



# Complex chemical reactions — A review

S. K. Scott\*, B. R. Johnson, A. F. Taylor, M. R. Tinsley

*School of Chemistry, University of Leeds, Leeds LS2 9JT, UK*

Received 29 March 1999; accepted 1 April 1999

## Abstract

Complex responses have been observed in a wide range of chemical and engineering systems: In well-stirred and unstirred solution-phase, in gels, in heterogeneous catalysis and dissolution reactions, in gas- and solid-phase combustion, widely in biological systems, accompanying phase transitions, in atmospheric kinetics and even in interstellar dust clouds. Complex behaviour does not, however, imply a necessarily complex underlying chemical mechanism. The appropriate feedback mechanisms, built on chain-branching, autocatalysis or self-heating, arise quite commonly in Nature. In many instances, it is appropriate first to attempt to find reduced mechanisms giving a semi-quantitative fit to observed responses. An example of such an approach applied to a model for complex oscillations of species concentrations in the mesosphere is presented, and the reduced model used to investigate the effects of longitudinal mixing in this system. Once a general understanding of a particular reaction system has been obtained, more detailed questions can be addressed. This is exemplified by a study of the development of three-dimensional scroll waves in the Belousov–Zhabotinsky reaction. Such detailed information for a specific reaction also informs the general understanding of the class of ‘excitable media’. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Atmospheric chemistry; Environment; Kinetics; Model reduction; Nonlinear dynamics; Chemical waves

## 1. Introduction

It is important to distinguish between *complex behaviour* and *complex reactions*. Perhaps the single most significant message from the last few decades of study of oscillating and other types of reaction is that, as well as existing as genuine phenomena, complex responses do not require complex or elaborate chemistry. Oscillations, bistability and even chaos can have relatively simple kinetic origins, arising through chemical or thermal feedback (Scott, 1994). In fact, cutting through the unnecessary detail to expose the underlying clockwork at its simplest is the most significant step in going from mere cataloguing to understanding. One only has to think of the vital roles played by simplified models — the Brusselator (Prigogine & Lefever, 1968) and Oregonator (Field & Noyes, 1974) in solution-phase systems, the FONI and its extensions in reactor engineering (Uppal, Ray & Poore, 1976; Farr & Aris, 1986), the Sel’kov (1968) and Schnackenberg (1979) models in biology — to appreciate the advantage of generic rather than system-specific

approaches. On the other hand, the theoretical and experimental ‘toolkits’ developed over this time and now available to the scientist and engineer, allow very detailed issues to be addressed in specific cases. In this paper, two example systems will be discussed: A model for atmospheric chemistry, for which the application of nonlinear methods is a relatively novel development, and the other involving an ‘old friend’, the Belousov–Zhabotinsky (BZ) reaction, investigating the onset of the so-called *scroll waves*.

## 2. Complex oscillatory responses in the mesosphere

The first suggestions that multiple steady states might exist in atmospheric chemical mechanisms were made by Fox, Wofsy, McFlroy and Prather (1982) and by White and Dietz (1984). The latter authors showed that a relatively simple photochemical model appropriate to the troposphere supported bistability, i.e. that there could be co-existing, different steady-state solutions for radical and other intermediate species concentrations for the same atmospheric conditions. These states may be linked to low and high NO<sub>x</sub> concentrations, respectively (Stewart, 1993,1995; Krol, 1995). Poppe and Lustfeld

\* Corresponding author.

E-mail address: s.k.scott@chem.leeds.ac.uk (S. K. Scott)

(1996) have also recently made the connection from bistability to oscillations in this model. Modelling of reactions in the stratospheric region has suggested a possible link between these dynamic chemical instabilities and the Antarctic ozone instability (Feigin & Kononov, 1996). Studies appropriate to the mesosphere have shown the existence of multiple steady states (Yang & Brasseur, 1994) and of oscillations, with a period-doubling bifurcation leading to chaos (Sonnemann & Fichtelmann, 1997; Fichtelmann & Sonnenmann, 1989,1992). The fluctuation in heating associated with the period-2 oscillation observed in this sequence has been proposed as a possible cause of the ‘quasi-two-day wind’ in the upper mesosphere (Mueller, 1978). Bistability and oscillations have also been reported in models of atmospheres on other planets and in interstellar environments (Le Bourlot, Pineau des Forets & Roueff, 1995).

The mesosphere is the name given to the region of the atmosphere with altitude between approximately 50 and 85 km and lies between the stratosphere and thermosphere. The region is thermally distinct from those above and below as the temperature decreases with altitude. The turning points in the temperature profile below and above that mark the boundaries of the mesosphere are known as the stratopause and mesopause, respectively. Within this region of the atmosphere, vertical stratification due to molecular diffusion is not significant. The mesosphere has a dynamic relationship with the other regions of the atmosphere and, in particular, the absorption of solar radiation by ozone in this region provides a significant route for the uptake of energy in the atmosphere as a whole (Wayne, 1991).

