

Chemical Oscillations

1. Basic Principles and Examples

Monika Sharma and Praveen Kumar

A chemical reaction is usually thought of as coming together of reactant molecules to form products. The concentrations of initial components (reactants) decrease, and concentrations of products increase until they reach a well defined state: the equilibrium. This process is accompanied by a decrease of the system free energy (compared at constant pressure and temperature), until it reaches a minimum in the equilibrium. Thus, it follows from the nature of the law of mass-action that every simple reaction approaches its equilibrium asymptotically, and the evolution of any physico-chemical system leads invariably to the steady state of maximum disorder in the universe. Normally, chemical systems approach equilibrium in a smooth, frequently exponential relaxation. Under special circumstances, however, coherent behavior such as sustained oscillations are observed and the oscillations of chemical origin have been present as long as life itself. Such reactions can be studied using mathematical models, the Lotka–Volterra model being the earliest and the simplest one.

1. Introduction

Every living system contains hundreds of chemical oscillators. Some examples are systems such as circadian clocks and rhythmic activity of central nervous system, and other biochemical processes at the cellular level like the glycolytic pathway, peroxidase-catalysed reaction or the biosynthesis of certain proteins. A systematic study of oscillating chemical reactions is of considerable interest, since these oscillating reactions can be used as prototype examples of the behaviours possible in reactions governed by non-linear dynamic laws that appear in chemistry,



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The phenomenological kinetics of oscillating chemical reactions shows that the concentrations of reactants, intermediates and products can vary periodically either in space, e.g., morphogenesis, or in time, e.g., circadian rhythms.

geology, biology and engineering. An understanding of oscillatory processes at molecular level is of great importance, as it holds the key to the mystery of complex phenomena like sleep induction in animals or migratory behaviour of birds, etc.

The phenomenological kinetics of oscillating chemical reactions shows that the concentrations of reactants, intermediates and products can vary periodically either in space, e.g., morphogenesis, or in time, e.g., circadian rhythms. It may seem that an oscillating reaction would require the free energy of the system to oscillate as the reactants were converted to products and then back to reactants, thus contradicting the Second Law of Thermodynamics. In fact, this behaviour is driven by the Gibbs-free-energy decrease of an overall chemical reaction occurring far from thermodynamic equilibrium. Such oscillating systems correspond to thermodynamically open systems. A biological cell is also an open system that can take in nutrients and excrete waste products of enzyme-catalysed reactions. These reactions are complex and take place via a number of elementary steps, most of which involve nonlinear kinetics. Long-lasting chemical oscillations can occur only if a proper feedback mechanism is present. This can be achieved by supplying reactants and removing products continuously from the reaction vessel.

In this article, we illustrate the interesting features of this now well studied area of complexity. We discuss autocatalysis, bistability and provide a recipe for observing oscillations in the laboratory.

Autocatalysis

Another important feature of most chemical systems that exhibit oscillations is autocatalysis, which is a way to provide positive feedback to an oscillatory reaction, i.e., the progress of the reaction is favoured by the product formed. Autocatalysis is the phenomenon of catalysis of reactions by products formed during a reaction.



The simplest example of autocatalysis is the reaction:



whose rate law is $-d[A]/dt = k[A][X]$.

The presence of one or more autocatalytic steps in a complex chemical mechanism leads to chemical oscillations. However, as the product concentration keeps building, autocatalysis can lead to explosion, so an inhibition step is also necessary. When autocatalysis and inhibition appear at the same time, the steady state can be stabilized, where the net rate of increase of all relevant species is zero. So, oscillations can appear only if the inhibition step is somehow delayed.

Example of an Autocatalytic Reaction

An example of autocatalysis is provided by Belousov–Zhabotinskii reaction (BZ reaction) (Box 1), the first oscillating reaction to be reported and studied systematically. This is also the first chemical reactions found to exhibit spatial and temporal oscillations, i.e., oscillations in time and space, respectively, even in a small beaker or in a Petri dish. The reaction solution spreads out as a thin film with a few millimeters thickness in a Petri dish and after a certain time, blue oxidation fronts propagating on a red background (reduced ferroin; see Box 1) develop (Figure 1).

Bistability and Hysteresis

Normally, only a single (monostable) steady state is expected for a particular set of reactant concentrations. However, equilib-



Figure 1. From left to right: Propagating oxidation waves in unstirred layer of the ferroin-malonic acid BZ reaction. When the wave is broken at a certain point, a pair of spiral waves develop at this point.

Courtesy: Peter Ruoff.

Source: www.ux.his.no/~ruoff/BZ_Phenomenology.html

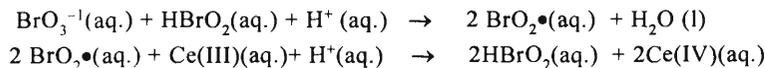


Box 1. BZ Reaction

In a classical form, BZ reaction is a case of oscillatory chemical reaction in homogeneous solution. Generally, it consists of oxidation of analogs of an organic acid (commonly malonic acid), by bromate ion in form of NaBrO₃ or KBrO₃ acidified by sulfuric or nitric acid. As catalyst, mostly Ce(III)/Ce(IV) salts, Mn(II) salts and ferroin are used.

