Oscillations in Simple Models of Chemical Systems

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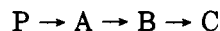
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1. Introduction

Oscillatory reactions, in which the concentrations of some intermediate species show regular periodic increases and decreases, have a surprisingly long history. Earliest reports go back as far as 1834,[1,2] and oscillations in apparently homogeneous systems have been known since 1921.[3] Today, a wide range of such reactions have been well established. The most famous of these is the Belousov–Zhabotinskii (B–Z) reaction,[4,5] which involves the reduction of bromate by bromide ions. In the presence of ferroin, the color of the reacting mixture will oscillate spontaneously for several hours between red and blue with a period of 1–2 min. We now know how to design a wide range of variations on this basic redox reaction theme.[6] A recent multiauthor book gives a detailed introduction to the behavior of such inorganic solution-phase oscillators.[7]

Other areas in which oscillatory reactions arise include biochemical and biological systems,[8] gas-phase reactions (including the oxidation of simple fuels[9]), and heterogeneous processes.[10] Indeed, so widespread is this phenomenon that it is long overdue a place in standard kinetics courses at undergraduate and graduate levels. In fact, many modern texts now find room for a dozen or so pages[11] which usually discuss the B–Z reaction. Perhaps the main reason for it not having become a fully established part of our courses is that there is still a need for a very simple example of a "kinetic mechanism" through which it can be taught. The need for such modeling also holds in the research field. By paring away all unnecessary complications, we will be able most clearly to see the underlying chemistry in greatest detail. The aim of this article is, therefore, not to attempt the explanation of any particular chemical system but rather to provide the simplest of all models, based on a somewhat hypothetical but clearly recognizable chemical set of reactions, which is capable of reproducing many of the features exhibited by such systems. We shall look at two typical experimental setups: (i) reaction in a beaker, closed to the transport of matter (in particular, closed to the inflow of fresh reactants; we are less concerned about the possible escape of any gaseous products), and (ii) reaction in the chemical engineers' continuously fed, well-stirred tank reactor (CSTR).

All we require is the conversion of a reactant or precursor P to a final, stable product C via two intermediate species A and B. Thus, the reaction chain may be represented as

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$$P \rightarrow A \rightarrow B \rightarrow C$$

The analysis of consecutive first-order reactions of this form is covered in elementary kinetics courses. This tells us that even then the concentrations of A and B will one after the other show an initial increase to a maximum value followed by a decrease. This can be taken as a first but frustrated indication of oscillatory behavior.

For the present purpose the middle step in this process will be taken to occur through two parallel routes. One will be a direct, first-order reaction converting A to B. The other will involve chemical autocatalysis (a commonly observed feature of oscillatory reactions). For the latter we suppose that an increase in the concentration of the product of the reaction (i.e., B) increases the rate of the reaction. Thus, we might find empirically a rate law for the catalyzed route of the form

$$\text{rate} = k_1 a b^2$$

Here a and b are the concentrations of species A and B.

Oscillatory behavior represents only one of the possible complex phenomena which can be displayed by "nonlinear" chemical systems. We may also find multiple states (i.e., differing extents of reaction for otherwise identical experimental conditions), ignitions, extinctions, "washout", hysteresis, slowing down, propagating fronts, spatial structures, and birhythmicity to name but a few. Simple adaptations of the prototype scheme mentioned above may be used to understand many of these additional patterns.[12]

2. Background: Kinetic Requirements

In this section the basic chemical requirements for an oscillatory reaction are discussed briefly, and some of the special terms used in the literature are explained. The reader will then be encouraged to believe that the mathematical procedures to be employed include little beyond algebraic manipulation.

