An Integrated and Open-ended Experiment

Study of Chemical Waves in Time and Space

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In this article we discuss an exciting experiment in non-linear dynamics. This provides an imaginative platform for bringing in chemical, physical, biological, mathematical and computational sciences together. There are implications for earth sciences as well.

1. Introduction

Chemistry is a subject combining magic, logic and aesthetics. Unfortunately, the laboratory programme has remained the weakest link in chemical education in our country at the university level. It is employed mainly for teaching techniques/skills or for illustrating theory. While these are undoubtedly necessary, the pleasure of learning by actually doing chemistry with a coordination of one's mind and hands tends to get submerged under the monotony of repetitive experiments. Furthermore, the emphasis on studying phenomena, as opposed to just determining a value, appears to be missing. Adequate intellectual efforts should therefore be made for designing instructive and exciting experiments based on the research literature, drawing upon the works of Indian and global researchers wherever possible. In an optimum way, this can be done at any level of university education, from first-year BSc to final-year MSc. The purpose of this article is to describe an integrated and open-ended experiment which has been taught by one of us at various levels for more than thirty years.

Keywords
Integrated open-ended experiments, birhythmicity, UV-visible spectrophotometer, period doubling, metastable equilibrium, molecular switch, autocatalysis, anharmonic oscillations.

An integrated experiment in chemical sciences should interlink various techniques/skills, concepts and phenomena from different areas of chemistry (e.g., from inorganic, organic and physical chemistry). It should also link chemistry to physics, mathematics, biology, earth sciences, computer simulation and computer control, emphasizing the beautiful internal harmony in chemistry and the essential ‘one-ness’ of all sciences. An open-ended experiment can be continued in different directions by students depending on their inclination, thereby fostering his learning by self-discovery and self-design as well as bringing in a flavour of exploration, research and adventure. It may, however, be noted that an integrated experiment is not necessarily open-ended and vice versa.

An experiment should excite the student visually and aesthetically, for example, through dynamic colour changes. Student’s initiative and ingenuity should be built into the design of the experiment so that the experiment is not performed mechanically.

The design of an integrated and open-ended experiment in chemical sciences should try to satisfy the following criteria:

1. It should excite the student visually and aesthetically, for example, through dynamic colour changes.
2. It may seem simple to execute but should be backed by a fairly large network of concepts from different areas/disciplines.
3. It should involve relatively inexpensive chemicals and equipments so that any educational institution can afford to do the experiment. However, for detailed quantitative measurements, simple equipments should be replaced by sophisticated research equipments involving computer interface.
4. Student’s initiative and ingenuity should be built into the design of the experiment so that the experiment is not performed mechanically.

Below, we describe an experiment on chemical waves in time and space based on the Briggs–Rauscher (BR) oscillating chemical reaction [1] which was discovered by two school teachers in 1973. It will be clear later that this is a ‘non-classical’ classical system which is perhaps the most exciting and complicated reaction to study in chemistry. Thus, it is not yet fully understood. The BR reaction is an excellent medium for attempting an intellectual integration between different areas and disciplines as mentioned above, because it falls into the broad domain of non-linear dynamics which comes under mathematics, physics, chemistry, biology, computational sciences, etc. (*Box* 1). However, it can be tailored for students at any level, from the school to the university [2]. For simplification, we describe the experiment,

The BR reaction is an excellent medium for attempting an intellectual integration between different areas and disciplines because it falls into the broad domain of non-linear dynamics which comes under mathematics, physics, chemistry, biology, computational sciences, etc.

Box 1. Some Examples of Non-linear Oscillations in Chemical, Biological, Physical and Other Systems

In linear (harmonic) oscillations, the restoring force is proportional to displacement and the oscillation amplitude as well as frequency are independent of time. In contrast, non-linear (anharmonic) oscillations are characterized by the restoring force varying non-linearly with displacement. As a result, the oscillation amplitude and/or frequency can change with time (Section 4.1). There are numerous examples of non-linear oscillations of which only a cross-section is listed below. They are frequently marked by *self-organization* which is manifested through exciting geometrical patterns.

Chemical: Bray–Liebhafsky reaction, Belousov–Zhabotinsky reaction, Briggs–Rauscher reaction, chlorite-iodate-arsenite reaction, chlorite-iodide-malonic acid reaction, hydrogen peroxide-sulfide reaction, cobalt-catalysed aerial oxidation of benzaldehyde, oscillators based on manganese chemistry, pH-driven oscillators, oscillating electrical current generated by an electrochemical cell, dissolution of chromium in acid, mercury beating heart, etc. Published observations on chemical oscillations go back to 1828.

Biological: Enzyme activity associated with metabolism (time-period about a minute); epigenetic activity (time-period about an hour); glycolytic cycle (time-period varies depending on the system); circadian (about 24 hours) rhythms in the physiology of bacteria, fungi, plants and animals; heartbeats, sleep, hunger, functions of the central nervous system, cell regeneration, reproduction; large-scale migrations of birds, turtles, whales of time-period about one year; prey-predator systems; striking patterns on the bodies of insects, birds and animals, etc. The formal study of temporal rhythms including daily, weekly, monthly and seasonal rhythms in living systems is called chronobiology. Such rhythms partly depend on external perturbations such as sunlight and temperature, with their own mechanisms for adjustment.

***Physical, including Atmospheric and Meteorological*:** Damped and driven pendulums, vibrations in molecules and solids, plasma oscillations, ocean tides, monsoon, El Nino and La Nina temperature fluctuations in the surface waters of the Eastern Pacific Ocean, Southern Oscillations (monthly or seasonal fluctuations in the air pressure in the Southern Hemisphere), quasi-biennial oscillations of the equatorial zonal wind in the tropical stratosphere with a mean period of 28 months, the Chandler Wobble (a variation of 0.7 arc-second of the earth's axis of rotation with a mean period of 433 days), *Aurora borealis* and *Aurora australis* in the northern and southern latitudes respectively (spectacular colour displays or 'paintings in the sky' caused by fluctuations in electro-magnetic fields), etc.

Geological, Ecological and Economical: Spatial patterns formed in naturally occurring minerals; population dynamics of various species; occurrence of disasters such as earthquakes, epidemics, famine, flood, etc.; ups and downs in market economy.

briefly discussing various concepts and explanations so that the present article can serve as a manual and source material for both students and teachers of not only chemistry but other sciences as well. We believe that some of the results, especially the spatial patterns, might be reported here for the first time.

The pedagogical plan of this article is the following: Section 2 describes how to do this experiment. Particular attention is drawn to *Box* 2 which emphasizes how the student, armed with only a few known facts, may proceed to investigate a new phenomenon based on his /her logical and intuitive faculties. This implies self-discovery and self-design by the student (see point 4 of 'design of an open-ended ...'), bringing in a sense of adventure. Such an approach comes into play whenever a scientist discovers and studies a hitherto unknown phenomenon. Section 3 lists the areas and concepts relevant to this experiment while Section 4 briefly

Box 2. Self-discovery and Self-planning of the Experiment by the Student with a Few Surprises in Store

(i) Do one or more trial runs of the reaction (steps 1 and 2 in Section 2.3). Observe the phenomenon. Follow it to completion.

(ii) You are observing chemical oscillations or waves. Are the oscillations linear or non-linear? Check if the time-period and amplitude of oscillations change with time. For linear oscillations (e.g., classical linear harmonic oscillator), where the restoring force is linear in displacement, both remain constant in time (Section 4.1).

(iii) For acquiring insights into this phenomenon, you need to think and plan to carefully gather as many facts about the phenomenon as you can (as Sherlock Holmes said to Watson, "It is a capital mistake to theorize without data" !). First, based on your trial runs, you need to speculate about what could be happening and then decide on a logical approach to probe the system/phenomenon in as much detail as possible.

(iv) You need to study the nature of these non-linear oscillations in both time and space. For oscillations in time, probes could be optical (spectrophotometric), electrochemical, thermal, etc. Which parameters might oscillate in time? For electrode probes, a little thinking will make you realize that in the reaction mixture a few redox couples might be generated, e.g., I_2/I^-, Mn^{3+}/Mn^{2+}, H_2O_2/H_2O, etc. Therefore, with suitable electrode probes, an oscillating emf may be obtained. Since the temperature of the reaction mixture changes during the reaction, could the temperature also oscillate? Other quantities which might oscillate are pH, volume of evolved gases, the rate of gas evolution, etc.