The two pictures on the left (*Figure A*) and right (*Figure B*) show the BZ reaction with malonic acid as a substrate in a stirred beaker with ferroin as a catalyst. Oxidized ferroin has a blue colour and reduced ferroin is red. The solution shows periodic colour changes due to the alternations between the oxidized state (*Figure A*) and reduced state (*Figure B*). The time period of BZ systems ranges from a fraction of a minute up to many minutes depending on the amounts of mineral acid, organic compound, catalyst, bromate ion and temperature.

The simplest description of the reaction is in terms of two elementary steps:



The product HBrO₂ is reactant in the first step and provides a feedback mechanism that enhances the rate of formation of HBrO₂.

Figure A (top). Oxidized ferroin system.
Figure B (bottom). Reduced ferroin system.

Courtesy: Peter Ruoff

Source: www.ux.his.no/~ruoff/BZ_Phenomenology.html



Bistability has an analogy in electronic circuitry, such as in bistable multivibrators, flip-flop, etc., where induction of bistable circuit to make an abrupt transition from one state to the other by means of external excitation is well known.

rium systems operating far from equilibrium (autocatalytic reactions) can exhibit a number of steady states, say three or more. The simplest of these is the existence of a system in two equally likely (but different) stable states – bistability, a situation arising out of three steady states, of which two may be stable locally and experimentally observable, and the third is always unstable.

This bistability has an analogy in electronic circuitry, such as in bistable multivibrators, flip-flop, etc., where induction of bistable circuit to make an abrupt transition from one state to the other by means of external excitation is well known. It can be used for performance of many digital operations, such as counting and storing of binary information.



Bistability occurs over a range of values of a suitable control parameter. This means that the existence of the system in either of the steady states is decided by a limited range of values of the parameter. Variation in the value of such an experimental parameter can possibly move the system between the steady states. Perturbing the system from the bistability range will effect the transition of the system to one or the other of the steady states. This behaviour is described by curves obtained in the $[X]$ - $[Y]$ plot (Figure 2). The upper and lower curves SSII and SSI are the set of stable steady states for different values of $[X]$, obtained far from equilibrium. The concentrations $[X]$ represent the reactant supplied to the reactor and $[Y]$ represent the concentrations of the product removed from the reactor, continuously.

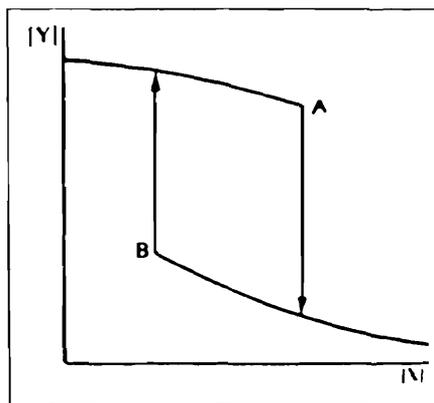


Figure 2. System showing bistability.

Moving along a curve for one steady state, say the lower one, if the system is brought to the range of values of $[X]$ for which bistability exists (from SSII to SSI in Figure 2), it will remain in that state until the limiting value of $[X]$ for this state is reached. Thus, to effect a transition in one direction, we must pass beyond the range of parameters for bistability. If we follow the curve for the other steady state in the reverse direction, we reach a different limit of the value of $[X]$, at which the reverse transition takes place, indicating that the system retains memory of the direction of the bistability region it left or re-entered. This peculiar behaviour is called hysteresis and has its analogy in magnetism, where the retention of magnetism by the iron sample, leads to the complete cycle of magnetisation and demagnetisation in the form of a loop.

When we introduce an intermediate Z to the reactor, which reacts with both X and Y , to produce Y and X , respectively, we observe that the system switches periodically between the upper and the lower curves (Figure 3), giving rise to oscillations. This added intermediate must show two features: the rates of reactions of the intermediate with one or more species present in the

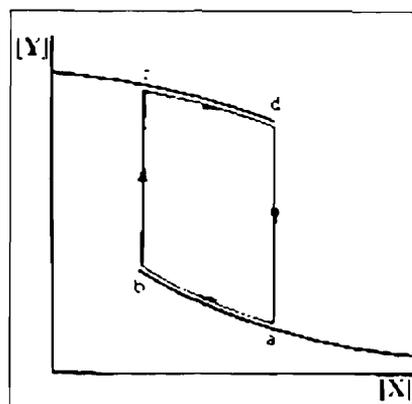


Figure 3. When an intermediate Z is added to reactor system X - Y .

Box 2. Recipe for Briggs–Rauscher Reaction

Solution I: [H₂SO₄] 0.0265M + [MnSO₄] 0.0067M + [Malonic acid] 0.0500M

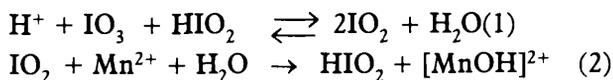
Solution II: [KIO₃] 0.0670M + [Starch] 0.0300M

Solution III: [H₂O₂] 30% solution

initial bistable system on the two steady state branches must differ to a considerable extent; and its reactions with the bistable system must be slower than the reactions of the constituents of the system with each other. The oscillation is seen as the periodic depletion of the reactants and surge of products. The existence of bistability is an interesting aspect in the occurrence of oscillations.

