

Chemical Oscillations

2. Mathematical Modelling

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The law of mass-action led chemists to the belief that reactions approach equilibrium steadily. So the discovery of chemical oscillations came as a surprise. Now chemists are very familiar with reactions that oscillate in time and/or space. Experimental and theoretical studies of such reactions showing temporal and spatial oscillations attract the interest of many laboratories world-wide. The Lotka–Volterra model is the simplest mathematical model which exhibits such oscillations. In this article, we use this model to illustrate chemical oscillations with the help of a computer program.

Introduction

In the earlier article¹ on chemical oscillations, we discussed the behaviour of a few complex chemical systems. We observed that these chemical oscillators are basically nonlinear systems driven far from equilibrium, having interesting physical and mathematical concepts underlying their evolution. The connection between the theory and experiment is made through mathematical models derived from the mechanisms of chemical oscillators. The simplest such model is the Lotka–Volterra model. This is perhaps the earliest proposed explanation for why a reaction oscillates, based on sound mathematical principles. This model was proposed by American biophysicist Alfred Lotka (1880–1949) and Italian mathematician, Vito Volterra (1860–1940). Lotka developed a model for chemical reactions, whereas Volterra developed a model for oscillations found in population dynamics.

Lotka proposed the following reaction mechanism: each reaction step refers to a molecular mechanism by which reactant



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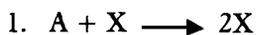
Part 1. Basic Principles and Examples, *Resonance*, Vol.11, No.2, pp.43–50, 2006.

Keywords

Lotka–Volterra model, non-linear oscillations, autocatalysis.

The predator-prey model is the simplest system exhibiting autocatalysis.

molecules combine to produce intermediates or products. He considered a series of consecutive reactions, each of which is supposed to be irreversible



Step contributions to rate laws:

$$d[A]/dt = -d[X]/dt = k_1 [A][X].$$



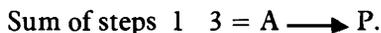
Step contributions to rate laws:

$$d[X]/dt = -d[Y]/dt = k_2 [X][Y].$$



Step contributions to rate laws:

$$d[Y]/dt = -d[P]/dt = k_3 [Y].$$



Steps 1 and 2 are autocatalytic, since X and Y accelerate their own production. This model is also known as the prey-predator model. (See *Box 1*.)

Overall, this chemical reaction is merely A going to B with two transient intermediates X and Y. The different rate equations then, are:

$$d[A]/dt = -k_1 [A][X]$$

$$d[X]/dt = k_1 [A][X] - k_2 [X][Y]$$

$$d[Y]/dt = k_2 [X][Y] - k_3 [Y]$$

$$d[P]/dt = k_3 [Y]$$

This autocatalytic system can reach a steady state; where the rate of reproduction of rabbits is exactly balanced by the consumption of species by foxes and foxes die at the same rate that baby foxes are born. Mathematically, we find such a state by setting all the time derivatives equal to zero and solving the resulting algebraic equations. Thus putting

$$d[X]/dt = k_1 [A][X] - k_2 [X][Y] = 0 \quad (1)$$

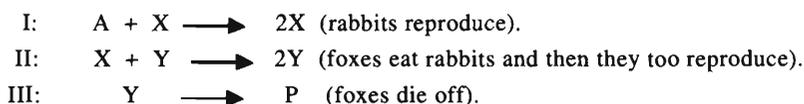


Box 1. Prey-Predator Model

The model describes the change of the number of rabbits (X) and the number of foxes (Y) in an island. The island has plenty of grass on which the rabbits can feed. A is used to denote the amount of grass, which is assumed to be available in plenty and hence change in its amount is not considered. In the absence of the foxes, rabbits will multiply (step I below) and X will increase exponentially. Foxes feed on rabbits and reproduce (step II) and of course, die off (step III). If there are no rabbits, then the number of foxes will decrease exponentially. Each step is irreversible: rabbits will never turn back into grass, nor dead foxes into live ones. Notice that

- X is consumed only by Y , and Y has nothing else to feed on.
- The rate of change of Y depends on the availability of prey.