(v) For studying oscillations in space, you need to decide on the reaction vessel. Does the reaction depend on the geometry of the reaction vessel, under certain conditions? If yes, then different regions of the reacting mixture should behave differently and you should then allow the phenomenon of diffusion (a slow process) to control the overall reaction. In other words, for establishing concentration gradients of various entities in space as the oscillations progress, do not stir or disturb the reaction mixture which now represents a reaction-diffusion system.

Box 2. continued...

Box 2. continued...

(vi) If the reaction depends on the geometry of the reacting vessel, then a simple way of playing with geometry is to 'maximize' and 'minimize' the vertical dimension. Therefore, you might do the reaction in a 50 ml burette (with a white background) as well as a large Petridish. In both cases, do you observe any striking oscillations in space?

(vii) If the reaction mixture is not to be disturbed, does the reaction depend on the sequence in which the reactants are mixed ? If yes, what does this mean?

(viii) In all your experiments, does the reaction show you the same 'face' twice, even when performed under supposedly 'identical' conditions ? If not, what does this mean and how can you probe this further? Are (vii) and (viii) related ?

(ix) Why are the reactant concentrations (note that starch is not a reactant, only an indicator for iodine) so specific? Can the concentrations be played with? Can any of the reactants be replaced by a related substance?

(x) The final goal of fully understanding this phenomenon involves speculating on a complete set of reaction steps with their own rate constants, leading to the final outcome, which can explain all the observed facts. For every oscillating parameter, one needs to find its appropriate non-linear differential equation of motion, solve it numerically (because analytical solution may not be possible) by using a computer and compare with the observed results. Computer graphics would play a significant role in creating various geometrical patterns out of the equations of motion and comparing them with the observed rich patterns. Note that although considerable progress has been made over the years, a complete understanding of this reaction is not yet available.

describes the essence of several areas/concepts directly involved in the experiment. Finally, Section 5 makes a few concluding remarks on structure, dynamics and function.

2. How to Do the Experiment

2.1 *Chemicals Required*

Prepare the following solutions at room temperature in volumetric flasks. Solutions (a) and (b) can be stored for at least two weeks. The original bottle of H_2O_2 should be kept in a fridge.

(a) 250 ml of 0.15 M malonic acid and 0.02 M $MnSO_4.H_2O$ in 0.159 N H_2SO_4 (solvent).
(b) 250 ml of 0.2 M KIO_3 in 0.1% freshly prepared, almost clear starch solution (solvent).
(c) 250 ml of 12.5% H_2O_2.

2.2 *Main Equipments and Other Materials Required*

UV-visible spectrophotometer (or a colorimeter with various filters), digital voltmeter, oscilloscope (preferably automatic recording and plotting), two Ag/AgI electrodes (iodide-specific), magnetic stirrer, graduated pipettes (1, 2 and 5 ml) and 50 ml burette with white background. If possible, a thermostat, thermally insulated container, rapid-sensor digital temperature recorder and rapid-sensor digital pH recorder may also be procured; however, these have not been employed in the present study.

Oscillations may be regarded as a result of the 'tug-of-war' between two opposing sets of reactions.

2.3 *Actual Experimental Steps*

The experiment may be performed in 8 – 12 hours. Each aspect of the experiment may be repeated by the student to obtain satisfactory results.

A. *Oscillations in Time*

1. In a 50 ml beaker, placed on a white tile, mix 3 ml each of solutions (a), (b) and (c) given in Section 2.1. Spectacular colour oscillations from colourless → golden yellow → blue → colourless take place (*Figure* 1) with a time-period (blue to blue, first appearance) of several seconds. Follow the reaction to its equilibrium, *viz*. solid iodine precipitated out with the solution getting warm due to the release of lattice energy. Sometimes, the reaction might be trapped in a metastable equilibrium of a colourless solution which on standing for several minutes gives way to iodine precipitation.

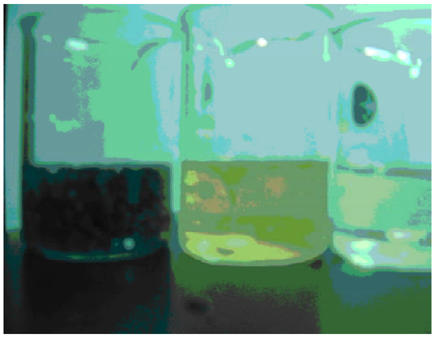


Figure 1. Three beakers showing sequential colour changes in the BR reaction at a particular time, viz., colourless, golden yellow and blue from right to left. This instantaneous phase matching in the three adjacent beakers occurs after a number of oscillations.

2. Using graduated pipettes, adjust the relative proportions of the three solutions in the reaction mixture so that around 50 oscillations are observed. These proportions should be employed for all subsequent experiments. For logically playing with the solutions, one should first realize that the oscillations may be regarded as a result of the 'tug-of-war' between two opposing sets of reactions, one set generating iodine (consuming iodide) and the other set consuming iodine (generating

iodide). This may be represented naively as

$$I^{-} \overset{\mathrm{MS}}{\langle\sim\sim\sim\sim\rangle} I_2$$

where MS is a molecular switch generated by the overall reaction (Section 4.7 for mechanism); here we have used an oscillating arrow pointing in two directions. When iodide production reaches a maximum, the switch is thrown in the forward direction and iodine generation begins. When iodine production reaches a maximum, the switch is thrown in the backward direction and iodine consumption (iodide generation) begins. The MS is an intermediate molecule which produces autocatalysis or feedback. Initially, I^- is generated from IO_3^- ; then I_2 is generated. I_2 is consumed mainly by the dicarboxylic malonic acid, containing a reactive methylene group ($=CH_2$) flanked between two $=CO$ groups, to form iodomalonic acid and iodide. Note that adding/ not adding appropriate amounts of water to vary the reactant concentrations in the reaction mixture is also an option (C – altering reactant concentrations ...).

At this point, the student should go to *Box* 2, dealing with self-discovery and self-planning, before proceeding with the following steps. As mentioned in Section 1, this encourages the student to approach the phenomenon based on only a few known facts and thereby maximizes her enjoyment from the experiment.

3. One may expect malonic acid to lead to the evolution of CO_2. Perform the reaction in a test tube fitted with a cork and a U-tube. Pass the outgoing gas mixture into another test tube containing lime water which would turn milky. Similarly, H_2O_2 should lead to the evolution of O_2.

4. Under constant stirring conditions (use a magnetic stirrer), plot the time-period of oscillations against time (*Figure* 2). Note that in this and all subsequent plots against time, you must fix zero-time; this is the instant when all the reactants are mixed together, e.g., it could be the time when a pipette adding the last reactant is half-empty or when a beaker adding the last reactant is quickly

emptied. Also, visually record the variation of amplitude of oscillation (intensity of blue colour) with time. If any of the two parameters varies with time, the oscillations are non-linear (anharmonic). Here, both parameters vary with time (Section 4.1). In certain situations, a non-linear oscillating system may double its period (for period doubling and related bifurcation phenomena, Section 4.5). This completes visual observations in time. Now come the instrumental recordings.

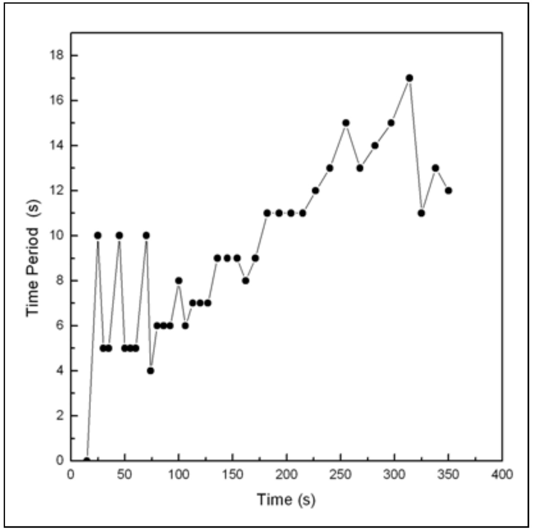
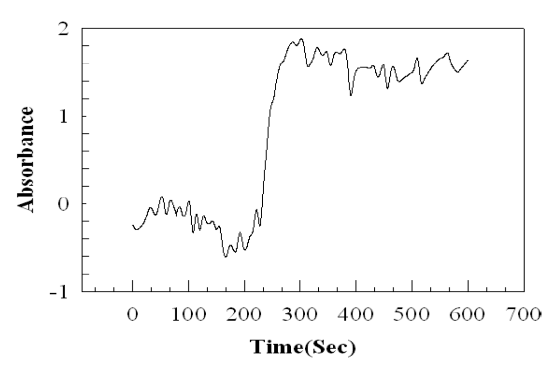


Figure 2. The time period of oscillations as a function of time.