Elsewhere, we have shown (Johnson, Scott & Tinsley, 1998) that the chemical mechanism appropriate to the upper region of the mesosphere proposed by Sonnemann and Fichtelmann (1997; 1989,1992) can be reduced to the 12 reaction-step scheme given in Table 1. Two species, H and O, are treated as full dynamic variables, with the quasi-steady-state approximation applied to OH, HO<sub>2</sub> and O<sub>3</sub>. The concentrations of O<sub>2</sub> and of the third body species *M* are taken to be imposed and constant, with [O<sub>2</sub>] = 6.5 × 10<sup>13</sup> molecule cm<sup>-3</sup> and [M] = 3.4 × 10<sup>14</sup> molecule cm<sup>-3</sup>. The concentration of water vapour is taken to be the main bifurcation parameter in this problem, with 1 < [H<sub>2</sub>O]/ppm < 5 typically the range of interest.

The rate coefficients *k<sub>i</sub>* are expressed in the appropriate (molecule cm<sup>-3</sup>)<sup>1-*n*</sup> s<sup>-1</sup> units, where *n* is the molecularity of the *i*th step. The numbering is chosen for consistency with reference to Johnson, Scott and Tinsley (1998).

Steps (16)–(18) provide a ‘radical input’ and depend on the photon intensity  $\phi$ , i.e. their rates vary between ‘day’ and ‘night’. For simplicity, the light intensity  $\phi$  can be modelled with a ‘square wave’:

$$\phi = \begin{cases} 0 & \text{for } t < 0.25 \text{ and } t > 0.75 \\ 1 & \text{for } 0.25 < t < 0.75, \end{cases}$$

Table 1  
Reduced mechanism for mesosphere

(2)	O <sub>3</sub> + H	→ O <sub>2</sub> + OH	$k_2 = 1.78 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(3)	O + OH	→ O <sub>2</sub> + H	$k_3 = 4.40 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(5)	O + HO <sub>2</sub>	→ O <sub>2</sub> + OH	$k_5 = 3.50 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(6)	H + HO <sub>2</sub>	→ O <sub>2</sub> + H <sub>2</sub>	$k_6 = 5.40 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
(9)	OH + HO <sub>2</sub>	→ O <sub>2</sub> + H <sub>2</sub> O	$k_9 = 4.00 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$
(10)	HO <sub>2</sub> + HO <sub>2</sub>	→ O <sub>2</sub> + H <sub>2</sub> O <sub>2</sub>	$k_{10} = 2.50 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$
(11)	O + O <sub>2</sub> + M	→ O <sub>3</sub> + M	$k_{11} = 1.05 \times 10^{-34} \text{ cm}^6 \text{ s}^{-1}$
(14)	H + O <sub>2</sub> + M	→ HO <sub>2</sub> + M	$k_{14} = 8.08 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$
(15)	OH + H + M	→ H <sub>2</sub> O + M	$k_{15} = 3.31 \times 10^{-27} \text{ cm}^6 \text{ s}^{-1}$
(16)	O <sub>2</sub> + <i>hν</i>	→ 2 O	$k_{16} = (1.26 \times 10^{-8} \text{ s}^{-1})\phi$
(17)	H <sub>2</sub> O + <i>hν</i>	→ H + OH	$k_{17} = (3.4 \times 10^{-6} \text{ s}^{-1})\phi$
(18)	O <sub>3</sub> + <i>hν</i>	→ O <sub>2</sub> + O	$k_{18} = (7.10 \times 10^{-8} \text{ s}^{-1})\phi$

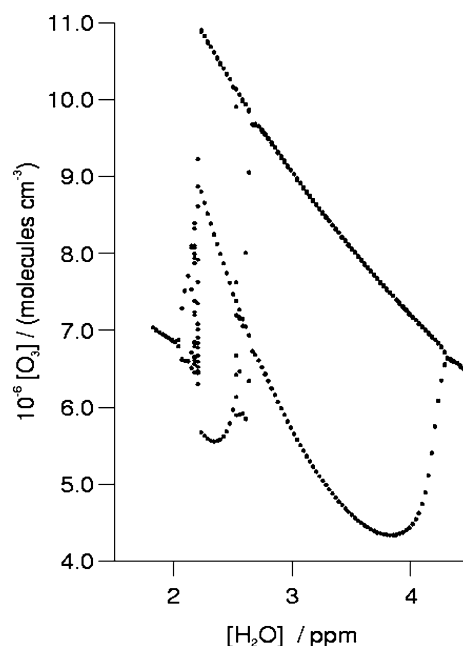


Fig. 1. Bifurcation diagram for reduced mesospheric chemistry model.

where  $t = \text{mod}(\text{time}/\text{day})$ , although the qualitative behaviour is relatively robust to other functional forms for this quantity. This time-dependence of the intensity imposes a periodic forcing on the system, with a forcing period of 1 day.

