

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1.2 Energy disposal in an exoergic chemical reaction

1.2.4 From specific energy disposal to the mode-selective control of chemical reactions

Consider the endoergic reaction

 $\rm I + \rm HCl \rightarrow \rm IH + \rm Cl$

The reverse exoergic Cl + HI reaction is observed specifically to populate the final vibrational states of HCl. Using our model and any other means, can we predict the *energy requirements* of this endoergic reaction and, in particular, can we enhance the reaction rate by a selective preparation of the reactants?

Since we are dealing with an isolated collision, the reaction endoergicity has to be supplied by the initial energy of the reactants, I and HCl. This energy can be provided by the relative translational energy of the colliding pair and/or by the internal energy of HCl. When the energy of the I and HCl reactants just exceeds the endoergicity, not enough energy is available to form a vibrationally excited HI product and the final momentum of the HI product is also small. If, Eq. (1.1), the momentum of the I atom is to be nearly unchanged during the collision, the necessary energy for the reaction cannot be provided by the relative translational energy of the I reactant relative to the center of mass. The reaction endoergicity, at least just above the energy threshold for reaction, must therefore be provided by the initial internal energy of the HCl.

The conclusion of a selective energy requirement, which is based on the model, can be much strengthened by consideration of the principle of *microscopic reversibility*.¹³ Recall that the experiments on Cl + HI showed that at low energies vibrationally **cold** HI leads mainly to the formation of vibrationally **hot** HCl, with only a smaller fraction of the energy released as translation. Because vibrationally cold HCl is formed with a very low probability in the forward reaction, it follows that for the reverse reaction involving the collision of vibrationally cold HCl with an I atom at high translational energies, most collisions are non-reactive. By this we mean that reaction will occur only rarely on such collisions. In contrast, collisions of vibrationally hot HCl molecules with I atoms will be fruitful even at low translational energies.

Selective preparation* of reactant energy states as a means for controlling not only the rate but also the chemical nature of the products has now been well

* How can reactions take place starting with bulk thermal reactants for which the proportion of molecules in the higher vibrational states is exponentially small? It is a requirement of chemical kinetics that reaction rates be measured for reactants that are maintained in thermal equilibrium. If necessary, a buffer gas is added whose role is to insure that thermal equilibrium is maintained, by collisions. In the bulk the very few vibrationally hot, i.e., excited, HCl molecules react with I atoms produced by thermal dissociation of I₂. This displaces the remaining HCl molecules from their thermal equilibrium because the mean vibrational energy is now lower. Collisions with the buffer gas restore the thermal equilibrium or, on a molecular level, collisions repopulate the higher vibrational states of HCl and also dissociate I₂ molecules. Next, the vibrationally hot HCl molecules are preferentially removed by reaction with I atoms. Equilibrium needs to be restored, and so on. All this is hidden when we just focus attention on the thermal reaction rate constant.

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demonstrated. As an example, the rate of the H + HOH \rightarrow H₂ + OH reaction is enhanced when the H–O stretch motion is excited.¹⁴ Say now that instead of H₂O one considers HOD where D is the heavy isotope of H. The O–H and O–D vibrations have sufficiently different frequencies that the two modes represent nearly independent vibrations of HOD. The reactions of H atoms with H–OD excited with four vibrational quanta produce primarily H₂ + OD, whereas reactions of H atoms with HO–D excited with five vibrational quanta produce primarily HO + DH:

 $H + {H \atop D} O \rightarrow \begin{cases} H_2 + OD \\ HO + DH \end{cases} \qquad \begin{array}{c} H - OD \text{ excited by four quanta} \\ HO - D \text{ excited by five quanta} \end{cases}$

The model introduced in Problem G concludes that the bond that is unaffected is a spectator in such reactions. Here we follow a more chemical argument: OH is isoelectronic with the F atom. The $F + H_2$ exoergic reaction selectively populates the vibrational states of the HF product. The H + H–(OH) reaction is expected to have similar forces to the H + HF reaction and the masses are also similar. Therefore, by microscopic reversibility, H–(OH) vibrational excitation should promote the endoergic H + H–(OH) reaction.

1.2.5 The experiment

The entire discussion in this section is based on the experimental determination of the vibrational energy partitioning in the nascent reaction products. The original experiment by John Polanyi and his coworkers was a tour de force. The background and the early results are described in his Nobel Prize lecture (Polanyi, 1987); for an early account, see Polanyi (1972). Nowadays we could use a pumpprobe technique. What we want is to be able to probe the nascent products before they undergo any relaxation by interaction with the surroundings. This condition can be achieved if we can slow time down so as to catch the products as soon as they emerge from the reactive collision. The technique of *pump and probe*, which uses two fast laser pulses delayed in time with respect to one another, can achieve this. We need a precursor that, upon photolysis, promptly dissociates to yield the reactive atom or radical. The photolysis pulse, known as the pump, is "on" for only a brief time interval. How brief we will see shortly, but the necessary short time pulses are nowadays routinely available. A short time after the pump a second short laser pulse, known as the probe, interrogates the nascent products. The experiment is in the bulk so that the time interval between the pump and probe pulses needs to be of the order of the time between two successive collisions that a molecule undergoes in the bulk. In this way we insure that the products arise from only those reactive atoms that have undergone one, reactive, collision. Prior to this one collision the reactive atoms have not been deflected or slowed down by collisions with other molecules. The same short delay between the pulses also