5. Optical Recordings: Using a UV-Visible spectrophotometer at $\lambda_{max} = 591$ nm, record the dynamical absorbance of the reaction mixture as a function of time over 700 secs (*Figure* 3). This will give both frequency and amplitude of colour oscillations as functions of time. For this, mix the reactants in a 50 ml beaker and stir well; quickly pipette about 3 ml of the reaction mixture into the spectrophotometer cell. Note the fine structure of the initial peaks and whether this structure persists throughout the duration of the reaction. If a spectrophotometer is not available, employ a colorimeter using the 590 nm filter and manually as well as quickly record the absorbance as a function of time up to the second decimal place as time progresses. The absorption 'spectrum' in *Figure* 3 indicates birhythmicity (Section 4.4).

Figure 3. The dynamical absorbance as a function of time, at $\lambda_{max} = 591$ nm.



6. Electrochemical Recordings: For generation of an oscillating emf, you may employ an iodide-specific electrode such as Ag/AgI (preparation given below) which would be sensitive only to the I_2/I^- couple and a clean platinum electrode (washed with boiling conc. HNO_3) which would be sensitive to all the redox couples. Take the Pt and Ag/AgI electrodes in a 100/150 ml beaker and connect the electrodes to a digital voltmeter (or an automatic recording

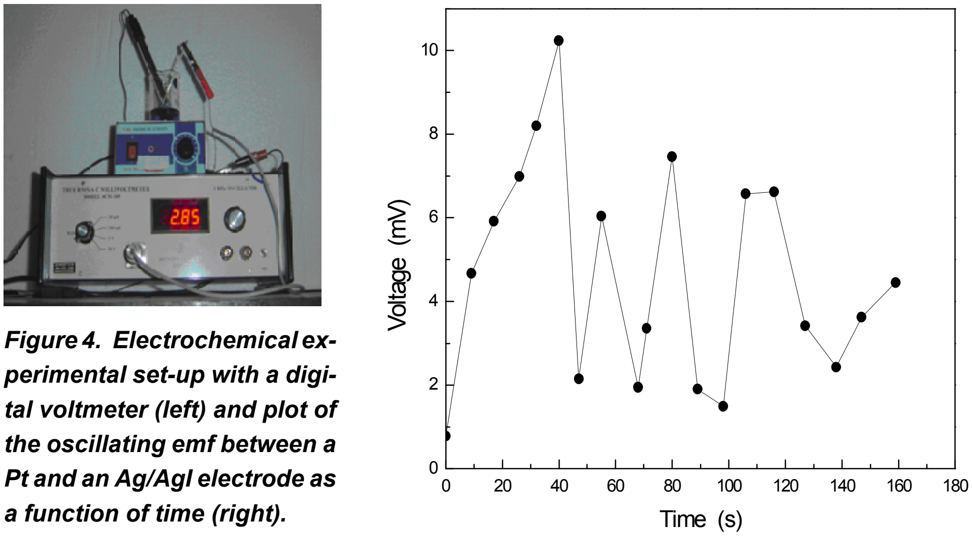
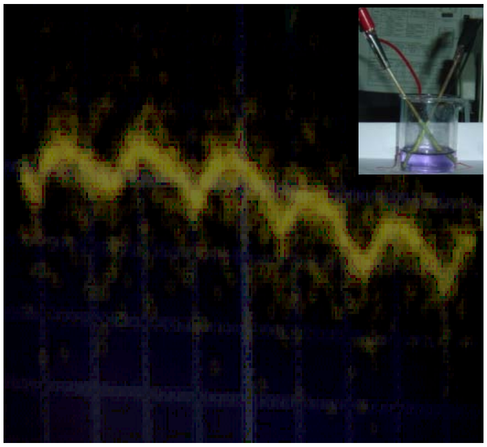


Figure 4. Electrochemical experimental set-up with a digital voltmeter (left) and plot of the oscillating emf between a Pt and an Ag/AgI electrode as a function of time (right).

and plotting voltmeter, if possible). Switch on the magnetic stirrer and prepare 50/75 ml of the reaction mixture in this beaker. Remembering that the oscillations are quite fast and using the code C, G, B for colourless, golden yellow and blue, quickly record as many readings of the voltmeter as you can for as many oscillations as possible. Plot voltage against time (*Figure* 4) and compare with the spectrophotometric plot against time.

Replace the digital voltmeter with an oscilloscope (automatic recording and plotting, if possible). Repeat the above experiment with a clean Pt electrode and a fresh Ag/AgI electrode (guard against the poisoning of electrodes). Keeping in mind the magnitudes of the time period and peak emf, adjust the oscilloscope voltage (DC) and time scales appropriately so that you can trace out several wave profiles of the oscillating emf in course of time. Record the oscilloscope pictures (*Figure* 5) and compare with the digital voltmeter plot. However, it may be noted that unscrambling oscillating potentials between pairs of redox couples from the above data is not possible unless one employs specific electrodes, each sensitive to only one redox couple.

Figure 5. The oscillating emf between a Pt and an Ag/AgI electrode as a function of time, as recorded by an automatic recording and plotting oscilloscope. Inset shows the reaction beaker with the electrode assembly.



Preparation of two Ag/AgI electrodes: Connect two thin, shining Ag rods (each 8 – 10 cm long) at one end with a copper wire so that the rods are in an inverted V-form. Place the rods away from a Pt electrode in a 250 ml beaker containing 125 ml of approx. 0.1 M KI solution. Using a 6 – 9 volt battery as well as making Ag the anode and Pt the cathode, perform electrolysis for about half an hour so that a thin yellow film of AgI is deposited on both the Ag rods (the film should not be grey or black). Store the two Ag/AgI electrodes in distilled water. After each determination of emf, the Ag rods can be cleaned and made shiny with sand paper.

7. Thermal Recordings (not reported here): Perform the reaction under constant stirring in an adiabatic enclosure (e.g., a thermos flask). Record the temperature of the reaction with an automatic, digital temperature recorder. The temperature might oscillate or might increase in a stepwise fashion.

8. pH Recordings (not reported here): Perform the reaction under constant stirring and record the pH with a quick-sensing automatic pH recorder. The pH might oscillate.

Experiments in 4, 5, 6 and 8 above may be performed at constant temperature, if possible, using a thermostat (not employed here) with a temperature control of $\pm 0.01^0$. However, note that the oscillation amplitudes are much larger than those caused by thermal fluctuations.

For automatically recording oscillations in time, a very convenient experimental device would be a PC with appropriate software along with specific rapid sensors for measuring colour intensity, voltage, pH, temperature, etc. Such a set-up represents many equipments in one.

9. Try to construct empirical functions of time from your recorded data/plots. This requires more mathematical knowledge than a chemistry student usually acquires at the BSc/MSc level.

10. Does repetition of steps 4 – 8 under identical conditions give you identical results?

The manner of propagation of the blue pulse(s), from either one end or both ends of the burette, is reminiscent of *solitary waves or solitons* which are highly interesting forms of non-linear waves.

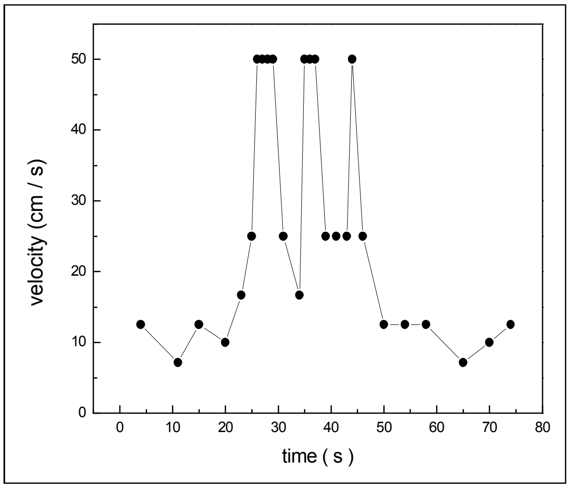
B. *Oscillations/Patterns in Space*: *Physical Manifestations of Chemical Waves*

1. Vertical Dimension 'Maximized': Prepare about 55 ml of the reaction mixture in a beaker, with or without stirring, and quickly pour the mixture into a 50 ml burette with a white background. You should observe a blue wave front traveling up and down, seemingly as a single pulse. The wave front may develop at the top/bottom/both ends of the burette. If two blue wave fronts develop at both ends of the burette, they propagate towards each other and appear to proceed further without any apparent change in form. Using a stop-watch, visually measure the velocity of propagation of the blue wave front over a distance of 50 cm on the burette and plot velocity against time (*Figure* 6). The velocity shows nonlinear oscillations.