The bifurcation diagram, showing the variation of the (post-transient) concentration of [O<sub>3</sub>] measured at sunset with the imposed water vapour concentration, for the reduced model is shown in Fig. 1. At the highest and lowest [H<sub>2</sub>O], the system exhibits a simple period-1 oscillation, with a period of 1 day, corresponding to the ‘forcing period’. In between, more complex responses are observed, including relatively large ranges of period-2 and -3 oscillations, each separated by smaller regions of higher periodicity or of chaos.

The calculations in earlier papers are essentially ‘zero-dimensional’ (well-stirred) or ‘one-dimensional’ (vertical

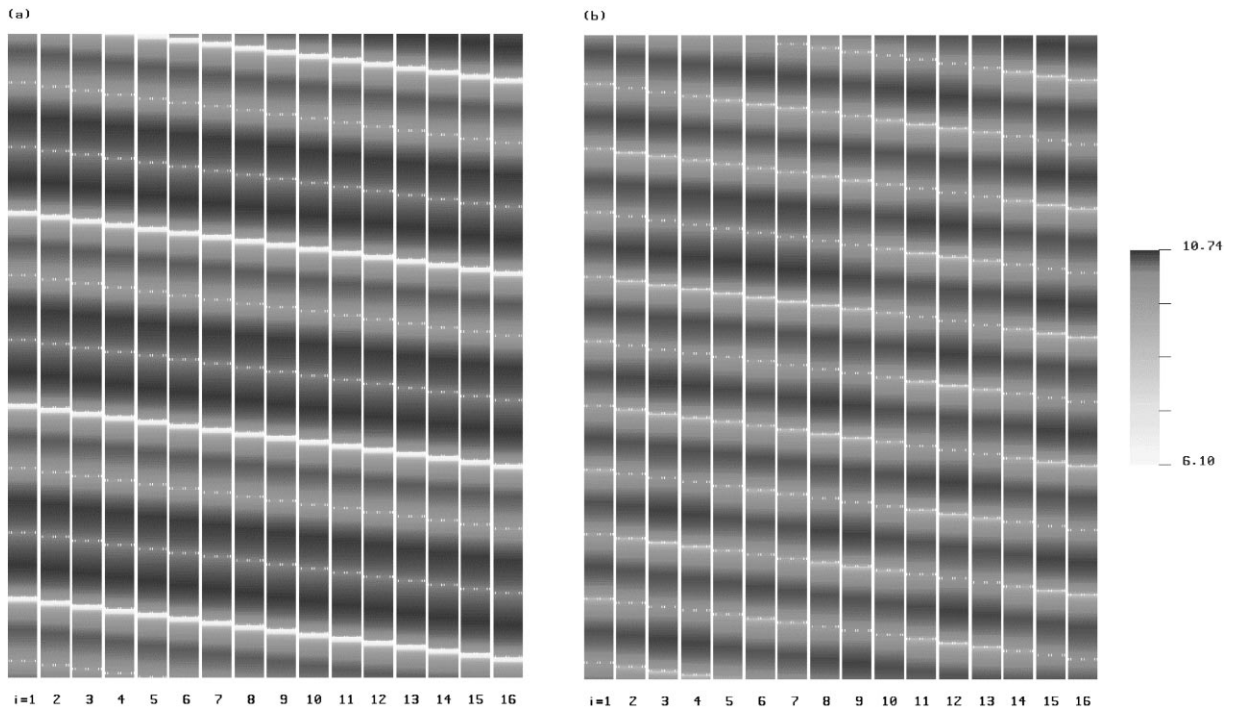


Fig. 2. Space-time plot showing the evolution of  $\log_{10}[\text{O}]$  over a 10 period for 16 coupled cells: (a) effectively uncoupled, with  $g = 10^{-15}$ , (b) coupled, with  $g = 10^{-5.3}$ ; grey-scale is indicated, with lightest regions corresponding to lowest  $[\text{O}]$ .