We can write down a system of differential equations to describe the behavior of the predator and prey species:



The net effect is the conversion of grass to dead foxes.

The model leads to the following two differential equations, one that describes the prey population, and another that describes the predator population.

$$\begin{aligned} d[X]/dt &= k_x [A][X] - k_y [X] [Y] \\ d[Y]/dt &= k_y [X] [Y] - k_d [Y] \end{aligned}$$

k_x is a rate constant reflecting how fast rabbits reproduce (for step I), k_y specifies how fast foxes reproduce for a given number X of rabbits to feed on (step II), and k_d indicates mortality rate of foxes (for step III).

Interestingly, for any set of values for these constants, the number of rabbits and foxes will oscillate with a period that depends upon k_x , k_y and k_d and A .

A key feature of the system is autocatalysis, which means that the rate of growth of any species, whether rabbits or foxes, increases with the population of that species.

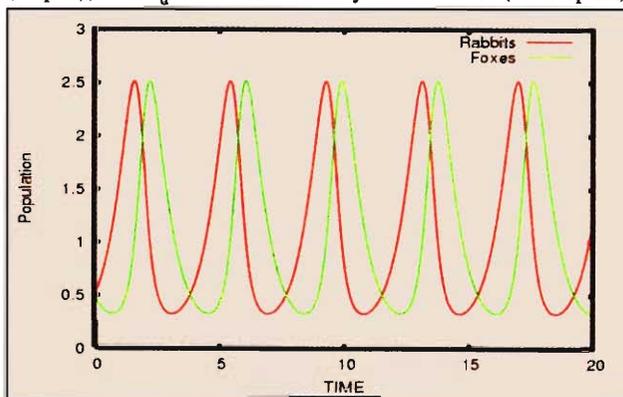


Figure A. Numerical solution of the Lotka-Volterra model with $A = k_x = k_y = k_d = 1$. Population vs. time plot showing oscillations in the population of the species (rabbits in red and foxes in green).

The predator-prey model cannot be solved analytically, but has to be integrated numerically on a computer. Its behavior near the equilibrium point can be studied analytically, and is found to be oscillatory.

$$d[Y]/dt = k_2 [X] [Y] - k_3 [Y] = 0, \quad (2)$$

we get the solutions

$$\begin{aligned} [Y] &= (k_1 / k_2)[A] \quad \text{and} \\ [X] &= k_3 / k_2. \end{aligned}$$

Mathematicians call these solutions the equilibrium points of the dynamical system defined by equations (1) and (2). If each concentration starts at the equilibrium point, then it does not change with time.

The qualitative features of the changes in $[X]$ and $[Y]$ near the equilibrium point can be investigated with a bit of mathematical analysis (see *Box 2*). Far from equilibrium however, the two equations defy analytical solution and hence we can integrate the two equations numerically on a computer. Numerical integration is essentially an exercise in curve-fitting. One uses information about the function to be integrated – its value and the values of its derivatives – at certain points to approximate the function over some interval by functions that we know how to integrate, usually polynomials. The results below are obtained using Runge–Kutta fourth order integration method to solve the Lotka–Volterra equation as per the Fortran program given in *Box 3*. This program can be run with different values of initial concentrations of X and Y , and the rate constants k_1 , k_2 and k_3 . The results can be depicted in two ways: one way is to plot X and Y versus time, and the second way is to plot one concentration (Y) versus the other (X). This is known as the phase plane representation. We have obtained these plots using the software **GNUPLOT**.

