Kinetics of Reactions in Solution

Most of the complications of kinetics and rate processes in liquid solutions arise from the much higher density of the liquid phase.

In a typical gas at atmospheric pressure, the molecules occupy only about 0.2 per cent of the volume; the other 99.8 percent is empty space. In a liquid, molecules may take up more than half the volume, and the "empty" spaces are irregular and ever-changing as the solvent molecules undergo thermal motions of their own.

In a typical liquid solution, the solvent molecules massively outnumber the reactant solute molecules, which tend to find themselves momentarily (~$10^{-11}$ sec) confined to a "hole" within the liquid. This trapping is especially important if the solvent is strongly hydrogen-bonded, as is the case with water or alcohol.

When thermal motions occasionally release a solute molecule from this trap, it jumps to a new location. The jumps are very fast ($10^{-12}$ - $10^{-13}$ sec) and short (usually a few solvent-molecule diameters), and follow an entirely random pattern, much like Brownian motion.
Consider a simple bimolecular process, \( A + B \rightarrow \text{products} \). The reactant molecules jump from between holes in the solvent matrix, only occasionally finding themselves in the same solvent cage, where thermal motions are likely to bring them into contact.

A pair of reactants end up in the same solvent cage, where they bounce around randomly and exchange kinetic energy with the solvent molecules. Eventually the two reactants form an encounter pair. If they fail to react the first time, they have many more opportunities during the lifetime of the cage. The products form and begin to move away from each other. Finally, after about \( 10^{-11} \) sec, the solvent cage breaks up and the products diffuse away.

The process can be represented as

\[
[A + B \rightarrow \{AB\} \rightarrow \text{products}]
\]

in which the \( \{\text{AB}\} \) term represents the caged reactants, including the encounter pair and the activated complex.

Compare this scenario with a similar reaction in the gas phase; the molecules involved in the reaction are often the only ones present, so a significant proportion of the collisions will be \( (A-B) \) encounters. However, if the collision is not energetically or geometrically viable, the reactant molecules fly apart and are unlikely to meet again quickly.

In a liquid, however, the solute molecules are effectively in a constant state of collision—if not with other reactants, then with solvent molecules which can exchange kinetic energy with the reactants. Once an A-B encounter pair forms, the two reactants have multiple chances to collide, greatly increasing the probability that they obtain the kinetic energy required to overcome activation energy hump before the encounter pair disintegrates.

### Diffusion and activation-control of reaction rates

The encounter pair model introduces some new rate parameters:

\[
A + B
\]
The first step is an equilibrium between the reactants outside and inside the solvent cage. The rate constants \( k_1 \) and \( k_2 \) refer to the diffusion of molecules through the solvent; their values are strongly dependent on the viscosity (and thus the temperature) of the solvent (Note that \( k_1 \)) is a second-order rate constant, whereas \( k_2 \) is first-order).

_Diffusion_ is the transport of a substance across a concentration gradient, moving from a region of higher concentration to one of lower concentration. This is observed in the way the color of tea spreads when a tea bag is immersed in hot water. Diffusion occurs because random thermal motions are statistically more likely to move molecules out of a region of higher concentration than in the reverse direction, simply because in the latter case fewer molecules are available to make the reverse trip. Eventually the concentrations become uniform and equilibrium is attained.

As molecules diffuse through a liquid, they shift neighboring molecules out of the way. The work required is essentially an activation energy, so diffusion can be thought of as a kinetic process with its own rate constant, \( k_d \), and activation energy. These parameters depend on the sizes of the solute and solvent molecules and on how strongly the latter interact with each other.

**Two important limiting cases for reactions in solution**

For water at room temperature, \( k_1 \) is typically \( 10^9 \cdot 10^{10} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \) and \( k_2 \) is around \( 10^{-9} \cdot 10^{-10} \text{ dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1} \). Given these values, \( (k_3 > 10^{12}) \) implies diffusion control, whereas values less than \( 10^9 \text{ s}^{-1} \) are indicative of activation control.

- **Diffusion controlled** (\( (k_3 >> k_2) \)). If the activation energy of the A+B reaction is very small or if the escape of molecules from the {AB} cage is difficult, the kinetics are dominated by \( k_1 \), and thus by the activation energy of diffusion. Such a process is said to be _diffusion controlled_. Reactions in aqueous solution in which \( E_a > 20 \text{ kJ/mol} \) are likely to fall into this category.

- **Activation-controlled** (\( (k_3 << k_2) \)). In the reverse case, the activation energy of the A+B reaction dominates the kinetics, and the reaction is _activation-controlled_.

Several general kinds of reactions are consistently very fast, and thus are diffusion-controlled in most solvents. Gas-phase rate constants are normally expressed in units of mol s\(^{-1}\), but rate constants of reactions in solution are conventionally given in units of mol L\(^{-1}\) or dm\(^3\) mol\(^{-1}\) s\(^{-1}\). Conversion between these units depends on a number of assumptions and is non-trivial.