For a chemical reaction to display oscillations there must be some mechanism for "feedback" within the

(1) Munck, P. S. *Ann. Phys. Chem.* 1834, 32.
(2) Joubert, M. J. *C. R. Hebd. Sceances Acad. Sci.* 1974, 78, 1853.
(3) Bray, W. C. *J. Am. Chem. Soc.* 1921, 43, 1262.
(4) Belousov, B. P. *Sb. Ref. Rad. Medit.* 1958, 145. See also ref 7, p 605.
(5) Zhabotinskii, A. M. *Biofizika* 1964, 9, 306; *Dokl. Akad. Nauk SSSR* 1964, 157, 392.
(6) De Kepper, P.; Epstein, I. R.; Kustin, K. *J. Am. Chem. Soc.* 1981, 103, 2133.
(7) Field, R. J.; Burger, M., Eds.; *Oscillations and Traveling Waves in Chemical Systems*; Wiley: New York, 1985.
(8) Murray, J. D. *Lectures on Nonlinear Differential Equation Models in Biology*; Oxford University Press: London, 1974.
(9) Griffiths, J. F. *Adv. Chem. Phys.* 1986, 64, 203.
(10) Sheintuch, M.; Schmitz, R. A. *Catal. Rev.—Sci. Eng.* 1977, 15, 107.
(11) Atkins, P. W. *Physical Chemistry*, 3rd ed.; Oxford University Press: London, 1986; pp 727–9.
(12) Gray, P.; Scott, S. K. *J. Phys. Chem.* 1985, 89, 22.

kinetics. This means that species formed somewhere along the chain must influence the rate of earlier reaction steps. Autocatalysis is a common realization of this requirement. Inhibition of a reaction by a product[13] can also play this role. In nonisothermal systems, the increase in temperature produced by heat released in an exothermic step can affect the reaction rate via the rate constant. Feedback implies "nonlinearity" in the reaction. This term relates to the reaction rate equations. Nonlinearities arise naturally in chemistry. Bimolecular reactions are quadratic, involving the product of two concentrations (or the square of one). Cubic terms may, in rare cases, arise from termolecular reactions. Along with even more complicated forms, they may also be found as empirical rate laws, hiding a coupled sequence of fast and slow steps. (The H_2 + Br_2 reaction is a well-known example involving fractional and inverse powers of H_2, Br_2, and HBr.)

Oscillatory behavior also requires at least two "independently variable" concentrations. In the simplest scheme

$$A \to B$$

the reacting mixture may contain two chemical species but has only one independent variable. This is the case because there is a stoichiometric relationship implied by the chemistry. As the initial concentrations of A and B (a_0 and b_0, respectively) are, in principle, knowable, the composition of the reaction is completely specified at any time by the concentration of only one species, e.g., b. The other is then given by $a = a_0 + b_0 - b$.
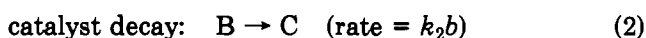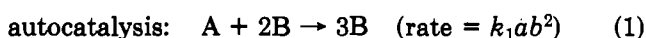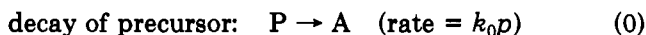
In the system

$$A \to B \to C$$
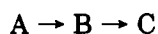
however, there are two independent concentrations. Now we have three chemical species but still only one stoichiometric, or mass-balance, equation, $a = a_0 + b_0 + c_0 - b - c$. Specifying the initial conditions and the value of b fixes the sum $a + c$. Only when two concentrations are specified is the third, and hence the whole system, uniquely determined.

In a well-stirred homogeneous system, kinetic rate equations involve derivatives of concentrations with respect to time, da/dt, etc. However we will see that a great deal of progress can be made in some circumstances by concentrating on the times when these rates of change become zero (remember the stationary-state hypothesis). Under such conditions we have to deal only with algebraic equations. For isothermal chemical reactions these usually mean polynomials, and in the present paper, we shall seek the solutions only of quadratic equations.

3. Model Kinetic Scheme for an Oscillatory Reaction

In order to represent the kinetic model in "chemical terms" and as an aid to visualization, we can write it as a series of four overall steps:

decay of precursor: P $\to$ A   (rate = $k_0 p$)   (0)

uncatalyzed step: A $\to$ B   (rate = $k_3 a$)   (3)

autocatalysis: A + 2B $\to$ 3B   (rate = $k_1 a b^2$)   (1)

catalyst decay: B $\to$ C   (rate = $k_2 b$)   (2)

(13) Higgins, J. *Ind. Eng. Chem.* 1967, *59*, 18.

