

COMPLEXITY IN CHEMICAL SYSTEMS

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Summary

The mechanistic origins of complex responses in chemical systems are traced to the role of chemical or thermal feedback arising from autocatalysis or self-heating. These simple building blocks, which occur widely in chemistry and biochemistry, support behavior ranging from simple clock reactions to sustained oscillations, chaos and spatial pattern formation. Examples discussed include the Belousov-Zhabotinsky reaction, with its spirals and target waves, combustion reactions and the formation of Turing structures.

1. Introduction: Chemical Kinetics

The complex behavior that occurs in reacting chemical systems stems from two basic features: chemical reactions do not occur instantaneously and they do not generally occur in a single step. As an example, the reaction between hydrogen H₂ and oxygen O₂ to form water H₂O is the simplest oxidation or combustion process. Most people, at some stage, learn how to write the balanced “stoichiometric” equation for this reaction:



This reaction does not occur at any measurable rate at room temperature and pressure, although at other conditions (see later) it occurs explosively fast. It also never occurs through the simple collision of two molecules of hydrogen and one of oxygen. Instead, there is a “mechanism” of chemical transformation in which, typically, one atom at a time is transferred from one molecule to another. In the course of this sequence, several new “intermediate” species are first formed and then destroyed. For instance, the very first step is believed to involve H₂ and O₂ reacting, with the H-H bond breaking and one H-atom transferring to the O₂ to produce the HO₂ radical and the other emerging as a

free H-atom.



This is an example of an “elementary step” -- a process that actually occurs, and which occurs through a single collision between the species on the left-hand side. The stoichiometric equation (1), in contrast, is simply a summary of the overall reaction, indicating the relative number of each reactant consumed and of products produced.

Both the HO₂ and H-atom species are radicals, and are more reactive species than the original reactants -- particularly so in the case of the H-atom. These species carry the reaction forwards by reacting with more of the reactants. For the H-atom, an important possible step involves reaction with O₂ to produce an O-atom and the hydroxyl radical OH,



This step is significant as the number of reactive intermediate species increases from one (H) to two (OH and O). This is a “chain branching” step. As the overall rate at which H₂ and O₂ are being consumed (and, hence, at which H₂O is ultimately being produced) depends on the reactive species concentrations, so the rate increases as a consequence of steps such as reaction (3).

The study of the rates at which chemical reactions occur, and of the way those rates depend on the concentrations of the species involved and on the temperature and other experimental conditions, is that of chemical kinetics. The above discussion might suggest that, even in the simplest cases, this is going to be a complicated endeavor, with the reaction rate depending on many species, several of which may be present at almost undetectably low concentrations. In many cases, however, despite the existence of a multi-step mechanism, the situation in terms of what determines the reaction rate turns out to be relatively straightforward. In part, this is because many of the elementary steps involving the most reactive species will occur very rapidly, and other steps involving the least reactive species will be very slow: the overall reaction rate then tends to be dominated by the steps that fall between these two extremes -- those perhaps involving one reactive and one relatively stable species. These are the so-called “rate determining” steps and the kinetics of the overall reaction will be determined by the kinetics of these steps alone. Even so, chemical reactions can support a wide range of “complex behavior”.

A convenient way of establishing the potential of a particular reaction, which we might write abstractly as



to support complex responses is to plot the reaction rate (e.g. the rate at which the concentration [A] of the reactant A is falling in time) as a function of “how far” the reaction has proceeded. The latter is made precise by considering the “extent of reaction” which is effectively the difference between the initial concentration [A]₀ of the reactant and its concentration [A] at any later time. Some example rate-extent plots are shown in figure 1(a,b).