stratification) box models. As a first step towards investigating the effect of spatial variation in the longitudinal direction, we have computed the evolution of the reduced model in a series of coupled domains, with a phase lag in the sunlight photon intensity term. For a domain consisting of  $n$  such cells, the phase lag in the sunrise time between neighbouring cells will be  $(24/n)$  h. We impose periodic boundary conditions between the first and  $n$ th cell, with simple linear coupling between other adjacent cells:

$$dx_{j,i}/dt = f_j(\mathbf{x})_i + g_l(x_{j,i-1} - x_{j,i}) + g_r(x_{j,i+1} - x_{j,i}),$$

where  $x_{j,i}$  represents the concentration of species  $j$  in cell  $i$ , the function  $f_j$  indicates the kinetic terms for the rates of formation and removal of species  $j$  and is evaluated in terms of the concentrations of all species  $\mathbf{x}$  in cell  $i$ . The final two terms indicate the coupling from the cells to the left ( $i - 1$ ) and right ( $i + 1$ ), respectively, and  $g_l$  and  $g_r$  are the coupling coefficients for these two directions. In the simplest case, we take  $g_l = g_r = g$ , but the above form allows different strengths of coupling in each direction, perhaps to allow for prevalent wind direction. An example of the behaviour of such a system with  $[\text{H}_2\text{O}] = 2.35$  ppm is shown in Fig. 2. For sufficiently low  $g$ , Fig. 2(a), the cells are effectively uncoupled and behave as isolated systems with a 1.5 h phase lag. At higher  $g$ , Fig. 2(b), the system develops a different, collective behaviour. The specific response depends on the actual value of the coupling coefficient. Typically, the

‘uncoupled’ state gives way to either quasi-periodic or chaotic behaviour as  $g$  increases, but at higher  $g$  the behaviour simplifies and approaches an entrained state in which each cell tends to the same state and the concentrations become independent of position and time.

### 3. Scroll waves and the influence of $\text{O}_2$ in the ferroin-catalysed BZ reaction

The BZ reaction is one of the most widely-studied chemical systems (Tyson, 1994; Zhabotinsky, 1995). A well-stirred solution may exhibit oscillations in various intermediate species concentrations or may be *excitable*. Excitable systems are characterised by a stable steady state. Small perturbations away from this state decay directly but if the amplitude of a perturbation exceeds some critical threshold value then the system responds with a single, large amplitude response or ‘excitation event’ before returning to the vicinity of the steady state. For a period following the excitation, the system is ‘refractory’ and hence insensitive to further perturbations. Typically, the refractory period is long compared to the excitation event. Eventually, the system recovers its excitability as it approaches the steady state and can respond to further perturbation. Excitable systems support reaction-diffusion wave structures such as target patterns — nested concentric expanding circular waves in two spatial dimensions. Excitable systems are prevalent and

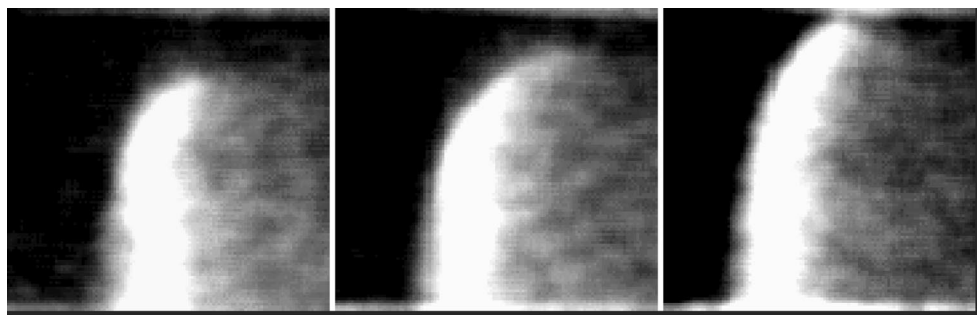


Fig. 3. Side view of wave propagation in thin cuvette initially under air. Wave is propagating from right to left.

important in biology (Winfree, Gray & Jaliffe, 1996; Glass, 1996) and also occur in combustion (Scott, Wang & Showalter, 1997) and other systems. It is well known that if a propagating front in such a system is broken, the two ‘ends’ can act as sources for a pair of spiral waves (Zaikin & Zhabotinsky, 1970; Winfree, 1972). The spiral is a characteristic spatiotemporal structure for excitable systems in 2D. In three dimensions, the equivalent structure (Winfree, 1973) is the *scroll* — which, in its simplest form, can be envisaged as a stack of spirals. Substantial progress in understanding the dynamical evolution of spirals and scrolls has been achieved through theory (Keener & Tyson, 1992), but experimental examples of scrolls are fewer. Jahnke, Henze and Winfree (1988) obtained scrolls in a gel matrix by allowing a circular wave to develop in a thin layer and then adding a second layer of excitable medium on top after the first wave had fully developed. Amemiya, Kadar, Kettunen and Showalter, 1996 obtained scrolls from a circular wave in the light-sensitive  $\text{Ru}(\text{bipy})_3^{2+}$  catalysed system by inhibiting a narrow layer with appropriate illumination until the wave was fully-developed and then allowing a segment to propagate into a masked region.