(The rather unusual numbering system is used to retain consistency with earlier work.[14-17]) The autocatalytic nature of the reaction is embodied in step 1, which will almost certainly not be an elementary process.

The kinetic rate equations for such a mechanism would then be

$$dp/dt = -k_0 p \qquad (3.1)$$

$$da/dt = k_0 p - k_1 a b^2 - k_3 a \qquad (3.2)$$

$$db/dt = k_1 a b^2 + k_3 a - k_2 b \qquad (3.3)$$

A very helpful simplification which can be used when studying model kinetic schemes such as these is to neglect the consumption of the reactant (in this case P). We may justify this chemically when reaction 0 is a slow process so k_0 is small. If A and B are relatively reactive intermediate species, then their maximum concentrations may be many orders of magnitude smaller that the initial concentration of the precursors. Thus, the depletion of P, at least during the initial period of the reaction, may be relatively unimportant. We will see later that results derived with this approximation are very useful in estimating the behavior of the full system both qualitatively and quantitatively.

Neglecting the reactant consumption replaces the term $k_0 p$ in eq 3.2 by $k_0 p_0$. This initial concentration of P is a constant for any given experiment but is also something which might be varied (a "parameter" of the system) over a series of experiments. With this approximation the kinetic equations are

$$da/dt = k_0 p_0 - k_1 a b^2 - k_3 a \qquad (3.4)$$

$$db/dt = k_1 a b^2 + k_3 a - k_2 b \qquad (3.5)$$

The simplest way to deduce the behavior of a chemical system described by equations such as these is to look for the "stationary states". These are values of the concentrations a and b at which both rates of change vanish simultaneously, i.e., for which

$$k_0 p_0 - k_1 a b^2 - k_3 a = 0 \qquad (3.6)$$

$$k_1 a b^2 + k_3 a - k_2 b = 0 \qquad (3.7)$$

Adding these two together leaves a simple result

$$b_{ss} = (k_0/k_2) p_0 \qquad (3.8)$$

for the stationary-state concentration of the autocatalyst in terms of the (initial) concentration of the reactant P and two of the rate constants.

The corresponding stationary-state concentration of A is obtained by rearranging (3.6) and substituting for b_{ss}

$$a_{ss} = k_0 p_0 / [k_1 (k_0 p_0 / k_2)^2 + k_3] \qquad (3.9)$$

Equation 3.8 shows that the concentration of the autocatalyst B at the stationary state is proportional to the reactant concentration (Figure 1a): b_{ss} increases as p_0 is increased. We have assumed, in neglecting reactant consumption, that step 0 is much slower than the other steps. Because of this, the factor k_0/k_2 will

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(16) D'Anna, A.; Lignola, P. G.; Scott, S. K. *Proc. R. Soc. London, A* 1986, *403*, 341.
(17) Merkin, J. H.; Needham, D. J.; Scott, S. K. *Proc. R. Soc. London, A* 1985, *398*, 81, 101. Scott, S. K. *J. Chem. Soc., Faraday Trans. 2* 1985, *81*, 789.
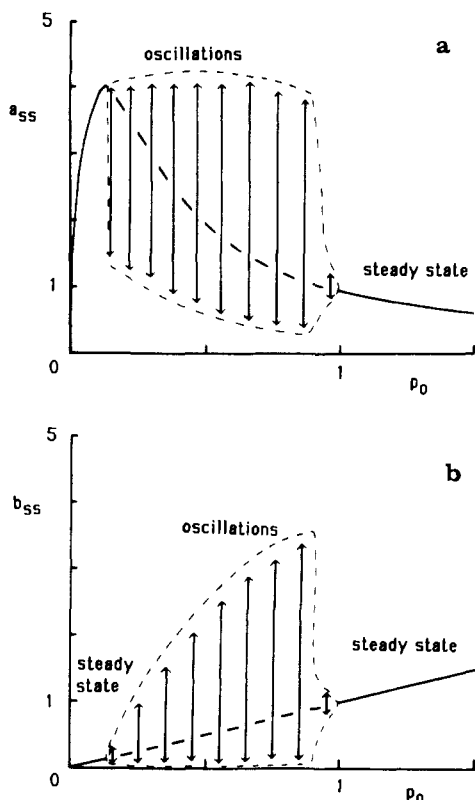
Figure 1. Stationary-state concentrations of a and b as functions of the initial reactant concentration. Stable states are shown as solid lines, and unstable states as broken lines. The amplitudes of the oscillations about unstable states are also indicated.

be small and b_{ss} is a small fraction of p_0.

