

Introduction to reaction dynamics

By now you should be well and truly used to the concepts involved in reaction kinetics on a macroscopic scale, the kinds of techniques used to measure rate constants and determine reaction orders, and the use of the steady-state approximation for determining rate laws once the sequence of elementary steps involved in a reaction is known. What you will probably not yet be familiar with is the idea that we can go much deeper than this and study these elementary reactions in much greater detail. Reaction dynamics looks at chemical reactions on the scale of single reactive collisions between molecules, and involves carrying out experiments and calculations with the aim of understanding chemical reactions at the most fundamental level possible.

This is one area of chemistry in which the link between theory and experiment is particularly strong, with the bridge between the two embodied by the reaction *potential energy surface*. A potential energy surface (or PES) is a multidimensional surface which gives the potential energy of a chemical system as a function of the nuclear coordinates of all the atoms involved in the reaction. Potential energy surfaces can be calculated using quantum mechanics, at least for simple systems. If you can remember a little classical mechanics, you will recall that the force in a particular direction is given by $F_x = -dV/dx$. The first derivative of the potential energy surface at a given point (i.e. a given nuclear configuration) therefore gives the forces acting on all the atoms at that configuration. Since the forces acting on an atom determine its motion, the potential energy surface for a reaction determines its course, including what (if any) products will be formed, in what direction(s) they are scattered, what their geometries and energies will be, how fast the reaction will proceed, and so on. Calculation of these potential energy surfaces is part of the theoreticians job.

The second part of the theoreticians job is to provide the link between these potential energy surfaces and the dynamics that would be observed for a reaction that proceeds over one of these surfaces. In practice, there are two ways to do this, quantum scattering calculations or quasi-classical trajectory (QCT) calculations. Quantum scattering theory is rather beyond the scope of this introduction to reaction dynamics, but a qualitative description of QCT calculations may be useful. As we said above, the potential energy surface for a reaction defines all the forces acting on each atom at any geometry of the reacting system. If we start from a particular point \mathbf{x}_1 on the surface (where \mathbf{x} is a vector containing all the nuclear coordinates) we can take the first derivative at that point (i.e. the gradient $\nabla V(\mathbf{x})$ for the mathematicians amongst you) at that point to find the forces. Once we know the forces, we can set up and solve Newton's classical equations of motion and determine the trajectory of the system at that geometry. We let the system follow that trajectory for a short time (i.e. a few femtoseconds), after which it has reached a new point \mathbf{x}_2 on the surface. We can then calculate the forces at this new point on the surface, set up and solve Newton's equations to move to a third point \mathbf{x}_3 , and so on. i.e. we can run a complete trajectory from the beginning to the end of the reaction. QCT calculations work by running a large number of these trajectories, each with slightly different starting conditions. The starting conditions are the positions and momenta of each of the atoms in the reaction system. If you think about it, you'll realise the defining these quantities is equivalent to defining the reactant geometries, velocities and internal energies at the start of the reaction. In practice these are usually sampled randomly from known internal state and velocity distributions. At the end of a trajectory, the nuclear positions and momenta are examined to see what products have formed (if any) and what energy they have. The 'quasi-classical' part of QCT calculations comes from the way in which quantisation is treated. The reactants are given the energy corresponding to the quantum state in which they begin the trajectory. At the end of a trajectory, once the contribution from translational motion has been subtracted from the total energy, the internal states of the products are determined from the (non-quantised) 'leftover' energy by finding

the closest energy states and assigning the product molecules to these states. QCT calculations essentially provide a large-scale simulation of a chemical reaction. By analysing all the trajectories, total reaction cross sections (the reaction cross section, usually given the symbol σ , is the microscopic equivalent of a rate constant; a cross section can be thought of as the effective area that one reactant presents to another, so, like a rate constant, it is related to the probability of reaction, and rate constants can be calculated from reaction cross sections), product quantum state distributions, angular scattering distributions (usually called 'differential cross sections', $d\sigma/d\theta$ since they describe the variation of the total cross section with scattering angle) and translational energy distributions, amongst other things, can be determined. These quantities can then be compared directly with the results of experimental measurements, allowing theory to guide experiment and vice-versa.

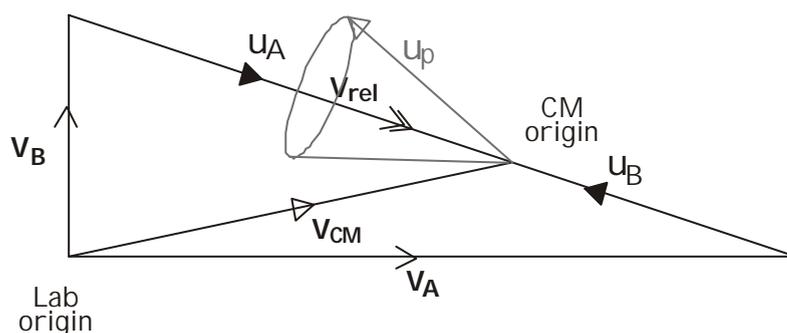
As for the experimentalists, their job is to set up experiments to measure the properties of a reaction that can be predicted once the potential energy surface is known. There are many different experimental techniques that have been used to obtain dynamical information on a chemical reaction, all of which require that the reaction takes place under *single collision conditions*. What this means is that the products of a reaction must be detected before they can collide with any other molecules. The kinds of properties you are trying to measure are in what direction the products recoil from the reaction centre and with how much energy, in what internal states they are populated and so on. Collisions can change the direction of motion of energy of a molecule, and in the extreme of multiple collisions between reaction and product detection, if single collision conditions were not used, you wouldn't be measuring properties characteristic of nascent ('newly born') reaction products at all, but properties characteristic of a thermalised molecular ensemble. For obvious reasons, these experiments are almost exclusively carried out in the gas phase.