The manner of propagation of the blue pulse(s), from either one end or both ends of the burette, is reminiscent of *solitary waves or solitons* which are highly interesting forms of non-linear waves. However, it would be very difficult to prove that these blue pulses are actually solitons (Section 4.6).

2. Vertical Dimension 'Minimized': Prepare the reaction mixture in a large Petridish of diameter 10 – 15 cm, placed on a white tile. First, decide the volume of the reaction mixture so that the dish is half-full. Do not disturb the reaction mixture once it is prepared so that as the oscillations progress, concentration gradients of the reactants and intermediates can develop between different spatial regions of the reaction; this is how diffusion can control the reaction. You may prepare the reaction mixture in various ways, e.g., (i) mix the three solutions first in a beaker, with or without stirring, and then pour the mixture into the dish; (ii) mix the three solutions directly into the dish, into the central region or near the periphery or along the sides of

Figure 6. Plot of the oscillating velocity of an advancing blue wave front in a 50 ml. burette as a function of time.



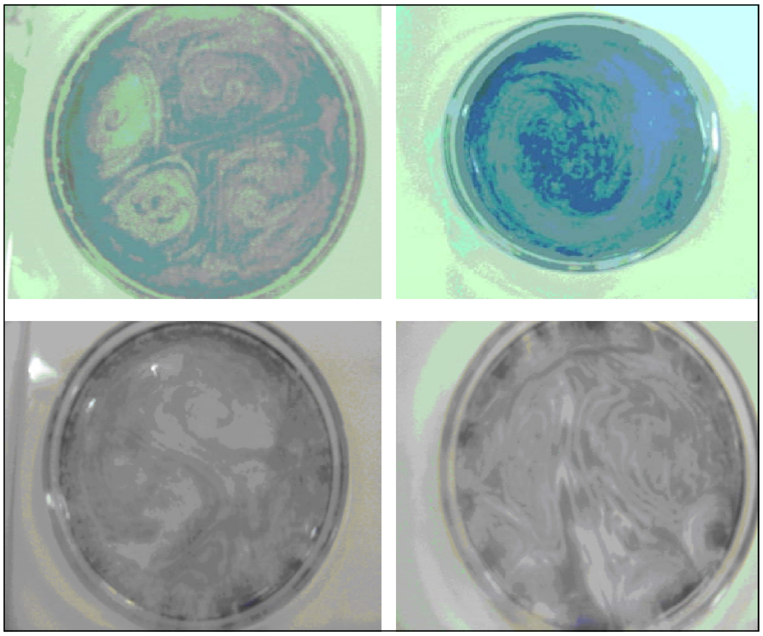
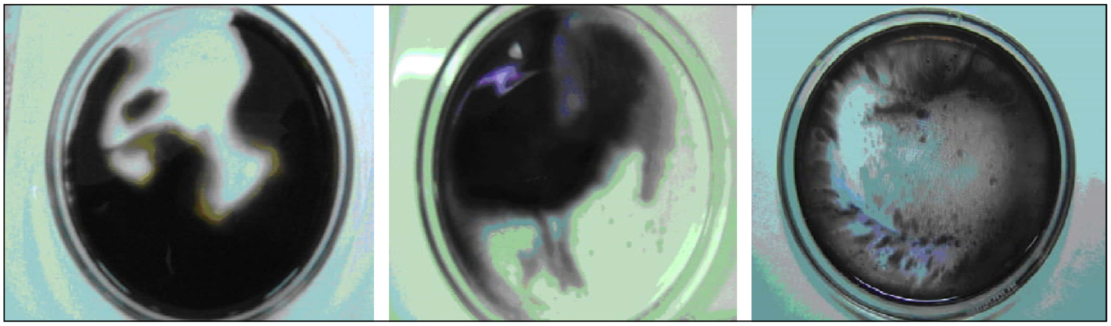


Figure 7. Iodine-starch blue geometrical patterns in a Petri dish. Clockwise from top left, 'd orbital', 'spiral', 'tapestry', 'paranoic face'.

the dish; (iii) alter the sequence of mixing of the three solutions for (i) and (ii), etc. The outcome varies from case to case. Once in a while, you may also prick the solution with a hot needle.

Fascinating and exhilarating geometrical patterns can be observed after a certain number of oscillations (A.2 above) when the solution is turning blue (*Figure* 7) and/or when iodine precipitation is taking place (*Figures* 8, 9). These patterns ('called' dissipative structures by I Prigogine) for the present system appear to be reported here for the first time for the BR reaction. They emerge and fade away quickly. The honeycomb is the most frequently observed pattern for iodine precipitation (*Figure* 9).

Figure 8. Geometrical patterns of iodine precipitation in a Petri dish. 'Baby in the womb' (left), 'flying chicken' (cenre), 'moon crater' showing very small hexagons and 'craters' (right).



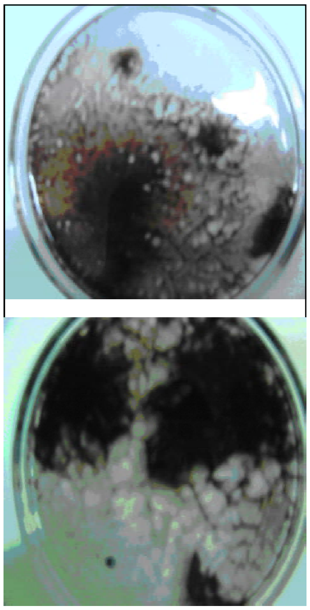


Figure 9. More geometrical patterns of iodine precipitation in a Petri dish. Small honeycomb (top), large honeycomb (bottom), with hexagonal patterns.

To generate other patterns requires repeated attempts and a great deal of patience because this reaction is classically chaotic and therefore highly sensitive to slight variations in initial conditions (Section 4.2). You may even observe patterns other than those reported here. These patterns appear due to the fact that different intermediate species are developing with different rates as well as concentrations and they have different diffusion rates. Some of these observed patterns, if not all, appear to be transient Turing patterns (Section 4.5) in reaction-diffusion systems. Therefore, they represent dynamical self-organization in the present system. Stationary Turing patterns seem to have been experimentally generated for the first time in 1990, nearly 40 years after their predicted occurrence by the mathematician Alan Turing.

Finally, the golden-yellow colour of the reaction mixture is due to iodine. We have verified that this colour occurs even in the presence of starch when iodine concentrations are very low *vis-a-vis* iodide concentrations in presence of excess H_2O_2.

In a test tube, prepare a solution of low iodine concentration *vis-a-vis* iodide concentration in presence of starch and H_2O_2 to obtain a blue-violet solution. Add excess H_2O_2 and a drop of iodine-iodide mixture, prepared by using a very small amount of elemental iodine in excess iodide solution, to obtain a persistent golden-yellow colour.

C. *Altering Reactant Concentrations and Replacing Reactants*

For the concentration of every reactant, there is a narrow range outside of which oscillations cannot be observed. Since oscillations occur due to a delicate balance of two opposing sets of reactions, and each reaction of either set has its own rate constant (the rate itself depending on concentration, in general), playing with reactant concentrations is difficult. You can replace Mn^{+2} with Ce^{+3} since the E_0 values of the redox couples Mn^{+2}/Mn^{+3} and Ce^{+3}/Ce^{+4} differ by only 7%. Malonic acid can be replaced by a substance containing a reactive methylene group, e.g., a β-diketone such as acetonyl acetone; it can certainly be replaced by methyl

For the concentration of every reactant, there is a narrow range outside of which oscillations cannot be observed.

malonic acid giving longer oscillation periods. Replacing H_2SO_4 by any other mineral acid can cause serious problems.

