Resolving Kinetics: Faster Methods

To investigate reactions that are complete in less than a millisecond, one can start with a pre-mixed sample in which one of active reactants is generated in situ. Alternatively, a rapid change in pressure or temperature can alter the composition of a reaction that has already achieved equilibrium.

**Flash photolysis**

Many reactions are known which do not take place without light of wavelength sufficiently short to supply the activation energy needed to break a bond, often leading to the creation of a highly reactive radical. A good example is the combination of gaseous Cl\textsubscript{2} with H\textsubscript{2}, which proceeds explosively when the system is illuminated with visible light. In flash photolysis, a short pulse of light is used to initiate a reaction whose progress can be observed by optical or other means.

Photolysis refers to the use of light to decompose a molecule into simpler units, often ions or free radicals. In contrast to thermolysis (decomposition induced by high temperature), photolysis is able to inject energy into a molecule almost instantaneously and can be much "cleaner," meaning that there are fewer side reactions that often lead to complex mixtures of products. Photolysis can also be highly specific; the wavelength of the light that triggers the reaction can often be adjusted to activate one particular kind of molecule without affecting others that might be present.

1. All this had been known for a very long time, but until the mid-1940's there was no practical way of studying the kinetics of the reactions involving the highly reactive species produced by photolysis.

In 1945, Ronald Norrish of Cambridge University and his graduate student George Porter conceived the idea of using a short-duration flash lamp to generate gas-phase CH\textsubscript{2} radicals, and then following the progress of the reaction of these radicals with other species by means of absorption spectroscopy.
In a flash photolysis experiment, recording of the absorbance of the sample cell contents is timed to follow the flash by an interval that can be varied in order to capture the effects produced by the product or intermediate as it is formed or decays.

Norrish and Porter shared the 1967 Nobel Prize in Chemistry for this work.

**Nanosecond flash photolysis setup**

Flash durations of around 1 millisecond permitted one to follow processes having lifetimes in the microsecond range, but the advent of fast lasers gradually extended this to picoseconds and femtoseconds. Flash photolysis revolutionized the study of organic photochemistry, especially that relating to the chemistry of free radicals and other reactive species that cannot be isolated or stored, but which can easily be produced by photolysis of a suitable precursor. It has proven invaluable for understanding the complicated kinetics relating to atmospheric chemistry and smog formation. More recently, flash photolysis has become an important tool in biochemistry and cellular physiology.

**Perturbation-relaxation methods**

Many reactions, especially those that take place in solution, occur too rapidly to follow by flow techniques, and can therefore only be observed when they are already at equilibrium. The classical examples of such reactions are two of the fastest ones ever observed, the dissociation of water

\[
2 \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}^- \]

and the formation of the triiodide ion in aqueous solution
Reactions of these kinds could not be studied until the mid-1950s when techniques were developed to shift the equilibrium by imposing an abrupt physical change on the system.

For example, if the reaction $A \xrightarrow{k_1} B$ is endothermic, then according to the Le Châtelier principle, subjecting the system to a rapid jump in temperature will shift the equilibrium state to one in which the product $B$ has a higher concentration. The composition of the system will then begin to shift toward the new equilibrium composition at a rate determined by the kinetics of the process.

For the general case illustrated here, the quantity "$x$" being plotted is a measurable quantity such as light absorption or electrical conductivity that varies linearly with the composition of the system. In a first-order process, $x$ will vary with time according to

$$x_t = x_0 e^{-kt}$$

After the abrupt perturbation at time $t_0$, the relaxation time $t^*$ is defined as the half-time for the return to equilibrium — that is, as the time required for $x_0$ to decrease by $\Delta x/e = \Delta x/2.718$. The derivation of $t^*$ and the relations highlighted in yellow can be found in most standard kinetics textbooks. Temperature jumps are likely most commonly used.
This is the method that Manfred Eigen (Germany, 1927-) pioneered when, in the early 1960's, he measured the rate constant of what was then the fastest reaction ever observed:

\[
H^+ + OH^- \rightarrow H_2O \quad k = 1.3 \times 10^{11} \; M^{-1} \; sec^{-1}
\]

- **high-voltage electric discharge**: A capacitor, charged to 5-10 kV, is discharged through a solution to which an electrolyte has been added to provide a conductive path.
- **laser irradiation**: The sample is irradiated with a laser whose wavelength corresponds to an absorption peak in the sample. Infrared lasers are often used for this purpose.
- **mixing of two pre-equilibrated solutions**: Two solutions, otherwise identical but at different temperatures, are rapidly mixed in a stopped-flow type of apparatus. Although this method is not as fast, it has the advantage of allowing
both negative and positive T-jumps. The device shown here uses 0.1-mL samples and provides jumps of up to ±40 °C over a few microseconds. Observation times, however, are limited to 1-2 milliseconds owing to thermal dissipation.

**Pressure jumps**

According to the Le Châtelier principle, a change in the applied pressure will shift the equilibrium state of any reaction which involves a change in the volume of a system. Aside from the obvious examples associated with changes in the number of moles of gases, there are many more subtle cases involving formation of complexes, hydration shells and surface adsorption, and phase changes. One area of considerable interest is the study of protein folding, which has implications in diseases such as Parkinson's and Alzheimer's.

The pressure-jump is applied to the cell through a flexible membrane that is activated by a high-pressure gas supply, or through an electrically-actuated piezoelectric crystal. The latter method is employed in the device shown here, which can produce P-jumps of around 1 GPa over sub-millisecond time intervals.

**Shock tubes: extreme jumping**

When a change in pressure propagates through a gas at a rate greater than the ordinary compressions and rarefactions associated with the travel of sound, a moving front (a *shock wave*) of very high pressure forms. This in turn generates an almost instantaneous rise in the temperature that can approach several thousand degrees in magnitude.

A shock tube is an apparatus in which shock waves can be generated and used to study the kinetics of gas-phase reactions that are otherwise inaccessible to kinetic measurements. Since all molecules tend to dissociate at high temperatures, shock tubes are widely used to study dissociation processes and the chemistry of the resulting fragments. For example, the shock-induced decomposition of carbon suboxide provides an efficient means of investigating carbon atom reactions:

\[ C_3O_2 \rightarrow C + CO \]

Shock tube techniques are also useful for studying combustion reactions, including those that proceed explosively.
The shock tube itself consists of two sections separated by a breakable diaphragm of metal or plastic. One section is filled with a "driver" gas at a very high pressure, commonly helium, but often mixed with other inert gases to adjust the properties of the shock. The other, longer section of the tube contains the "driven" gas—the reactants—at a low pressure, usually less than 1 atmosphere.

The reaction is initiated by causing the diaphragm to rupture, either by means of a mechanical plunger or by raising the pressure beyond its bursting point. The kinetics of the reaction are monitored by means of an absorption or other optical monitoring device that is positioned at a location along the reaction tube that is appropriate to the time course of the reaction.

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