The influence of  $\text{O}_2$  in the atmosphere above the solution or gel in which the BZ reaction is occurring has been noted previously (Zhabotinsky, Gyorgyi, Dolnik & Epstein, 1994; Bugrim, Zhabotinsky & Epstein, 1995; Johnson, Taylor & Scott, 1997; Taylor, Johnson & Scott, 1998). In a thin film of solution,  $\text{O}_2$  in air inhibits the propagation in the topmost layer, to a depth of approximately 0.4 mm (Taylor et al., 1998). We can exploit this inhibition to produce scroll waves. Experiments were conducted in a long, narrow rectangular cuvette of dimension 28 mm  $\times$  5 mm in which a thin layer of BZ reagent is maintained. The cuvette is loosely covered with a glass plate to minimise convection. An oxidation wave is initiated using an Ag wire at one end and allowed to develop and propagate along the domain under an atmosphere of air or  $\text{O}_2$  so an inhibited (sub-excitable) layer is established at the top of the solution. Once the wave has become established, the air or  $\text{O}_2$  is replaced by  $\text{N}_2$ . (This procedure is relatively demanding in terms of experi-

mental technique as disturbance of the liquid layer has to be avoided.) The removal of oxygen allows the previously inhibited, topmost layer to become excitable. In Fig. 3, a sequence is shown for an initial air/solution interface. The depth of the sub-excitable layer (ca. 0.4 mm) is sufficiently thin that, following the replacement of the air with  $\text{N}_2$ , the system eventually develops so as simply to produce a wave propagating in the original direction but now through the whole solution depth. For a system under  $\text{O}_2$ , Fig. 4, the inhibited layer is deeper and following the switch to  $\text{N}_2$  above the solution, the propagation of the wave into this newly excitable region occurs more slowly (as the dissolved  $\text{O}_2$  concentration decreases more slowly). The segment of the wave in this region has significant curvature, and the layer is sufficiently deep compared with the incipient curvature of the front for this wave-tip to ‘turn over’ and propagate in the opposite direction to the original wave, entering a region in which the system has recovered from its refractory period. The curved nature of the tip persists, as it propagates into the lower region of the solution, allowing it to turn over again. This process repeats: On each turn, part of the wave breaks as it reaches the upper or lower surface of the solution, but the side-on view in the figure shows the spiral projection of a scroll wave in the cuvette.

#### 4. Modelling

The effect of  $\text{O}_2$  on the propagation of BZ waves and the existence of an inhibited layer can be rationalised with a relatively simple modification of the accepted model for this reaction. The ferroin-catalysed system is well fit by a model first proposed by Rovinsky and Zhabotinsky (1984) and subsequently modified by Zhabotinsky, Buchholtz, Kiyatin and Epstein (1993), as listed in Table 2.

The scheme has been augmented here with an extra step (10) in which the malonyl radical MA is able to react with dissolved  $\text{O}_2$  to produce more radicals. It is understood that this involves some chain-branching cycle, with a net branching factor given by  $\phi - 1$ . The rate