3. Areas Involved in the Phenomenon

1. Thermodynamics of equilibrium systems (Classical Thermodynamics). This is unable to explain the phenomenon (Section 4.3).
2. Thermodynamics of open systems. Non-equilibrium thermodynamics. Systems far from equilibrium. These concepts are needed to explain the occurrence of chemical oscillations.
3. Chemical dynamics (Section 4.7).
4. Electrochemistry. Ion-specific electrodes.
5. Non-linear differential equations of motion. Solitary waves and solitons (wave-particle duality of classical waves, i.e., outside quantum mechanics; Section 4.6). Classical (deterministic) chaos. Bifurcations. Period doubling. Sections 4.2 and 4.5.
6. Feedback processes. Autocatalysis.
7. Molecular switches. Molecular electronics.
8. Computer programming and numerical methods.
9. Computer control of experiments. Automation.
10. Reactive methylene group in organic chemistry.
11. Chronobiology. Models of biological periodicity/clocks, for e.g., daily, monthly, seasonal and yearly rhythms.

4. Some Necessary Concepts :

In view of the relatively large number of areas mentioned above, we restrict ourselves to simplified discussions of only a few. For detailed and in-depth understanding, the student is encouraged to search the literature/internet for the different areas/concepts. As mentioned before, a complete explanation of all the observed facts for the BR reaction is not yet available.

4.1 *Nonlinear oscillations*

For a classical linear harmonic oscillator, the restoring force on the particle is directed towards a point and proportional to its displacement from that point, k being the proportionality constant.

The differential equation of motion for such linear oscillations is given by

$$d^2x/dt^2 = -\omega^2 x \qquad (1)$$

where $x = a$ at $t = 0$, a being the amplitude of oscillations, and is the angular frequency; both amplitude and frequency remain constant in time. The following expressions give complete information about the state of motion of the oscillator:

$$x = a \cos [\omega t] \qquad (2)$$

$$p = - \; m\,a \;\sin [\omega t] \qquad (3)$$

$$E = p^2 / 2m + ½ \; k\,x^2 \,; \; k = m\omega^2 \qquad (4)$$

Equation (4) shows that for a particular value of the total energy E, the phase space orbit or trajectory (obtained by plotting linear momentum p against position x) is an ellipse which may be oblate or prolate depending on the relative values of m and k. For all E ≥ 0, the family of phase-space trajectories completely describes the motion of the system. The force constant k (spring constant in Hooke's law of elasticity) has been connected to, e.g., bond strengths of diatomic molecules.

For non-linear oscillations (see *Box* 2), one may formally write

$$d^2x / dt^2 = -\, a_1 x + a_2 x^2 + a_3 x^3 + \dots \,. \qquad (5)$$

$$x = a(t) \cos [\omega(t) t] \qquad (6)$$

so that a and/or ω are now functions of time; they might also oscillate non-linearly. Period doubling (Section 4.5) in course of oscillations is associated with classical chaos (Section 4.2). The above considerations can be extended to higher dimensional systems. Non-linear oscillations/dynamics were discovered in the 1820's but initially faced strong skepticism.

The multidisciplinary science of non-linear dynamics has spawned a huge amount of scientific literature, with numerous exciting phenomena many of which are actually observed. Below, we restrict ourselves to elementary discussions of only a few features concerning the present system.

4.2 *Classical or Deterministic Chaos*

A non-linear dynamical system manifests this phenomenon under certain conditions. Given its non-linear equation of motion, the chaotic behaviour of a system, no matter how surprising and counter-intuitive, can be completely predicted. The conditions for chaos are: (i) Sensitivity to initial conditions (SIC); (ii) topological mixing; (iii) dense nature of periodic orbits in phase space.

Consider two trajectories in phase space which start from two close-lying points at the initial time t_0 (*Figure* 10a, b), since they differ very slightly in the initial conditions. Let their distance of separation R(t) be proportional to exp[λt], where λ has been called the Lyapunov exponent. If $\lambda > 0$, then R(t) would diverge when $t \to \infty$, if the system is classically chaotic (*Figure* 10 b). In other words, SIC (condition (i)) implies that although two identical systems may appear nearly identical at a time t_0, depending on slight changes in initial conditions, the final outcomes can be dramatically different if the phenomenon is classically chaotic. Thus, condition (i) implies that a positive Lyapunov exponent is a confirmatory signature of classical chaos. For a non-chaotic system, R(t) does not diverge (*Figure* 10a).

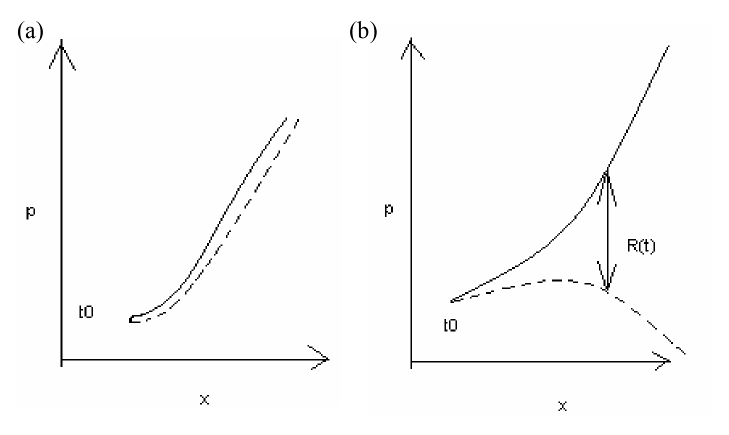


Figure 10. Depiction of the phase space of a system by plotting the momentum p against the position x. At an initial time t_0, two trajectories (solid and dashed lines) of the system, differing slightly in initial conditions, start from two points close to each other.

(a) Non-chaotic system.

(b) Chaotic system with a positive Lyapunov exponent.

Conditions (ii) and (iii) imply that, given a sufficiently large time, the system evolves in such a way that any given region in phase space will eventually overlap with any other region. Expressed simply, this means that it will not be possible to discern where one region of phase space ends and another region begins. A classic example of this is the *Lorenz Butterfly* (Section 4.4) in phase space which led to the term 'Butterfly Effect' ("If a butterfly flutters its wings in Beijing, a storm might brew in Washington, DC"). For chemically reacting systems which are chaotic, the fact that no matter how carefully you prepare the reaction mixtures you can never make two reaction mixtures identical, can have startling consequences. Apart from chemical oscillations, there are numerous other examples of classically chaotic systems; one such example is cardiac arrest which can be brought about by electrical impulses in the heart becoming chaotic (ventricular fibrillation). (Section 2.3 and *Box* 2).

4.3 *Why Classical Thermodynamics Does Not Permit Oscillations Around a Chemical Equilibrium*

Consider a chemical reaction $A \rightleftharpoons B$. Define the free energy G of a mixture of n_A moles of A and n_B moles of B, with μ_A and μ_B as the chemical potentials,

$$G = n_A \mu_A + n_B \mu_B \tag{7}$$

Let n_A^0 be the initial number of moles of pure A in its standard state. Define

$$G/n_A^0 = g\,; \quad n_A = n_A^0 - n_B\,; \quad \varepsilon = n_B/n_A^0 \tag{8}$$

Then g can be expressed as a function of the extent of reaction ε $(0 \le \varepsilon \le 1)$, as

$$g = \mu_A^0 + \varepsilon(\mu_B^0 - \mu_A^0) + RT\,[(1-\varepsilon)\ln(1-\varepsilon) + \varepsilon\ln\varepsilon] \tag{9}$$

(For the derivation of (9), see D H Everett, *An Introduction to the Study of Chemical Thermodynamics*, Ch.7, Longman Group Limited, London, 1971). *Figure* 11

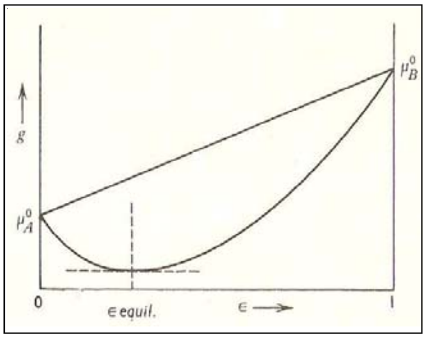


Figure 11. Plot of molar free energy (g) against the extent of reaction (ε). Reproduced with permission from D H Everett, *An Introduction to the Study of Chemical Thermodynamics,* Longman Group, London, Ch. 7, 1971.

gives the plot of g against ε for the case $\mu_A^0 < \mu_B^0$. The straight line denotes $\mu_A^0 + \varepsilon\,(\mu_B^0 - \mu_A^0)$. The minimum represents the equilibrium state and the reaction is spontaneous from either A or B because $dg/d\varepsilon < 0$ until it vanishes at equilibrium. From either side, once the equilibrium is reached, the system cannot overshoot the equilibrium because then the free energy will increase; even if the free energy increases infinitesimally, it will be spontaneously brought back to the minimum. This is consistent with the principle of microscopic reversibility enunciated by R C Tolman in 1925 for systems in thermodynamic equilibrium (this principle had been invoked by experts in classical thermodynamics to argue that oscillations cannot occur around a chemical equilibrium). Tolman's statement of the principle is the following: "In the case of a system in thermodynamic equilibrium not only… the total number of molecules leaving a given state in unit time shall on the average equal the number arriving in that state in unit time, but also … the number leaving by any particular path shall on the average be equal to the number arriving by the reverse of that particular path, thus excluding any cyclical maintenance of the equilibrium state".

