

## Kinetics

The value of the rate constant will be different for different reactions. Consider the reaction of HCl and a water molecule discussed in the last section. Even with the same concentrations, the almost identical reaction where hydrogen is replaced by deuterium will proceed at a different rate (Chapter 19). To understand this we need to think again about what needs to happen for a reaction to occur. It is not enough for the two species to simply collide. We know that for this reaction to work the proton must come into contact with the *oxygen* atom in the water molecule, not the hydrogen atoms, that is, there is some sort of steric requirement. We have also seen that most reactions need to overcome an energy barrier. In other words, it is not enough for the two species just to collide for a reaction to proceed, they must collide in the right way and with enough force.

You can see now how the overall rate equation for our example reaction

$$\text{rate of reaction} = k \times [\text{HCl}] \times [\text{H}_2\text{O}]$$

contains all the points needed to work out how fast the reaction will proceed. The most important point concerns the concentrations of the reacting species—which are expressed directly in the rate equation. Other considerations, such as how large the species are or whether or not they collide in the right way with the right energy, are contained in the rate constant,  $k$ . Notice once again that not only is  $k$  different for different reactions (for all of the above reasons), but that it also varies with temperature. It is essential when quoting a rate constant that the temperature is also quoted. That part of chemistry that deals with reaction *rates* rather than equilibria is known as **kinetics**.

### Activation barriers

In the same way that we define  $\Delta G^\ddagger$  to be the difference in energy between the starting materials and the transition state (that is, activation energy), we can define the entropy of activation,  $\Delta S^\ddagger$ , and the enthalpy of activation,  $\Delta H^\ddagger$ , as being the entropy and enthalpy differences between the starting materials and transition state. These quantities are directly analogous to the entropy and enthalpy of the reaction but instead refer to the difference between starting material and *transition state* rather than starting material and *products*.

In a similar manner, we could also define an equilibrium constant between the reactants and the transition state

$$K^\ddagger = \frac{[\text{AB}^\ddagger]}{[\text{A}][\text{B}]}$$

Our all-important thermodynamic equations apply equally well to these activation functions so that we may write

$$\Delta G^\ddagger = -RT \ln K^\ddagger \text{ and } \Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger.$$

It is possible to relate these functions with the rate constant for the reaction,  $k$ , by using a model known as **transition state theory**. We will not go into any details here, but the net result is that

$$k = \frac{k_B T}{h} K^\ddagger$$

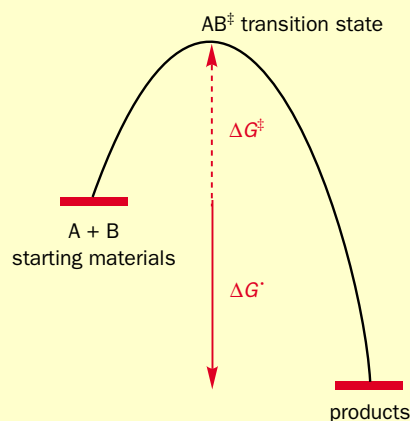
where  $k_B$  and  $h$  are universal constants known as Boltzmann's constant and Planck's constant, respectively

By substituting in the equation  $K^\ddagger = e^{\frac{-\Delta G^\ddagger}{RT}}$  the rearranged form of  $\Delta G^\ddagger = -RT \ln K^\ddagger$  we arrive at an equation, known as the **Eyring equation**, which relates how fast a reaction goes ( $k$ ) to the activation energy ( $\Delta G^\ddagger$ )

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}}$$

This can be rearranged and the numerical values of the constants inserted to give an alternative form

$$\Delta G^\ddagger \text{ (in J mol}^{-1}\text{)} = 8.314 \times T \times [23.76 + \ln(T/k)]$$



## Kinetics gives us an insight into the mechanism of a reaction

Now for some of the reactions you have seen in the last few chapters. Starting with carbonyl substitution reactions, the first example is the conversion of acid chlorides into esters. The simplest mechanism to understand is that involved when the anion of an alcohol (a metal alkoxide  $\text{RO}^-$ ) reacts with an acid chloride. The kinetics are bimolecular:  $\text{rate} = k[\text{MeCOCl}][\text{RO}^-]$ . The mechanism is the simple addition-elimination process with a tetrahedral intermediate.

The formation of the tetrahedral intermediate by the combination of the two reagents is the rate-determining step and so the highest transition state will be the one leading from the starting materials to that intermediate.