This is illustrated by the Briggs–Rauscher (BR) [1] reaction (*Box 2*), a variant of the BZ reaction. When we mix the three solutions given in the recipe (see *Box 2*) and the mixture is stirred vigorously with a magnetic stirrer, the initial colourless solution turns amber immediately. Then it turns blue-black, which fades out to colourless, which again changes to amber. The colour of the solution thus oscillates between the colourless, amber, and blue black for some time. The main feedback specie recognized in this reaction is malonic acid and, bistability is generated from an autocatalytic decomposition of H₂O₂ by IO₃⁻. Upon initial mixing of the solutions, IO₃⁻ reacts with H₂O₂ to give HIO₂. This step is autocatalytic, assumed to result from a radical mechanism activated by the presence of Mn²⁺ ions.

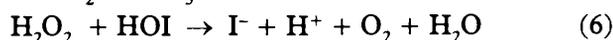
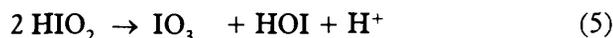
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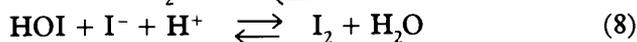
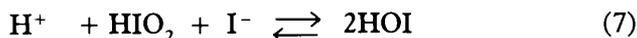
[MnOH]²⁺ eventually generates oxygen



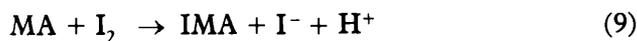
This autocatalytic production of HIO₂ is finally limited by



The HOI produced in equations (5), (6) and (10) reacts with I^- producing I_2



The I_2 reacts slowly with malonic acid



This shows that BR reaction involves two stoichiometric radical and non-radical reduction processes. These reactions give rise to bistability under appropriate flow conditions. The non-radical sequence (equations 7-10) lowers the concentrations of I_2 and I^- , denoted by $[I_2]$ and $[I^-]$, respectively. This makes the system undergo a switchover to the radical sequence (equations 1-4). The decreased $[I^-]$ and increased $[HIO_2]$ (equations 1-2), result in increase of $[HOI]$ by radical reactions to such an extent that Equation 6 begins and $[I^-]$ increases. The presence of amber colour corresponds to the concentrations of HOI greater than I^- concentrations. The increase in $[I^-]$ switches the system to non-radical mode, thereby increasing $[I_2]$ (by equation 8). The blue-black colour is present when $[I^-]$ is greater than $[HOI]$ due to the formation of a blue starch-iodide complex. $[I_2]$ reaches a maximum and begins to fall with $[I^-]$ still rising as $[I_2]$ continues to drop until the solution finally fades out. When $[I^-]$ reaches a critical level, $[HIO_2]$ falls suddenly, increasing $[I^-]$, switching the system back to the non-radical path, and the cycle is again allowed to repeat. Thus, the switching of reaction between the radical and non-radical modes is dictated by the $[I^-]$, i.e., whether the $[HIO_2]$ finds enough $[I^-]$ to react through nonradical mode, or gets involved in the radical autocatalytic step.

The Briggs-Rauscher reaction, like the BZ reaction, has been studied extensively. In experiments using the continuous-flow, stirred-tank reactor (CSTR)², the complex oscillations as well as the bistability involved in the BR reaction have been seen. The bistability observed can also be explained by the phase diagram

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(Figure 2 with $[X]$ and $[Y]$ as input-flow concentration $[I_2]_0$ and steady state iodine concentration $[I_2]_{SS}$, respectively). Curves SSII and SSI denote steady state II and steady state I, respectively. The steady state $[I_2]_{SS}$ can either be higher or lower than $[I_2]_0$, depending upon the branch of hysteresis attained. At low input flow, system attains SSII where $[I_2]_{SSII} > [I_2]_0$. On the other hand, at high input flow, the system reaches SSI where $[I_2]_{SSI} < [I_2]_0$. Under some conditions, a curious phenomenon is observed, known as inverse regulation² of $[I_2]$, where it is seen that increasing $[I_2]_0$ beyond its critical value results in a drop in $[I_2]$ in the reactor, and the reverse is observed when $[I_2]_0$ is decreased below the critical value.

Concluding Remarks

The BR oscillator studied above is one of the most spectacular elementary chemical oscillators. It can be used for the purpose of lecture demonstrations, and it appears like a magic show! There are many other kinds of oscillating systems known and studied at present. All of these have underlying plans of evolution; they all have autocatalytic components. Often the reaction is carried out in a continuous-flow reactor; the conditions are varied to find the bistability region; and another substance exerting significant by different effects on the two branches of steady states of system may be added to the original oscillatory system. In Part II of this article, we describe a very simple mathematical model, the prey-predator model, of an oscillatory chemical reaction. We carry out detailed analysis of this model and show a few results.

Suggested Reading

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