In contrast to the above thermodynamical example, imagine an iron ball has been rolled from any side down a mountain slope similar to that depicted in *Figure* 11. It will oscillate up and down around the equilibrium position until it comes to rest at equilibrium. Thus, we have conclusively argued that oscillations can take place around a mechanical equilibrium but not around a chemical equilibrium. In the BR reaction, under carefully controlled conditions, the concentrations of reactants or products do not oscillate but those of some intermediate products do, when the overall reaction is far from equilibrium.

4.4 *Why Do Chemical Oscillations Occur? Bistability/ Multistability*

The conditions necessary for non-linear oscillations in a number of chemical systems are as follows: (a) The system concerned should be far from equilibrium. Note, however, that the BR reaction may be performed as a closed system far from equilibrium, although the oscillations will die down after a while. In contrast, the oscillations can be sustained in an open system. (b) The overall reaction should involve one or more autocatalytic steps (feedback) which can act as a molecular switch. (c) The system should exist in two (or even more) steady states (non-equilibrium states).

To understand condition (b) briefly, consider the well-known Lotka–Volterra mechanism for a reaction A → B, where the concentration of the reactant A is kept constant by supplying it to the reaction vessel from outside and the product B may be removed as it is formed (X and Y are intermediate products while k_1, k_2 and k_3 are rate constants):

$$\mathrm{A + X \rightarrow X + X}\ ;\ -\mathrm{d[A]/dt} = k_1\,\mathrm{[A]\,[X]}. \qquad (10)$$

$$\mathrm{X + Y \rightarrow Y + Y};\ -\mathrm{d[X]/dt} = k_2\mathrm{[X][Y]}. \qquad (11)$$

$$\mathrm{Y \rightarrow B}\ ;\ \mathrm{d[B]/dt} = k_3\,\mathrm{[Y]}. \qquad (12)$$

It is clear that steps (10) and (11) involve autocatalysis (feedback). One can solve the Lotka–Volterra equations, arising out of the above scheme, numerically and obtain the concentrations of the intermediates X and Y as functions of time. Define a 'phase space' (Section 4.1) by plotting [Y] against [X] to obtain the trajectory of the system as a closed orbit. This signifies non-linear oscillations (c.f. the closed phase-space orbits of the classical linear harmonic oscillator mentioned in Section 4.1). Different initial conditions give rise to different orbits.

However, as happens with the Brusselator and Oregonator models of non-linear chemical oscillations, the closed orbit may be a limit cycle to which the system migrates whatever be the initial concentrations of X and Y. A limit cycle may also be an attractor which appears to attract trajectories in its vicinity to itself. The visually stunning Lorenz Butterfly (*Figure* 12), discovered by Edward Lorenz in the 1960's during his researches on climate dynamics, is perhaps the most dramatic example of a strange

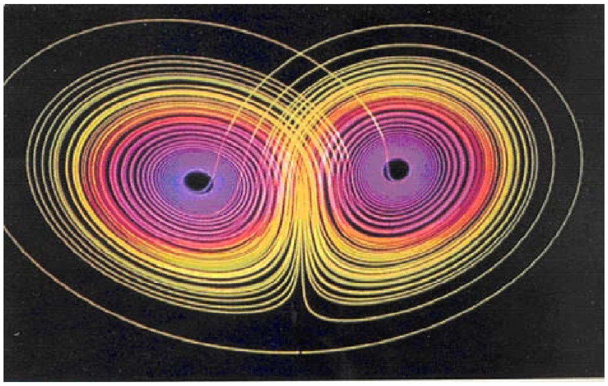
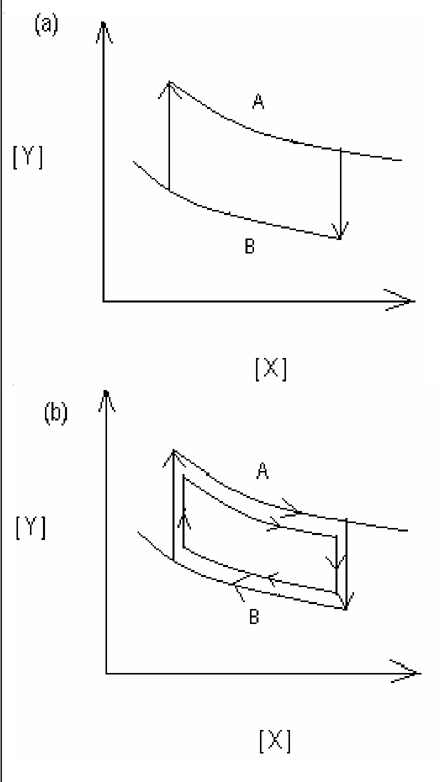


Figure 12. The Lorenz Butterfly in phase space. Reproduced with permission from J Gleick, *Chaos: Making a New Science*, Sphere Books, London, 1989.

attractor (an incredibly complicated tangle of trajectories) lurking in phase space. Strange attractors are associated with classical chaos (Sections 4.2 and 4.5) while both of them can be associated with fractals (sprawling, self-similar patterns whose topological dimensions are less than their fractal dimensions which may be either fractions or integers, e.g., the path of a Brownian particle, a tree, a cloud, etc.). Like black holes in the universe, strange attractors can inspire science fiction; chaos and fractals can do so as well.

Figure 13. Plots of [Y] against [X] showing (a) bistability, (b) oscillations caused by the addition of an autocatalytic cycle.



Condition (C) above signifies bistability (or multistability, as the case may be). To understand bistability briefly, consider *Figure* 13a, depicting a plot of [Y] *versus* [X]. The two curves A and B denote two steady states far from equilibrium involving hysteresis (retention of memory). When [X] has increased to a certain value, corresponding to a decrease in [Y], the system may jump from curve A to curve B. Likewise, when [Y] has increased to a certain value, corresponding to a decrease in [X], the system may jump from curve B to curve A. However, this by itself cannot cause chemical oscillations unless an autocatalytic cycle is added to it (*Figure* 13b). If the two steady states are themselves oscillatory, then the phenomenon is called birhythmicity (a special case of bistability). The BR reaction involves bistability. *Figure* 3 indicates birhythmicity.

4.5 *Bifurcations and Period Doubling*

In a naive way, when the solution to a non-linear dynamical problem changes from there being only one possible solution to there being two solutions, the phenomenon is called bifurcation. A bifurcation takes place when a small change made in the value of a parameter (bifurcation parameter) brings about a sudden qualitative change in the system's long-term dynamical behaviour. Bifurcations can occur in both continuous (represented by ordinary and partial differential equations) and discrete (represented by what are known as logistic maps) dynamical systems. They can be of local and global types, each type having several subtypes of its own. There are numerous examples of bifurcations, e.g., in fluid flow, population dynamics (ecology), irregular heartbeats, chemical oscillations, certain symmetry-breaking phenomena, etc. It has been speculated that the emergence of life on earth out of the prebiotic 'soup' could have been a bifurcation. Below, we consider an example of local period-doubling bifurcations in a discrete, non-linear dynamical system, which eventually leads to chaos (Section 4.1).