The dependence of a_{ss} on p_0 is also shown in Figure 1. With low (initial) concentrations of the reactant P the stationary-state concentration of A is very small but increases as p_0 is increased. However, a_{ss} does not increase indefinitely; instead, it attains a maximum value

$$a_{ss,max} = k_2/2(k_1 k_3)^{1/2} \quad \text{when } p_0 = k_2 k_3^{1/2}/k_0 k_1^{1/2}$$

For larger values of the reactant concentration the stationary-state concentration of A decreases. The loci for a_{ss} and b_{ss} cross with

$$a_{ss} = b_{ss} = ((k_2 - k_3)/k_1)^{1/2} \quad \text{at } p_0 =$$
$$(k_2 - k_3)^{1/2} k_2/k_1^{1/2} k_0$$

Stationary states are places at which all the time derivatives vanish. By analogy with systems in mechanics,[18] we may thus expect these to be the conditions to which concentrations tend and at which they will then remain. However, this presumes that such states are "stable". Stationary states may also be "unstable", and it is common that oscillations begin as stability is lost. Stability and the method for its assessment are discussed in the next section.

4. Local Stability of Stationary States and Oscillation

The term "stability of a stationary state" refers to how the system reacts to small fluctuations or perturbations

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(19) Merkin, J. H.; Needham, D. J.; Scott, S. K. *Proc. R. Soc. London, A* 1986, *406*, 299.
(20) Farr, W. W.; Scott, S. K. *Chem. Eng. Sci.*, in press.

when it is sitting at that state. If small displacements tend to decay back to the original stationary state, then it is a stable state. If, however, the state is unstable, these perturbations will grow in time. Stability or instability is determined by the sensitivity of the reaction rate equations to changes in the concentrations a and b.

In particular, we need to find out how the rate of production of A varies as the concentration of A changes and how the rate of production of B depends upon the concentration of B. Mathematically, we are concerned with the partial derivatives $\partial(da/dt)/\partial a$ and $\partial(db/dt)/\partial b$. If increases in the concentrations a and b lead to decreases in both the net rates of production of A and of B, then both partial derivatives will be negative and the stationary state will be stable.

In the present case $\partial(da/dt)/\partial a$ is always negative. For the autocatalyst, $\partial(db/dt)/\partial b$ may be negative or positive depending on the experimental conditions. The stationary state will be stable if the sum of the partial derivatives is negative. It will be unstable if the sum becomes positive. The changes in stability as p_0 is varied for a typical set of the rate constants k_0, etc., are indicated in Figure 1: where the stationary state is unstable it is shown as a broken line.

The stationary state loses stability when $\partial(da/dt)/\partial a + \partial(db/dt)/\partial b$ becomes zero. We may use this condition and the rate equations (3.4) and (3.5) to locate the conditions for the onset of instability:

$$p_0^2 = (k_2^2/2k_0^2 k_1)\{k_2 - 2k_3 \pm [k_2(k_2 - 8k_3)]^{1/2}\} \quad (4.1)$$

This equation will have two positive real roots, p_1 and p_2, provided $k_2 > 8k_3$. The higher root p_1 lies close to the value at which the a_{ss} and b_{ss} curves cross. The other p_2 occurs close to where the a_{ss} curve has its maximum.

In between the two roots of (4.1) the stationary state is unstable. The system will not remain at such a state. However, there is no other set of concentrations for which the rates of change vanish simultaneously and hence there is no other stationary state to which the system can tend. Thus, the concentrations of A and B vary continuously in this region, describing sustained oscillatory behavior. If we plot the concentrations a and b against each other rather than against time, we see that they form a closed path or "limit cycle" in the "a–b phase plane". We may also plot the stationary state as a point on such a diagram to show that the system oscillates around it.