In the ideal experiment, you'd set up a collision in which the internal states, velocities and orientations of the reactants were completely specified and then detect the product velocities, scattering angles, internal states, and so on. In practice, it is not usually possible to do all of this at the same time, though the 'perfect' experiment is getting closer to becoming a possibility. Laser and/or molecular beam techniques can be used to control the reactant velocities (or at least the reactant velocity distributions), and internal states, and electric fields can be used to control reactant orientation for some types of molecules (e.g. symmetric top molecules can be oriented using hexapole fields, heteronuclear diatomics using quadrupole fields or very strong uniform fields). Products can be detected as a function of angle and time-of-flight (and therefore velocity) using a rotatable mass spectrometer in the simplest case. In this case all product quantum states are detected at the same time and the three dimensional product velocity distribution obtained is averaged over all product internal states. This type of experiment is usually done under very low pressure conditions, so that no further collisions occur during the time the product travels from the reaction centre to the detector. Another approach is to use a laser to probe the product(s) spectroscopically, making use of the Doppler effect to obtain velocity information (some examples and results using this method can be found on Mark Brouard's web page: <http://physchem.ox.ac.uk/~mb/>). In this case it is possible to look at one product state at a time by 'sitting' on a single spectroscopic transition, and get the 3D product velocity distribution as a function of quantum state. These 3D velocity distributions can be thought of as a 'scattering map', which shows the preferred direction(s) in which the products scatter, and their velocity (and therefore energy) distribution. This information can be traced back in time to infer what must have happened during the reaction event itself. Reactions can usually be classified as 'direct' or 'indirect'. Examples of direct reaction mechanisms are the 'rebound' and 'harpoon' or 'spectator stripping' mechanisms. In the rebound mechanism, one reactant must hit the other more-or-less 'head on' for reaction to occur, and is strongly backward scattered. In the harpoon mechanism one reactant (usually a fairly heavy atom) plucks a light atom from the other reactant as it passes, with the result that the newly formed diatomic is forward-scattered with respect to the original atom

(since its momentum is changed little by the addition of a light atom) and the other reactant acts as a spectator during the reaction, apart from the loss of an atom. Indirect reactions proceed through a long-lived intermediate complex. If the lifetime of the complex is longer than its rotational period, it will have lost all memory of the reactant motion by the time it dissociates, and the products are scattered isotropically from the reaction centre.

As an example, consider an S_N2 type reaction (e.g. $F^- + CH_3Cl \rightarrow CH_3F + Cl^-$) and think about what type of scattering dynamics you might expect to see. If you could control the reactant orientation so that the F^- struck either the Cl or the CH_3 end of the methyl chloride molecule (which is not beyond current experimental technology) you might expect to find that in the former case you'd see very little reaction, while in the latter case you'd see Cl^- products scattered forwards with respect to the initial direction of the F^- ion. These products should have fairly high velocities since they will receive most of the energy released in the reaction as the C-Cl bond breaks. You might find that exciting the C-Cl stretch (say with a laser) would lead to a much higher reaction cross section by making the bond easier to break, or that increasing the velocity of the attacking F^- would increase the range of angles over which reaction could occur (often called the 'cone of acceptance'). The latter would occur if it is the velocity component along the breaking bond that is important for reaction, and would lead to a broader angular distribution for the scattered Cl^- product.

One last thing that should be mentioned is that product differential cross sections and/or velocity distributions must be determined in the centre of mass (CM) frame (i.e. the frame of reference whose origin is moving along with the velocity of the centre of mass of the system) since this is the frame which is meaningful when describing molecular properties. In this frame, the reactants approach along their relative velocity vector (i.e. the collision is 'head on') and scattering is symmetric about this vector. However, experimental data is measured in the lab frame, so some mechanism is required for transforming the results of experiments into the CM frame. In some cases, for example crossed molecular beam experiments, this is relatively simple; in other cases it can be considerably more complicated. To see the effect of the frame transformation on measured data consider the figure below.



This is a *Newton diagram* for a crossed beam experiment. v_A and v_B are the velocities of the two reagents in the molecular beams, which cross at 90° and $v_{rel} = v_A - v_B$ is their relative velocity. The velocities in the CM frame are $u_A = v_{rel}m_B/(m_A+m_B)$ and $u_B = v_{rel}m_A/(m_A+m_B)$. v_{CM} is the velocity of the centre of mass of the two reactants as they approach each other and the origin of the CM frame is the point at which the reactants collide. Also shown is a cone corresponding to a product scattering at a particular angle from the reaction with a centre of mass frame velocity u_p (as stated previously, scattering is symmetric about the relative velocity vector). In the lab frame, the measured velocity would correspond to a vector pointing from the lab origin to the tip of the CM frame

Further information can be found in the following:

Levine and Bernstein, *Molecular Reaction Dynamics* (1974)

Bradley, *Fast Reactions*, Oxford Chemistry Series (Oxford: Clarendon Press, 1975)

Bernstein, *Chemical dynamics via molecular beam and laser techniques* (1982)

Fluendy and Lawley, *Chemical Applications of Molecular Beam Scattering* (Chapman and Hall 1973)

Mark Brouard, *Reaction Dynamics* (Oxford Chemistry Primer)