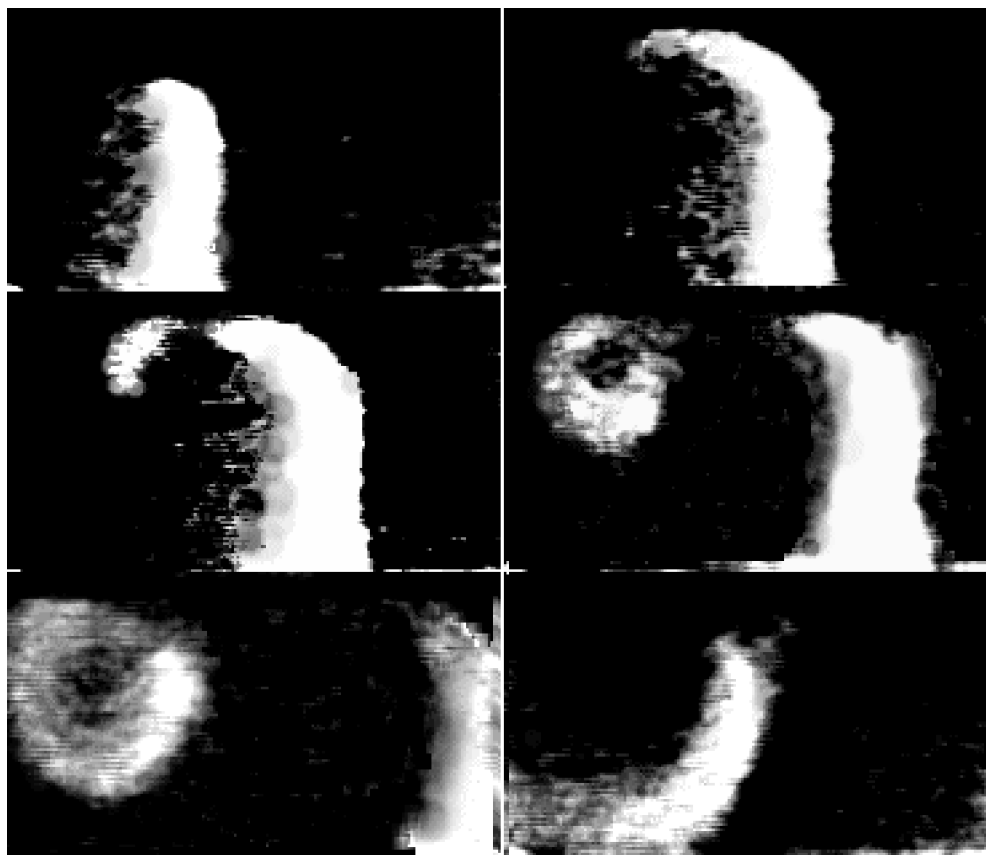


Fig. 4. As Fig. 3. but initially under  $O_2$  so inhibited layer is deeper. Initial wave is propagating from left to right in this sequence.

Table 2  
The Rovinsky–Zhabotinsky model

(3)	$BrO_3^- + 2H^+ + Br^- \rightarrow HBrO_2 + HOBr$
(2)	$HBrO_2 + Br^- + H^+ \rightarrow 2HOBr$
(4)	$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$
(5)	$BrO_3^- + HBrO_2 + H^+ \rightleftharpoons 2BrO_2$
(6)	$BrO_2 + M_{red} + H^+ \rightarrow HBrO_2 + M_{ox}$
(7)	$M_{ox} + Org \rightleftharpoons M_{red} + MA^{\cdot} + H^+$
(8)	$MA^{\cdot} \rightarrow gBr^-$
(10)	$MA^{\cdot} + O_2 \rightarrow \phi MA^{\cdot}$

coefficient  $k_{10}$  is expected to be proportional to  $[O_2]_{aq}$ . For simplicity at this stage, we will ignore the reversibility of steps (5) and (7) and assume that a dynamic steady-state approximation can be applied to the concentration of  $Br^-$  and the malonyl radical. Invoking the scaling and dimensionless groups first suggested by Tyson (1982), the equations governing the evolution of  $[HBrO_2]$  as  $x$  and  $[M_{ox}]$  as  $y$  can be written here in the form

$$\varepsilon \frac{dx}{d\tau} = x(1-x) - \frac{(x-q)}{(x+q)} f v_{ss}, \quad \frac{dz}{d\tau} = x - z,$$

where the ‘stoichiometric factor’  $f = 2g$  and  $v_{ss}$  is the steady-state dimensionless concentration of the malonyl

radical and is given by

$$v_{ss} = z \left/ \left[ 1 - (\phi - 1) \frac{k_{10}}{k_8} \right] \right.$$

Substituting this expression into  $dx/d\tau$ , we obtain an equation of the ‘classic Oregonator’ form

$$\varepsilon \frac{dx}{d\tau} = x(1-x) - \frac{(x-q)}{(x+q)} f_{eff} z, \quad \frac{dz}{d\tau} = x - z,$$

where the ‘effective stoichiometric factor’  $f_{eff}$  is given by

$$f_{eff} = f \left/ \left[ 1 - (\phi - 1) \frac{k_{10}}{k_8} \right] \right.$$

with  $\phi > 1$ ,  $f_{eff}$  increases as  $k_{10}$  increases, which is expected to occur with increasing  $[O_2]_{aq}$ . For a system with  $f = 2$ , the o.d.e. model above shows sustained oscillations in the absence of  $O_2$ , but oscillation is lost and an excitable system is obtained as  $k_{10}$  is increased such that  $f_{eff}$  reaches the value  $2.4 \approx 1 + 2^{1/2}$ . A further increase in  $k_{10}$  would see a decrease in the excitability of the stable steady state.