When p_0 lies just inside the region of unstable states, the oscillations are of small amplitude and are virtually sinusoidal. As the reactant concentration is moved further into this region, however, the amplitudes increase. We may indicate economically both the stationary-state and the oscillatory behavior about it as shown in Figure 1a,b. In the region of instability (dashed stationary-state locus) the maximum and minimum values achieved by the concentrations during the limit cycle oscillations for any given reactant concentration are marked. These points form an envelope around the unstable part of the curves and indicate the growth in size as p_0 varies.

Figure 1 can give no indication of the period between successive oscillations. This also varies with the value of p_0. At the upper end of the oscillatory region near p_1 the period is approximately $2\pi/k_2$. This lengthens

as p_0 is decreased to $2^{3/2}\pi/(k_2k_3)^{1/2}$ at p_2.

5. Reactant Consumption Acknowledged: The Behavior with Decaying Concentration of Precursor

The assumption that the concentration of the precursor or reactant P does not vary but is given by p_0 at all times is useful, but it is clearly only an approximation. In reality, the concentration will fall as P is converted to A. For the simple system chosen here there is a first-order decay, so at any time t after the start of the experiment ($t = 0$), the concentration of P will be

$$p(t) = p(t{=}0) \exp(-k_0 t) = p_0 \exp(-k_0 t) \quad (5.1)$$

A complete description of the behavior of the full set of rate equations requires numerical computation.[19] However, for small values of k_0 (in fact this turns out to mean small compared with k_2) the results of the previous sections can be used to avoid this. Provided the concentration of P changes via reaction 0 on a much slower time scale than a and b change via the remaining steps, the latter may still see a pseudostationary value for p. Thus, we may expect that the time-dependent forms for the concentrations of the intermediates are the stationary-state equations, (3.8) and (3.9), but with the constant p_0 replaced by $p(t)$ given by eq 5.1. This indeed is what is found, at least over the values of p_0 $\exp(-k_0 t)$ for which the stationary state was stable in the previous section.

Thus, if a system of pure P is set up with some initial concentration p_0 (relatively large), there is a rapid initial increase in the concentrations of the intermediates from zero to the values given by eq 3.8 and 3.9. Following this there is a period of much slower change: the concentration of the reactant falls exponentially while that of A increases and that of B decreases according to

$$a(t) =$$
$$k_0 k_2{}^2 p_0 \exp(-k_0 t)/[k_1 k_0{}^2 p_0{}^2 \exp(-2k_0 t) + k_2{}^2 k_3] \quad (5.2)$$

$$b(t) = (k_0/k_2)p_0 \exp(-k_0 t) \quad (5.3)$$

This behavior persists until the concentration of the reactant has fallen to a value equal to p_1, the condition at which instability arose in the previous section. Here the time-dependent concentrations of a and b move away from the pseudostationary-state trajectories (5.2) and (5.3). Oscillations begin. In fact, they do not become apparent immediately; rather, they require a finite time to develop. This development time may be quite significant, and the concentration of P will continue to fall during this period. Nevertheless, provided k_0/k_2 and k_3/k_2 are both much less than unity, oscillatory excursions in the concentrations of A and B will be observed (see Figure 2). The concentration of the final product C increases smoothly during the pseudostationary stage. During the oscillatory behavior, there are stepwise increases in c. The oscillatory period lasts as long as $p(t)$ remains between the numerical values of p_1 and p_2. Once the concentration of the reactant falls below the latter, however, the system moves back toward pseudosteady behavior. The concentrations of A and B show a damped oscillatory return to the solutions (5.2) and (5.3): $a(t)$ then achieves its maximum value, and after that all three concentrations p, a, and b fall monotonically to zero as t tends to infinity. The con-
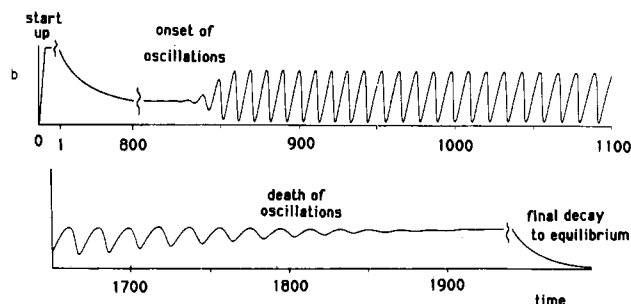