Let the system be represented by a variable $0 \leq x \leq 1$, with values $x_0, x_1, x_2, \ldots$ .etc, at times $t_0, t_1, t_2, \ldots$, etc.; x may be the mole fraction of a species generated in a set of chemical reactions. Assuming x_0 as known, consider the cubic logistic map which allows us to predict the next value from the present one,

$$x_{n+1} = A\, x_n (1 - x_n)^2, \tag{13}$$

where $1 \leq \mathrm{A} \leq 27/4$ is a constant which can take different preassigned values. The non-zero, stationary-state solution $x_{s.s}$ for a given A is obtained by taking $x_{n+1} = x_n$, *viz.*

$$x_{s.s} = 1 - A^{-1/2} \tag{14}$$

ignoring the larger root. *Figure* 14 shows plots of x_n against n, for $A = 3$ (period 1), 4.5 (period 2), 5.1 (period 4), 5.25 (period 8), 5.29 (period 16) and 5.298 (period 32). The term 'period 2' means that the value of x is repeated at every second iteration. This

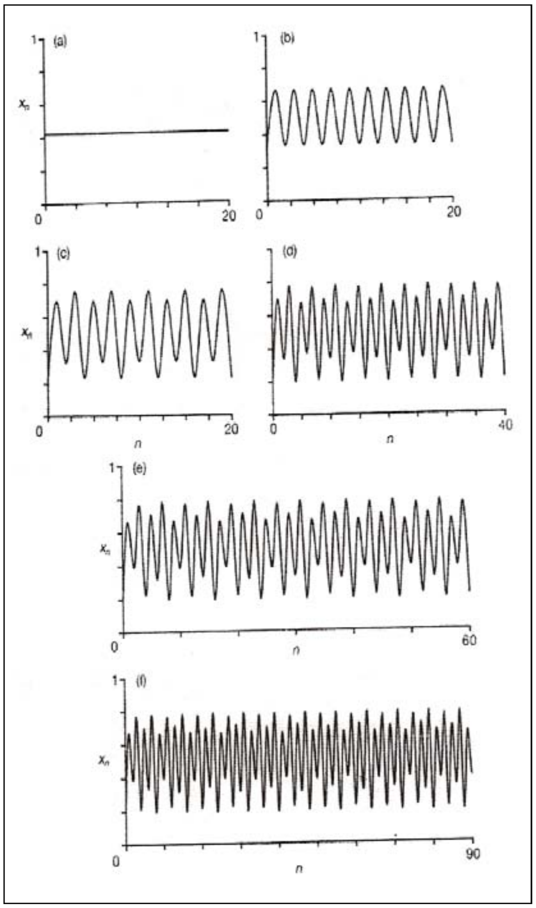


***Figure* 14. Plot of x_n against n, the iteration number, showing period doubling with variation in the bifurcation parameter A.**
(a) A = 3, period 1;
(b) A = 4.5, period 2;
(c) A = 5.1, period 4;
(d) A = 5.25, period 8;
(e) A = 5.29, period 16,
(f) A = 5.298, period 32.

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phenomenon is period-doubling bifurcation. *Figure* 15 shows the plot of x_n against the bifurcation parameter A. Note the values of

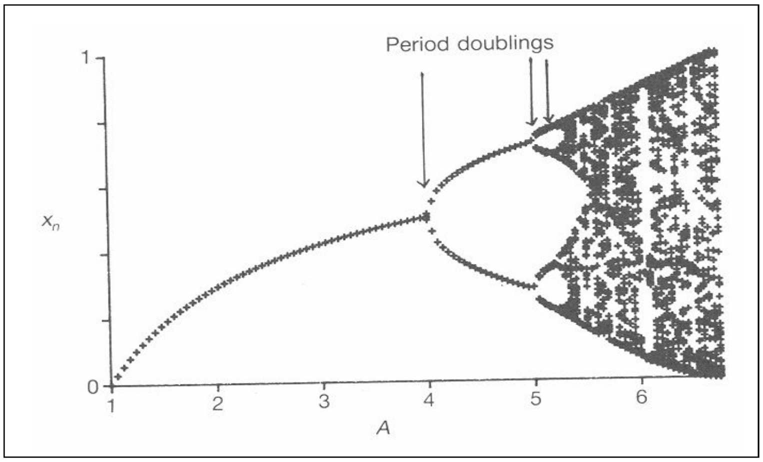

***Figure* 15. Plot of x_n against the bifurcation parameter A, showing cascading period-doubling bifurcations from left to right, leading eventually to chaos.**

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A where the cascading period-doubling bifurcations take place, eventually leading to chaos (Section 4.2) on the far right of the plot. Bifurcations can cause both stationary and transient Turing structures. It would be instructive for the students to do these simple calculations as well as plot *Figures* 14 and 15 themselves.

4.6 *Solitary Waves and Solitons*

"A soliton may be described as a self-reinforcing solitary wave (a wave packet or a pulse) that maintains its shape while it travels at constant speed. It is caused by a delicate balance between non-linear and dispersive effects in the medium. 'Dispersive effects' refer to a relationship between the frequency and speed of waves in the medium. Solitons arise as the solutions of a widespread class of non-linear dispersive partial differential equations. They have three important properties, [*viz*., they] (1) represent waves of permanent form, (2) are localized, so that they decay or approach a constant at infinity, (3) can interact strongly with other solitons, but they emerge from the collision unchanged apart from a phase shift" [11]. Property (3) is analogous to the collision and separation of two particles. For this reason, these wave forms have been named solitons (*Box* 3) and may be regarded as representing wave-particle duality in the classical, non-quantum mechanical world.

Box 3.

Solitons were discovered by John Scott Russell, an engineer, in 1834. He found them moving "in splendid isolation, steadfastly holding their shape", but faced only scathing skepticism from his contemporaries.

All solitons are solitary waves but all solitary waves are not solitons (Section 2.3). To qualify as a soliton, a solitary wave has to fulfill certain necessary and sufficient mathematical conditions which are, however, beyond the scope of the present article.

Some examples of solitons: Certain types of tidal bore, undersea internal waves, Morning Glory Cloud of the Gulf of Carpentaria (near northern Australia), the Great Red Spot on Jupiter's atmosphere, signal conduction within neurons, screw dislocations in a crystal lattice, acoustic waves in a crystal lattice, magnetic monopole, cosmic strings, solitons in optical fibres, possible solitons/ solitary waves in the curious striations (observed in satellite images) in the Andaman Sea near Thailand, Bose–Einstein condensate, wave-modes of plasmas, Davydov solitons in α-helix proteins, solitons in liquid crystals and high-T_c superconductors, solitons in electronic polymers such as polyanilines, spin solitons in organic charge-transfer salts, etc. Solitons constitute a broad, very active multidisciplinary area of research. For an inquisitive student, it would be worthwhile to investigate whether the blue wave fronts observed in Section 2.3 can indeed be solitons.

The most extensively studied equations yielding soliton solutions are the Korteweg-de Vries (KdV) equation, (cubic) non-linear Schrödinger (NLS) equation, sine–Gordon (SG) equation and the Kadomtsev–Petviashvili (KP) equation as well as their variants. Below, we describe these equations and their solutions very briefly, for the mathematically inclined student.

The most extensively studied equations yielding soliton solutions are the Korteweg-de Vries (KdV) equation, (cubic) non-linear Schrödinger (NLS) equation, sine–Gordon (SG) equation and the Kadomtsev–Petviashvili (KP) equation as well as their variants.

(i) *KdV Equation*: This is a third-order differential equation,

$$\partial\omega/\partial t + \partial^3\omega/\partial x^3 - 6\omega\,\partial\omega/\partial x = 0 \tag{15}$$

Its one-soliton solution is

$$\omega(x,t) = -a/\{2\cosh^2[\tfrac{1}{2}a^{1/2}(x-at-b)]\} \tag{16}$$

where a and b are arbitrary constants.

(ii) *NLS Equation*: This is a second-order differential equation,

$$i\,\partial\omega/\partial t + \partial^2\omega/\partial x^2 + k|\omega|^2\omega = 0;\ i^2 = -1 \tag{17}$$

where k is a real constant. For $k > 0$, its one-soliton solution is

$$\omega(x,t) = \pm a\,(2/k)^{1/2}\exp[ibx + i\,(a^2 - b^2)\,t + i\,c_1]/\{\cosh(ax - 2abt + c_2)\} \tag{18}$$

where a, b, c_1, c_2 are arbitrary real constants. The well-known Gross–Pitaevskii equation for Bose–Einstein condensate is a kind of (cubic) NLS equation. The NLS equation has been extended to two and three spatial dimensions. A generalized NLS equation in three spatial dimensions has been employed to obtain the static and dynamic electron densities of atoms and molecules.

(iii) *SG Equation*: In contrast to the KdV and NLS equations, the SG equation maintains 'space-time symmetry' in the sense that it is second-order in both x and t, *viz*.,

$$\partial^2\omega/\partial t^2 - a\,\partial^2\omega/\partial x^2 - b\sin(\lambda\omega) = 0 \tag{19}$$

Its one-soliton solution is

$$\omega(x, \mathrm{t}) = (4/\lambda)\tan^{-1}\{\exp[\pm b\lambda (kx + c\mathrm{t} + d)/(b\lambda)^{1/2} (c^2 - ak^2)^{1/2}]\}, \quad (20)$$

where $b\lambda(c^2 - ak^2) > 0$ and d is an arbitrary real constant.