This analysis is clearly over-simplified, but indicates the appropriate trend. To proceed further, we must resort to numerical computation. The above scheme was taken

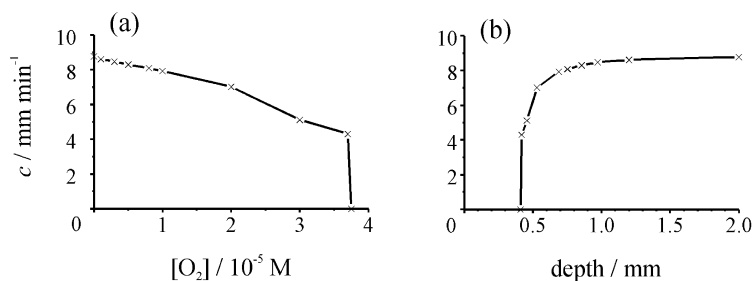


Fig. 5. Computed dependence of wave speed on (a)  $[\text{O}_2]$  and (b) depth.

in its fully reversible form, and the involvement of BrMA as an explicit variable is also included by assuming this species (i) is produced rapidly from HOBr, (ii) participates in step (8) and (iii) that there is also a removal step through which BrMA reacts without producing  $\text{Br}^-$ . These computations confirm that for a system with  $f = 3$ , wave propagation is possible from a suitable initial stimulus provided  $[\text{O}_2]_{\text{aq}}$  (i.e.  $k_{10}$ ) is below some critical value  $[\text{O}_2]_{\text{cr}}$  but that for  $[\text{O}_2]_{\text{aq}} > [\text{O}_2]_{\text{cr}}$  wave propagation is completely inhibited. The dependence of the wave speed on  $[\text{O}_2]$  computed in this manner is shown in Fig. 5(a) and is consistent with the experimental observations that the wave speed is the highest, and approximately constant, in the deepest part of the solution where  $[\text{O}_2]_{\text{aq}} \sim 0$ , but that it decreases as the inhibited layer is approached. Using the expression for the dissolved oxygen concentration as a function of depth derived in Bugrim et al. (1995), we can predict the variation of speed with depth, Fig. 5(b) and also estimate the depth of the inhibited layer. Based on previous estimates for the rate coefficients, where available, we predict a critical depth of 0.5 mm for the experimental conditions in our experiments, in good agreement with the observed value.

## 5. Conclusions

The methods available for analysing the behaviour of 'complex chemical reactions' are well developed. Complexity of response does not, in fact, imply particularly high degrees of complexity of the underlying chemical mechanism. Feedback through autocatalysis, chain-branching, radical-cycles or self-heating occurs widely in physical, biological and engineering systems. Much value can be obtained by seeking reduced mechanisms that capture the semi-quantitative spirit of the observed behaviour but which are sufficiently simple to allow an understanding of the important feedback processes to be identified. Once this has been done, then more detailed aspects can be analysed: numerical methods are generally important in these later stages. Two examples have been discussed — one from each of the above categories. Non-trivial dynamical responses have been known for

some time in realistic models of atmospheric and interstellar chemistry, but the application of nonlinear methods is only just developing. The example presented here is associated with the chemistry of the mesosphere. At present there are no meaningful experimental data to allow us to judge whether the predicted behaviour is realised or especially relevant to the actual response in that region, but theory always has a role in guiding experiments or observations as they become feasible. The 'linear exchange' model for molecular transport is clearly a first-order approximation, but such simplified approaches have repeatedly provided insight not possible from full-blow computations of reaction-diffusion-advection equations, especially in situations where the absence of specific experimental data precludes parameter estimation. The BZ reaction, on the other hand, has been one of the paradigms on which nonlinear methods have been developed and tested. An intricate understanding of this system has been achieved through the efforts of many workers. This understanding has been of more than particular interest as the BZ reaction represents a whole class of system — excitable or 'active' media — that occur throughout Nature. Many other important areas have benefited from nonlinear dynamical approaches. Others that offer the prospect of reward in this way include the recent reports of oscillatory kinetics accompanying phase transitions in complex fluids (Vollmer, Strey & Vollmer, 1997) and in catalytic reactions under industrial operating conditions (Hadden, Sakakini, Tabatabaei & Waugh, 1997; Werner, Herein, Schultz, Wild & Schlogl, 1997).

## Acknowledgements

AFT and MRT thanks the EPSRC and BRJ thanks the University of Leeds for financial support.

## References

- Amemiya, T., Kadar, S., Kettunen, P., & Showalter, K. (1996). *Physics Review Letters*, 77, 3244.