Figure 2. Onset, growth, and decay of oscillations for system with decaying reactant concentration. (Parameters used for computation: $k_0 = 1 \times 10^{-3}$ s^{-1}, $k_1 = 10^8$ dm^6 mol^{-2} s^{-1}, $k_2 = 1$ s^{-1}, $k_3 = 0.05$ s^{-1}, $p_0 = 0.1$ mol dm^{-3}.)

centration of C continues to increase, smoothly again, during this final period, tending to a value equal to p_0. Thus, we can image the time-dependent system moving from right to left across Figure 1a, b as p decreases. Provided the rate constant for the uncatalyzed conversion of A to B (k_3) is relatively small compared with that for the decay of the autocatalyst (k_2), the preoscillatory period and the number of oscillations observed depend most strongly on k_0. As an example, a system with $k_0 = 10^{-2}$ s^{-1} shows 13 excursions. If k_0 is decreased to 10^{-3} s^{-1}, the oscillatory train has 130 peaks: for k_0 = 0.1 s^{-1} there is only one pulse. In a closed system, oscillations must eventually cease because of the exhaustion of the reactants. The remaining sections of this Account will go on to deal with "open" systems—those with a constant supply of fresh reactants and a route for the removal of the products.

6. Autocatalysis in a Well-Stirred, Continuous Flow Reactor

The CSTR can be easily visualized as a well-stirred tank with inflow tubes along which the various reactants are pumped at a total volumetric flow rate v and an outflow or exchaust with the same v. The constant inflow of material allows us to reduce our kinetic model when seeking the simplest oscillator. We no longer need a chemical precursor reactant P. Our model comprises, therefore, the following reactions:

$$A + 2B \rightarrow 3B \quad (1)$$
$$B \rightarrow C \quad (2)$$
$$A \rightarrow B \quad (3)$$

The rate equations for a CSTR of volume V are then

$$\frac{da}{dt} = \frac{a_0 - a}{t_{res}} - k_1 ab^2 - k_3 a \quad (6.1)$$

$$\frac{db}{dt} = \frac{b_0 - b}{t_{res}} + k_1 ab^2 - k_2 b + k_3 a \quad (6.2)$$

where $t_{res} = V/v$ is the mean residence time of a molecule in the reactor and a_0 and b_0 are the concentrations of A and B in the inflow (allowing for the dilution as the two streams mix, if necessary).

In section 3, pseudosteady states were created artificially by neglecting reactant consumption. Equations 6.1 and 6.2 for a CSTR allow true steady or stationary states. The time derivatives may both become zero together, corresponding to time-independent conditions, without any approximation. The concentrations of A and B at the stationary state vary with the values of the
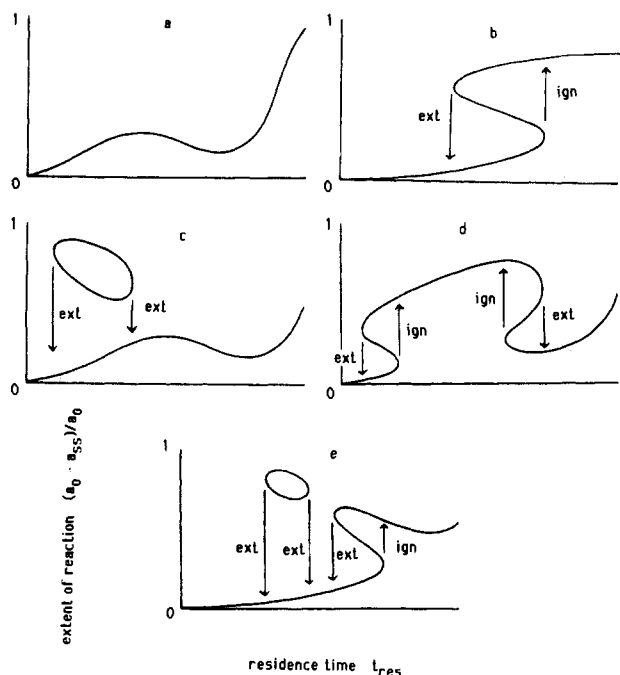
Figure 3. (a) Unique, (b) breaking wave, (c) isola, (d) mushroom, and (e) breaking wave + isola patterns for dependence of stationary-state extent of reaction on residence time for CSTR.