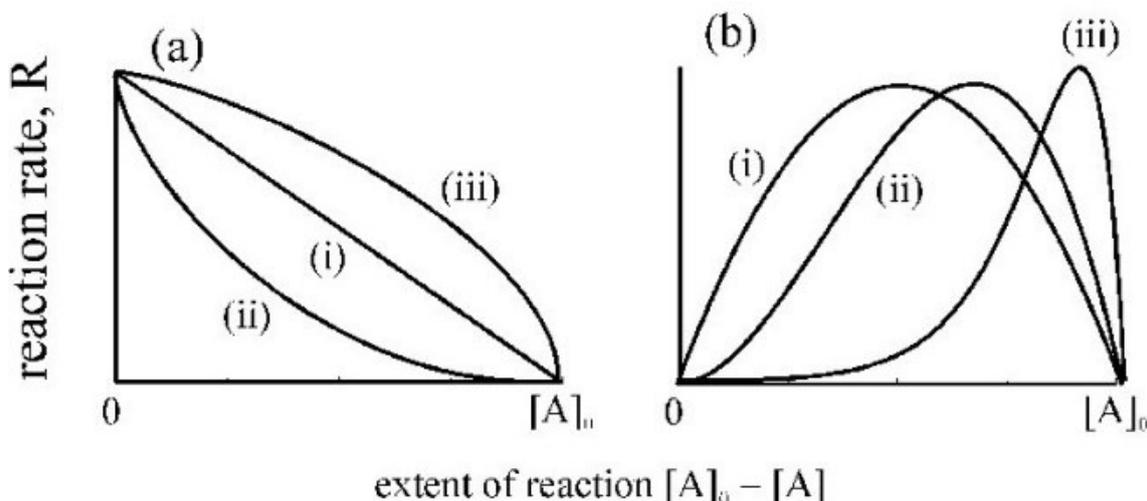


Figure 1: Typical rate-extent plots (a) for deceleratory chemical systems with (i) first-order, (ii) second-order and (iii) half-order kinetics; (b) for acceleratory systems exhibiting feedback such as (i) and (ii) chemical autocatalysis or (iii) thermal feedback

Plot (i) in figure 1(a) shows a reaction for which the reaction rate decreases in a linear (straight line) manner as the reactant is used up. This is an example of a “first-order” process, with the rate being simply proportional to the concentration of the one reactant. The other plots in figure 1(a) indicate rates that depend on different powers of the concentration -- specifically (ii) shows a “second-order” case with the rate depending on the square of the concentration and (iii) shows “half-order” kinetics, with the rate proportional to the square root of the concentration. The rate-extent plots in figure 1(a) all share a characteristic feature: the rate is highest at the beginning of the reaction (zero extent of conversion) and falls monotonically as the extent increases. These, then, are examples of “deceleratory” reaction kinetics. The rate-extent plots in figure 1(b), however, are characteristic of “acceleratory” systems, those in which there is a period over which the reaction rate *increases* with increasing extent of conversion. The origin of such acceleratory behavior is typically that described in the opening paragraphs of this article -- the increasing production of reactive intermediate species through chain-branching. Curves (i) and (ii) in figure 1(b) are typical of the two “shapes” found for acceleratory systems. They can be modeled by imagining that the conversion of A to B is, in some way, “catalyzed” by the product B -- giving an “autocatalytic” process. The very low reaction rate at low extent of conversion (i.e. at the beginning of the reaction) noticeable especially for curve (ii) means that the reaction is “kinetically frozen”. Curve (iii) is characteristic of a different type of feedback -- that which occurs when a chemical reaction gives out heat (an exothermic reaction). Unless this heat is transferred with perfect efficiency to the surroundings, there will be a rise in the temperature of the reacting species. Most chemical reactions are temperature-sensitive, showing an increasing rate as the temperature increases. The increasing reaction rate will lead to an increasing rate of heat evolution, and so to a further increase in temperature. This “thermal feedback” is responsible for many instances of spontaneous ignition in combustion.

The rate-extent curves can be used as a basis for the introduction of the various complex

responses exhibited by reacting chemical systems.

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Biographical Sketch

Professor **Steve Scott** is Head of the Department of Chemistry at the University of Leeds. He leads a research group investigating nonlinear kinetics in chemical reactions, with recent emphasis on controlling chaos in combustion reactions and pattern formation in solution-phase reactions. His research extends from experiment to theory and involves collaboration across Europe and the USA. He gained his PhD in 1982 from Leeds and spent periods at universities in Australia and the USA before returning to Leeds. From 1997 to 1999 he was Scientific Editor of the journal *Faraday Transactions*, published by the Royal Society of Chemistry. He was awarded the Harrison Memorial Prize and the Marlow Medal by the Royal Society of Chemistry.