- Bugrim, A. E., Zhabotinsky, A. M., & Epstein, I. R. (1995). *Journal of Physical Chemistry*, 99, 15930.
- Farr, W. W., & Aris, R. (1986). *Chemical Engineering Science*, 41, 1385.
- Feigin, A. M., & Konovalov, I. B. (1996). *Journal of Geophysical Research*, 101, 26023.
- Fichtelmann, B., & Sonnenmann, G. (1989). *Zeitschrift fuer Meteorologie*, 39, 297.
- Fichtelmann, B., & Sonnenmann, G. (1992). *Annals in Geophysics*, 10, 719.
- Field, R. J., & Noyes, R. M. (1974). *Journal of Chemical Physics*, 60, 1877.
- Fox, J. L., Wofsy, S. C., McElroy, M. B., & Prather, M. J. (1982). *Journal of Geophysical Research*, 87, 11126.
- Glass, L. (1996). *Physics Today*, 49(8), 40.
- Hadden, R. A., Sakakini, B., Tabatabaei, J., & Waugh, K. C. (1997). *Catalysis Letters*, 44, 145.
- Jahnke, W., Henze, C., & Winfree, A. T. (1988). *Nature*, 336, 662.
- Johnson, B. R., Scott, S. K., & Tinsley, M. R. (1998). *Journal of the Chemical Society of Faraday Transactions*, 94, 2709.
- Johnson, B. R., Taylor, A. F., & Scott, S. K. (1997). *Journal of the Chemical Society of Faraday Transactions*, 93, 3733.
- Keener, J. P., & Tyson, J. J. (1992). *SIAM Review*, 34, 1.
- Krol, M. C. (1995). *Journal of Geophysical Research*, 100, 11699.
- Le Bourlot, J., Pineau des Forets, G., & Roueff, E. (1995). *Astronomy and Astrophysics*, 297, 251.
- Mueller, H. G. (1978). *Philosophical Transactions of the Royal Society A*, 271, 585.
- Poppe, D., & Lustfeld, H. (1996). *Journal of Geophysical Research*, 101, 14373.
- Prigogine, I., & Lefever, R. (1968). *Journal of Chemical Physics*, 48, 1695.
- Rovinsky, A. B., & Zhabotinsky, A. M. (1984). *Journal of Physical Chemistry*, 88, 6081.
- Schnackenberg, J. (1979). *Journal of Theoretical Biology*, 81, 389.
- Scott, S. K. (1994). *Oscillations, waves and chaos in chemical kinetics*. Oxford: Oxford University Press.
- Scott, S. K., Wang, J., & Showalter, K. (1997). *Journal of Chemical Society of Faraday Transactions*, 93, 1733.
- Sel'kov, E. E. (1968). *European Journal of Biochemistry*, 4, 79.
- Sonnemann, G., & Fichtelmann, B. (1997). *Journal of Geophysical Research*, 102, 1193.
- Stewart, R. W. (1993). *Journal of Geophysical Research*, 98, 20601.
- Stewart, R. W. (1995). *Journal of Geophysical Research*, 100, 8929.
- Taylor, A. F., Johnson, B. R., & Scott, S. K. (1998). *Journal of Chemical Society of Faraday Transactions*, 94, 1029.
- Tyson, J. J. (1982). *Journal of Physical Chemistry*, 86, 3006.
- Tyson, J. J. (1994). In S. A. Levin, *Lecture notes in biomathematics*, vol. 100. Berlin: Springer.
- Uppal, A., Ray, W. H., & Poore, A. B. (1976). *Chemical Engineering Science*, 31, 205.
- Vollmer, D., Strey, R., & Vollmer, J. (1997). *Journal of Chemical Physics*, 107, 3619.
- Wayne, R. P. (1991). *Chemistry of atmospheres*. Oxford: Oxford University Press.
- Werner, H., Herein, D., Schulz, G., Wild, U., & Schlogl, R. (1997). *Catalysis Letters*, 49, 109.
- Winfree, A. T. (1972). *Science*, 175, 634.
- Winfree, A. T. (1973). *Science*, 181, 937.
- Winfree, A. T., Gray, R. A., & Jaliffe, J. (1996). *International Journal of Bifurcation Chaos*, 6, 415.
- White, W. H., & Dietz, D. (1984). *Nature*, 309, 242.
- Yang, P., & Brasseur, G. P. (1994). *Journal of Geophysical Research*, 99, 20955.
- Zaikin, A. N., & Zhabotinsky, A. M. (1970). *Nature*, 225, 535.
- Zhabotinsky, A. M. (1995). In R. Kapral, & K. Showalter, *Chemical waves and patterns* (p. 401). Dordrecht: Kluwer.
- Zhabotinsky, A. M., Buchholtz, F., Kiyatin, A. B., & Epstein, I. R. (1993). *Journal of Physical Chemistry*, 97, 7578.
- Zhabotinsky, A. M., Gyorgyi, L., Dolnik, M., & Epstein, I. R. (1994). *Journal of Physical Chemistry*, 98, 7981.