Results of Computer Simulation

We give detailed plots showing the results of computer calculations of the prey-predator model that can be reproduced easily with the help of the program provided (see *Box 3*) and the scientific plotting software **GNUPLOT**. At the steady state, calculated from the equations (1) and (2) (and with values of



Box 2. Analysis of the Solution of the Differential Equations near the Steady State

Equations (1) and (2) can be simplified by introducing the dimensionless quantities, defined by

$$\tau = k_3 t; \quad x = (k_2 / k_3)[X]; \quad y = (k_2 / k_3)[Y]; \quad a = (k_1 / k_3)[A]$$

Then the rate equations (1) and (2) become:

$$dx/d\tau = ax - xy \quad (a)$$

$$dy/d\tau = xy - y \quad (b)$$

At the steady states, $x_0 = 1; [X] = k_3 / k_2$
 $y_0 = a; [Y] = (k_1 / k_2) [A]$

When the system is close to the steady-state, we can write

$$x(t) = x_0 + \Delta_x e^{\omega t} \quad (c)$$

$$y(t) = y_0 + \Delta_y e^{\omega t} \quad (d)$$

where Δ_x and Δ_y are assumed to be small. This is a standard way of analyzing the behaviour of a system close to the steady state. Notice that if ω is real and $\omega > 0$, $e^{\omega t}$ is an increasing function and the quantities x and y (and hence the concentrations of X and Y) go away from the steady state progressively and exponentially. On the other hand, if ω is real and $\omega < 0$, the system comes closer and closer (converges) to the steady state. When ω is a complex number, the system oscillates around the steady state, spiralling outwards away from the steady state if the real part of ω , denoted by $\text{Re}(\omega) > 0$ and spiralling towards the steady state if $\text{Re}(\omega) < 0$.

Substituting equations (c) and (d) into (a) and (b) and simplifying by assuming small values of Δ_x and Δ_y (i.e. neglecting higher order terms), we get

$$\omega^2 + k_1 k_3 a = 0$$

$$\text{or, } \omega = \pm i (k_1 k_3 a)^{1/2}$$

$\text{Re}(\omega) = 0$ and the imaginary part $\text{Im}(\omega) = \pm i (k_1 k_3 a)^{1/2}$. Thus ω is a purely imaginary number giving rise to oscillatory behaviour of the concentrations without any asymptotic convergence or divergence. This means that near the steady state, the values of X and Y will always oscillate.

[A], k_1 , k_2 and k_3 set in arbitrary units as 2, 1, 2 and 2, respectively) with the initial concentration of X and Y both as 1.0 unit, we locate the equilibrium point of dynamics, whereafter concentrations remain constant in time. This can be seen from *Figure 1*, where the concentrations remain constant.



Box 3. PROGRAM (in FORTRAN 77 can be used as such with a F90 compiler)

!PROGRAM TO SOLVE THE PREY-PREDATOR PROBLEM (See [2])

```

parameter(n=2)
implicit double precision(a-h,o-z)
real*8 conc(n),dconcdtime(n),concout(n) !conc(1)=[X], conc[2]=[Y]; dconcdtime is the time
derivative
external der
common a,rk1,rk2,rk3
a=2.0d0
rk1=1.d0
rk2=2.d0
rk3=2.d0
write(*,*)'input conc(1),conc(2)'
read(*,*)conc(1),conc(2)
time=0.d0
nm=1000
h=1.d0/dfloat(nm)           ! time-step for integration
call der(time,conc,dconcdtime) ! Subroutine der provides the derivatives at each point of time
write(4,*)conc(1),conc(2),time
do l=1,5000   !outer loop to write data after every nm/100 integrations
do k=1,nm/100 ! integration loop
time=time+h
call der(time,conc,dconcdtime)
call rk(conc,dconcdtime,n,time,h,concout,der) !rk is the Runge Kutta numerical integration
routine
conc(1)=concout(1)
conc(2)=concout(2)
enddo
write(4,999)conc(1),conc(2),time
enddo
999 format (2x,f8.3,2x,f8.3,2x,f8.3)
end
SUBROUTINE der(time,conc,dconcdtime) ! routine to calculate the derivatives
implicit double precision(a-h,o-z)
dimension conc(*),dconcdtime(*)
common a,rk1,rk2,rk3
dconcdtime(1)=rk1*a*conc(1)-rk2*conc(1)*conc(2)
dconcdtime(2)=rk2*conc(1)*conc(2)-rk3*conc(2)
return
end

```

Box 3. continued...