rate constants, etc. It is of particular interest to establish how they vary as the residence time (or, equivalently, the flow rate) is changed. For some values of k_1, etc., there is one, and only one, stationary-state composition for any given residence time (e.g., Figure 3a). Under different experimental conditions, however, a new phenomenon emerges. The derivatives become zero together for more than one set of a and b for the same k_1, t_{res}, etc.: there is more than one stationary state possible for some residence times. In these cases in order to decide how much A will be converted to B or C it is no longer sufficient only to specify the experimental or boundary conditions. These are the same for each of the states. We need also to know something about the history of the reaction; i.e., we must also consider the initial conditions before we can decide which of the possible states will be realized.

This phenomenon is known as musltiplicity. There are in fact four patterns of multiplicity for the present model, as shown in Figure 3b–e: these are known as (b) breaking wave, (c) isola, (d) mushroom, and (e) breaking wave + isola. The term $(a_0 - a)/a_0$ reflects the fraction of the inflowing reactant A which has reacted: it varies between 0 (no reaction) and 1 (complete conversion).

The breaking wave is a simple S-shaped hysteresis loop. With an isola, the highest and middle extents of reaction form a closed curve. We can fall off the upper branch, as indicated by the downward arrows in Figure 3c, either by increasing or decreasing t_{res}. When this happens, the system moves to the lowest branch, with a corresponding sudden decrease in the conversion. This is known as extinction (in combustion) or washout (in solution-phase and biochemical reactions). Once the lowest branch has been reached, no variation of the residence time will cause a jump back to the upper branch. There is also no such way in which this system can be induced to jump to the middle branch.

Mushroom patterns (Figure 3d) have two ranges of multiple stationary states, an S-shaped loop at low

residence times (high flow rates) and a Z-shaped loop at longer residence times. These are separated by a region over which there is only one stationary state, that corresponding to the upper branch. As well as two extinctions, there are two points at which the system jumps from a low conversion state to one of high conversion. In combustion systems these are called ignitions. For the S shape, ignition accompanies an increase in the residence time: at the other end of the mushroom it occurs as t_{res} is reduced.

The simple origins of these interesting phenomena are revealed in ref 12. Which of the five patterns will be observed in any given experiment is determined by (i) the ratio of the inflow concentrations b_0/a_0, (ii) the relative rates of the two reactions $k_2/k_1a_0^2$, and (iii) the ratio $k_3/k_1a_0^2$.

As well as showing multiple stationary states, the CSTR system allows instability. In fact, the middle solution is always unstable. One or both of the other two solutions may also lose stability under some conditions (known as points of Hopf bifurcation), and again these are often (but not always) the conditions at which oscillation begin. For example, if the system is sitting on the top branch of an isola or of a mushroom, the stationary state may become unstable as t_{res} is increased. The concentrations of A and B then have three choices: (i) they may oscillate about the unstable state; (ii) if the other two stationary states exist, a and b may oscillate about all three states; (iii) if the lowest state exists and it is stable, the system may move to that. In case i and ii plotting a against b during the oscillations describes a stable limit cycle in the concentration phase plane (see section 4).

Limit cycles which are unstable may also exist. The system cannot remain on such a cycle as even the smallest perturbations away from it grow. Unstable limit cycles do not therefore lead to observable, sustained oscillations. They do, however, play a significant role. They act as a boundary in the phase plane, separating different regions of "attraction". If we start off inside the limit cycle, we must eventually move to the stable stationary state which it surrounds. The allowed variations in the concentration cannot lead to a path in the phase plane which crosses the limit cycle. Conversely, therefore, if the system starts from the outside of the cycle, it cannot approach the stationary state within. It must move either to a different stable state or to a stable limit cycle.