- **Recombinations of atoms and radicals**: for example, for the formation of \( (I_2) \) from I atoms in hexane at 298 K, \( k_3 = 1.3 \times 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \).

- **Acid-base reactions** that involve the transport of \( (H^+ \) and \( (OH^-) \) ions tend to be very fast. The most famous of these is one of the fastest reactions known:

\[
[H^+ + OH^- \rightarrow \text{H}_2\text{O}]
\]
for which \( k_3 = 1.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) at 298 K.

### Solvent polarity effects

Polar solvents such as water and alcohols interact with ions and polar molecules through attractive dipole-dipole and ion-dipole interactions, leading to lower-energy solvated forms which stabilize these species. In this way, a polar solvent can alter both the thermodynamics and kinetics of a reaction.

### Solvent thermodynamic effect

If the products of the reaction are markedly more or less polar than the reactants, solvent polarity can change the overall thermodynamics (equilibrium constant) of the reaction. Nowhere is this more apparent than when an ionic solid such as salt dissolves in water. The \( \text{Na}^{+} \) and \( \text{Cl}^{-} \) ions are bound together in the solid by strong coulombic forces; pulling the solid apart in a vacuum or in a nonpolar solvent is a highly endothermic process. In contrast, dissolution of \( \text{NaCl} \) in water is slightly exothermic and proceeds spontaneously.

![Solvent Thermodynamic Effect Diagram](image)

The water facilitates this process in two important ways. First, its high dielectric constant of 80 reduces the force between the separated ions to 1/80 of its normal value. Second, the water molecules form a solvation shell around the ions (lower left), rendering them energetically (thermodynamically) more stable than they are in the \( \text{NaCl} \) solid.

### Solvent Kinetic Effect

In the same way, the activation energy—and therefore rate—of a reaction whose mechanism involves the formation of an intermediate or activated complex with polar or ionic character is subject to change as the solvent polarity is altered. As an example, consider an important class of reactions in organic chemistry. When an aqueous solution of a strong base such as \( \text{KOH} \) is added to a solution of tertiary-butyl chloride in ethanol, the chlorine is replaced by a hydroxyl group, leaving \( t \)-butyl alcohol as a product:
This reaction is one of a large and important class known as \( SN_1 \) nucleophilic substitution processes. In these reactions, a species with a pair of non-bonding electrons (also called a nucleophile or Lewis base) uses them to form a new bond with an electrophile — a compound in which a carbon atom has a partial positive charge owing to its bonds to electron-withdrawing groups. In this example, other nucleophiles such as \((NH_3)\) or even \((H_2O)\) would serve as well.

To reflect the generality of this process and to focus on the major changes that take place, this reaction is represented as follows:

\[
\begin{align*}
\text{CH}_3\text{C}^-\text{Cl}^- + :\text{OH}^- & \rightarrow \text{CH}_3\text{C}^-\text{OH}^- + :\text{Cl}^- \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

Extensive studies of this class of reactions in the 1930's revealed that it proceeds in two activation energy-controlled steps, followed by a simple dissociation into the products:

In step 1, which is rate-determining, the chlorine leaves the alkyl chloride, leaving an intermediate known as a carbocation ("cat-ion"). These ions, in which the central carbon atom lacks a complete octet, are highly reactive, and in step 2 the carbocation is attacked by the (water molecule) which supplies the missing electron. The immediate product is another cation in which the positive charge is on the oxygen atom. This oxonium ion is unstable and rapidly dissociates into the alcohol and a hydrogen ion.

\[
\begin{align*}
\text{CH}_3\text{C}^-\text{X}^- + :\text{OH}^- & \rightarrow \text{CH}_3\text{C}^-\text{OH}^- + :\text{X}^- \\
\text{carbocation} & \quad \text{oxonium ion}
\end{align*}
\]
The reaction coordinate diagram illustrates the effect of solvent polarity on this reaction. Polar solvent molecules interact most strongly with species in which the electric charge is concentrated in one spot. Therefore, the carbocation is stabilized to a greater extent than are the activated complexes in which the charge is spread out between the positive and negative ends. As the heavy green arrows indicate, a more polar solvent stabilizes the carbocation more than it does either of the activated complexes; the effect is to materially reduce the activation energy of the rate-determining step, and thus speed up the reaction. Because neither the alkyl chloride nor the alcohol is charged, the change in solvent polarity has no effect on the equilibrium constant of the reaction. This is dramatically illustrated by observing the rate of the reaction in solvents composed of ethanol and water in varying amounts:

<table>
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<tr>
<th>% water</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
</tr>
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<tbody>
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<td>$k_1 \times 10^6$</td>
<td>1.7</td>
<td>9.1</td>
<td>40.3</td>
<td>126</td>
<td>367</td>
<td>1294</td>
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</table>

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