SUBROUTINE rk(conc,dconcdtime,n,time,h,concout,der) ! Runge-Kutta routine for integration

```

implicit double precision(a-h,o-z)
dimension conc(n),dconcdtime(n),concout(n),conct(n),concl(n),conc2(n)
h2=h/2.d0
h6=h/6.d0
timeh=time+h2
do i=1,n
conct(i)=conc(i)+h2*dconcdtime(i)
enddo
call der(timeh,conct,concl)
do i=1,n
conct(i)=conc(i)+h2*concl(i)
enddo
call der(timeh,conct,conc2)
do i=1,n
conct(i)=conc(i)+h*conc2(i)
conc2(i)=concl(i)+conc2(i)
enddo
call der(time+h,conct,concl)
do i=1,n
concout(i)=conc(i)+h6*(dconcdtime(i)+2.d0*conc2(i)+concl(i))
enddo
return
end

```

When viewing the same initial populations in the phase plot, (*Figure 2*) we see just an equilibrium point.

It can be seen that when both X and Y have the same concentration near the steady state, as A reacts with X, the production of even more X occurs autocatalytically. However, as X is formed, production of Y begins and initially, it occurs slowly (as can be seen from the gradually increasing slope of [Y]) because [Y] is small, but autocatalysis leads to surge of [Y] and thus, there is a sudden increase in the slope (*Figure 3*). The increase in [Y] removes [X] and so production of X slows down and less of X is produced. But less of X being available now, production of Y slows down at the same time. As less Y becomes available to



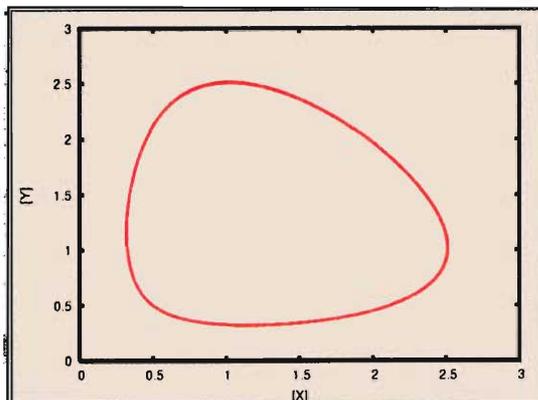
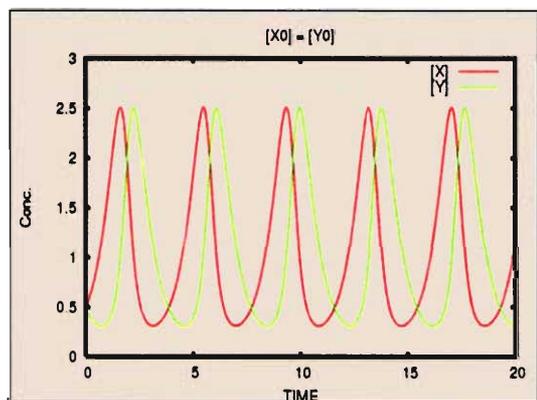
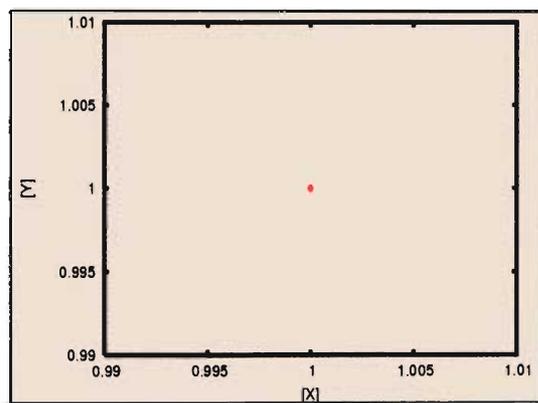
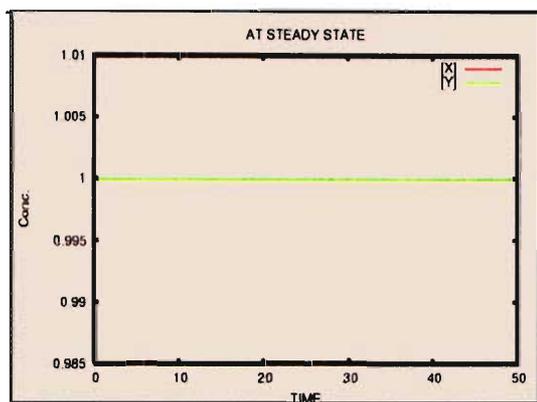