Figure 4 shows the different ways in which limit cycles and stationary states may be combined for the cubic autocatalator, different ones being obtained by varying the experimental conditions. Thus, in Figure 4f there are three stationary states available: one, corresponding to a high value of a_{ss} and low b_{ss}, is stable while the other two are unstable; the stationary state at lowest a_{ss} and high b_{ss} is surrounded by a stable limit cycle. Also indicated in the diagram is a boundary or "separatrix" passing through the middle, unstable state. The time-dependent behavior of such a system can be deduced as follows. The initial state corresponds to some point in the phase plane, and as the concentrations of A and B evolve in time they draw out a path. Such a path cannot cross the separatrix. Depending on which side the initial point is, the concentrations tend either to the stable stationary state or to the sustained
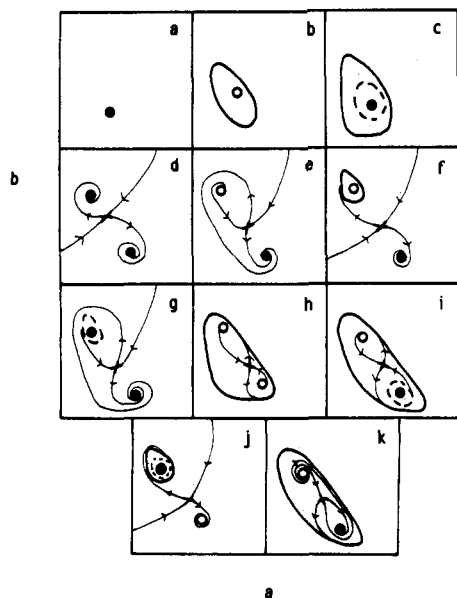
Figure 4. The 11 different "phase portraits" for the autocatalator.

oscillatory state corresponding to continuous motion around the stable limit cycle.

7. Conclusions and Future Extensions

A very simple scheme, based on a single autocatalytic step, has been shown to be capable of accounting for a wide variety of "nonlinear" behavior in two different experimental situations: closed vessel and well-stirred open reactor. Autocatalysis is not widely found in conventional chemical systems but is commonly observed in oscillatory reactions[21] and, along with auto-inhibition, is one of the results of the cooperative effects[13] which are so important in biochemical processes. It appears under another name in branched-chain reactions[22] such as the oxidations of almost all fuels. One difference between the present scheme and the behavior of some inorganic reactions systems, such as the B–Z reaction, is that the oscillations predicted are not of the relaxation type (periods of relatively slow change separated by sharp jumps in concentrations).

Recent work on the models discussed here has tended to focus upon their "robustness": ensuring that the various patterns survive such tests as elaborating the kinetic scheme by adding extra competing reactions and recognizing some of the more subtle requirements of thermodynamics.[23] These are important questions as many other models fail these examinations, and at the same time the answers provide greater insight to aspects such as the relationship between oscillations and multiple stationary states. (Despite what is stated elsewhere even now, there is no link and each can be found in models which do not display the other although both have their roots in the chemical nonlinearities.) In some cases these elaborations serve to increase the diversity of behavior.

An extension of the present work has involved studying the cubic autocatalysis model with reaction coupled to diffusion[24] either through a restricted zone (e.g., a simple cell) or the propagation of reactive fronts or chemical waves through an extended region. The ultimate goal, however, is to build a bridge between model and real chemical systems. Experiments with the iodate–arsenite reaction, which has an approximately cubic autocatalytic rate law, can be explained[25] in the terms of section 6, but the most exciting prospect remains the understanding of enzymatic and other biochemical systems to probe the regular oscillations such as circadian rhythms, including the human biological clock. In individual living systems or in collected populations, the choice between various possible stationary states in regions of multiplicity may literally prove the difference between life and death, in which case the term "extinction" becomes unnervingly appropriate. Other examples of biochemical oscillations include glycolysis[26] and cell division (mitosis):[27] spatial periodicity and structure arise in morphogenesis and embryo development.

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