(iv) *KP Equation*: While equations (15), (17) and (19) are all in one spatial dimension, the KP equation generalizes the KdV equation to two and three spatial dimensions. In two spatial dimensions, the KP equation may be written as a fourth-order differential equation,

$$(\partial/\partial x)(\partial\omega/\partial \mathrm{t} + 6\omega\,\partial\omega/\partial x + a^2\partial^3\omega/\partial x^3) + b\partial^2\omega/\partial y^2 = 0, \quad (21)$$

where $b = \pm 1$. Instead of writing the complicated soliton solution to equation (21), we depict in *Figure* 16 the collision and subsequent separation, with unchanged forms, of two two-dimensional solitons propagating along the x-axis with unequal amplitudes. Like colliding particles after separation, the two solitons go their own ways.

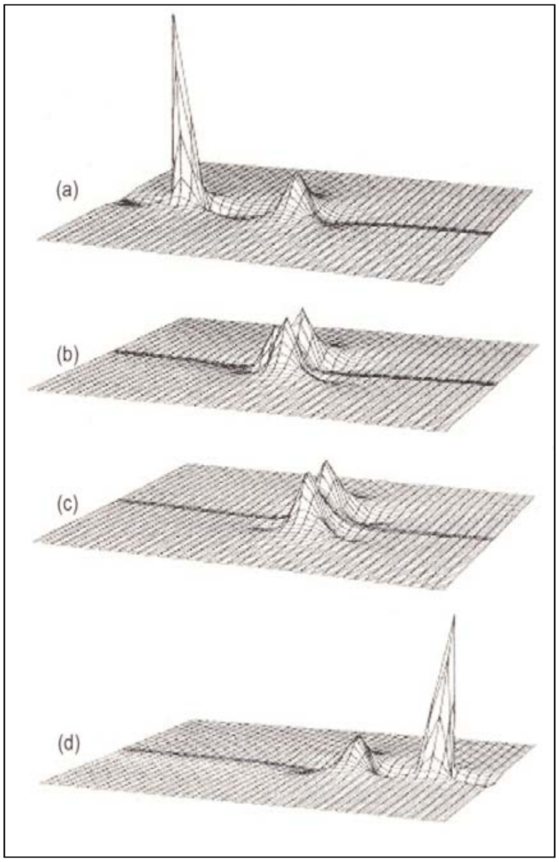

Figure 16. Two two-dimensional solitons of different amplitudes propagating along the x-direction. From (a) to (d), they approach each other, collide and then separate, going their own ways.

Reproduced with permission from V Yu Belashov and S V Vladimirov, *Solitary Waves in Dispersive Complex Media*, Springer, Berlin, 2005.

Students should try to depict the solitons and their collisions given by equations (16), (18) and (20) using computer graphics. Successive profiles of individual solitons along the x-axis can be drawn at different times, in the same diagram, in a way similar to *Figure* 16.

4.7 *A Suggested Mechanism for the BR Reaction*

As mentioned in Section 4, a complete reproduction of all the space-time features of the BR reaction is not yet available. However, the essential qualitative and semi-quantitative features of this oscillatory reaction have been reproduced through mechanistic studies by mainly I R Epstein *et al* [8,9] and R M

Noyes *et al* 10]. The important reaction steps in the mechanisms suggested by both the research groups are the same. The mechanisms are more complicated than the Lotka–Volterra, Brusselator and Oregonator models. The reaction steps involve radicals, the generation and consumption of iodide/iodine as well as autocatalysis through Mn^{+2}. Below, we describe the ten-step mechanism proposed by Epstein *et al*, with the corresponding rate laws and rate constants under the usual experimental conditions.

$$IO_3^- + I^- + 2H^+ \rightarrow HOI + HIO_2; \; -d[IO_3^-]/dt = k_1 [IO_3^-][I^-][H^+]^2; \; k_1 = 1.43 \times 10^3 \, M^{-3} s^{-1} \quad (22)$$

$$HIO_2 + I^- + H^+ \rightarrow 2\,HOI; \; -d[HIO_2]/dt = k_2 [HIO_2][I^-][H^+]; \; k_2 = 2 \times 10^{10} \, M^{-2} s^{-1} \quad (23)$$

$$HOI + I^- + H^+ \rightleftharpoons I_2 + H_2O; \; -d[HOI]/dt = k_3 [HOI][I^-][H^+] - k_{-3}[I_2] \quad (24)$$
$$k_3 = 3.1 \times 10^{12} \, M^{-2} s^{-1}; \; k_{-3} = 2.2 \, s^{-1}$$

$$IO_3^- + HIO_2 + H^+ \rightleftharpoons 2\,IO_2 + H_2O; \; -d[IO_3^-]/dt = k_4 [IO_3^-][HIO_2][H^+] - k_{-4}[IO_2]^2 \quad (25)$$
$$k_4 = 7.3 \times 10^3 \, M^{-2} s^{-1}; \; k_{-4} = 1.7 \times 10^7 \, M^{-1} s^{-1}$$

$$2\,HIO_2 \rightarrow HOI + IO_3^- + H^+; \; -\tfrac{1}{2} d[HIO_2]/dt = k_5 [HIO_2]^2; \; k_5 = 6 \times 10^5 \, M^{-1} s^{-1} \quad (26)$$

Autocatalysis :

$$IO_2 + Mn^{2+} + H_2O \rightarrow HIO_2 + MnOH^{2+}; \; -d[IO_2]/dt = k_6 [IO_2][Mn^{2+}]; \; k_6 = 1.0 \times 10^4 \, M^{-1} s^{-1} \quad (27)$$

$$MnOH^{2+} + H_2O_2 \rightarrow HO_2 + Mn^{2+} + H_2O; \; -d[MnOH^{2+}]/dt = k_7 [MnOH^{2+}][H_2O_2]; \; k_7 = 3.2 \times 10^4 \, M^{-1} s^{-1} \quad (28)$$

$$2\,HO_2 \rightarrow H_2O_2 + O_2; \; -\tfrac{1}{2} d[HO_2]/dt = k_8 [HO_2]^2; \; k_8 = 7.5 \times 10^5 \, M^{-1} s^{-1} \quad (29)$$
$$MA + I_2 \rightarrow IMA + I^- + H^+$$

This reaction itself occurs in two steps (MA and IMA are malonic acid and iodomalonic acid respectively), *viz.*,

Suggested Reading

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[10] R M Noyes and S D Furrow, *J. Am. Chem. Soc.*, Vol.104, p.45, 1982.

[11] www.wikipedia.org

$$\mathrm{MA} \rightleftharpoons \mathrm{Enol}$$

$$\mathrm{Enol} + I_2 \rightarrow \mathrm{IMA} + I^- + H^+;\ -d[I_2]/dt = k_9\,[\mathrm{MA}]\,[I_2]/\{1 + C_9\,[I_2]\}; \quad k_9 = 40\ M^{-1}\,s^{-1};\ C_9 = 10^4\,M^{-1} \tag{30}$$

$$\mathrm{HOI} + H_2O_2 \rightarrow I^- + H^+ + O_2 + H_2O;\ -d[\mathrm{HOI}]/dt = k_{10}\,[\mathrm{HOI}]\,[H_2O_2];\ k_{10} = 37\ M^{-1}\,s^{-1} \tag{31}$$

Reactions (22), (23) and (24) are iodide-consuming reactions while reactions (30) and (31) are the main iodide-generating reactions. In reactions (22), (23), (26) and (27), the reverse reactions are ignored due to low concentrations of the species on the right-hand side under the usual experimental conditions.

Based on the above rate laws and rate constants, bistability and temporal oscillations can be generated by employing numerical methods and computer graphics.

5. Conclusion

The present integrated experiment demonstrates that behind apparent simplicity can lurk a great deal of sophistication. It also illustrates the subtle interconnections between structure and dynamics that one observes in nature. The concept of structure in its manifold connotations is of crucial importance in all sciences and mathematics. Furthermore, it is well-known that in chemistry, physics and biology intricate relationships exist between structure and function (properties of various kinds) so that one can result from the other. However, in nature, structure is not static; rather, structure is actually a consequence of dynamics and vice versa. This is beautifully demonstrated by the present experiment.

We hope that aspects of this experiment would be utilized in chemical, physical, biological, mineralogical and computer simulation teaching laboratories.

Acknowledgement

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