Figure 1 (top-left). Trajectory obtained at steady state when $[X_0] = [Y_0] = 1$.

Figure 2 (top-right). Phase plot corresponding to Figure A (In Box 1).

Figure 3 (bottom-left). Plot obtained when initial concentrations of X and Y are same.

Figure 4 (bottom-right). Phase plot corresponding to Figure 3.

remove X, X gets the chance to autocatalyse its formation and its concentration again increases.

This can be seen from the closed orbit (Figure 4) obtained by plotting $[X]$ vs. $[Y]$ which means that as $[X]$ increases $[Y]$ increases. (A good exercise left for the reader is to find the direction of the dynamical trajectory in Figure 4. It can be obtained analytically from the sign of (dY/dX) obtained by dividing equations (a) by (b).) Here, both $[X]$ and $[Y]$ increase to the respective maximal values and then, decrease.

It is left as an exercise for the reader to draw plots for different initial conditions. One can also see the exponential growth or decay of one of the constituents in absence of the other, by setting the initial concentrations of either of the constituents, X or Y to zero in the program.

These plots of time trajectories (concentrations as functions of time) and the phase behaviour give equivalent ways of looking at the dynamics. The periodic variation is seen clearly and at the same time many interesting aspects related to the nonlinear dynamics surface (e.g., can we construct a Hamiltonian or a Lagrangian for the dynamical system?) that are left for the reader to explore on his/her own.

Conclusion

Lotka–Volterra model is an approximate description of the realistic oscillatory systems in nature. Here, the constancy of component A, results in exponential increase of the reactant X to infinity in the limit of vanishing amounts of Y, which is an absurd phenomenon. Also, the undamped oscillations taking place with equal concentrations of reactants X and Y do not seem realistic. More sophisticated theoretical models are now known and have been investigated by physical chemists and others extensively. Interested readers may find details in the references cited at the end. Higher accuracy demands larger number of variables and with fast computers available today, it has become possible to carry out such investigations. So, this model may not be useful for quantitative predictions, but it does give us insight into the phenomena of oscillations in reactive processes.

Suggested Reading

- [1] I R Epstein, K Kustin, P De Kepper and M Orban, *Sci. Am.*, Vol.248, No.3, pp.112-123, 1983.
- [2] Fortran Program developed by R Rai and H Singh, *Phys. Rev. E*, Vol.62, pp.8804-7, 2000, with integration subroutine from W H Press, S A Teukolsky, W H Vetterling and B P Flannery, *Numerical Recipes in FORTRAN*, Cambridge University Press, Cambridge, 2000.
- [3] S K Scott, *Oscillations, Waves and Chaos in Chemical Kinetics*, Oxford Chemistry Primer #18, Oxford University Press, Oxford, 1994.
- [4] R Rai, K Arora and H Singh, *Chem. Edu. Rev.*, Vol.14, No.3, pp.25-33, 1999.

Lotka–Volterra model is the simplest and it has only undamped oscillations. More complex models exhibiting damped oscillations are easy to construct and have been extensively studied.

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