28. Chemical Oscillations

The kinetics of chemical reactions can be modeled by a system of coupled first-order differential equations. As an example, consider the following reaction:

$$A + 2B \to 3B + C \tag{1}$$

where A, B, and C represent the concentrations of three different types of molecules. The corresponding rate equations for this reaction are:

$$\frac{dA}{dt} = -kAB^2 \tag{2a}$$
$$\frac{dB}{dt} = +kAB^2 \tag{2b}$$
$$\frac{dC}{dt} = +kAB^2 \tag{2c}$$

The rate at which the reaction proceeds is determined by the reaction constant k. The terms on the right-hand side of (2) are positive if the concentration of the molecule increases in (1) as it does for B and C, and negative if the concentration decreases as it does for A. Note that the term $2B$ in the reaction (1) appears as B^2 in the rate equation (2).

Most chemical reactions proceed to equilibrium, where the mean concentrations of all molecules are constant. However, if the concentrations of some molecules are replenished, it is possible to observe other kinds of behaviour, such as oscillations (see below) and chaotic behaviour. In (2) we have assumed that the reactants are well stirred, so that there are no spatial inhomogeneities.

To obtain chemical oscillations, it is essential to have a series of chemical reactions such that the products of some reactions are the reactants of others. In the following, we consider a simple set of reactions that can lead to oscillations under certain conditions:

$$A \to X \tag{3a}$$
$$B + X \to Y + D \tag{3b}$$
$$2X + Y \to 3X \tag{3c}$$
$$X \to C \tag{3d}$$

If we assume that the reverse reactions are negligible and A and B are held constant by an external source, the corresponding rate equations are:

$$\frac{dX}{dt} = A - (B+1)X + X^2Y \tag{4a}$$
$$\frac{dY}{dt} = BX - X^2Y \tag{4b}$$

For simplicity, we have chosen the rate constants to be unity.

1. The steady state solution of (4) can be found by setting the left-hand side equal to zero. Show that the steady state values for (X, Y) are $(A, \frac{B}{A})$.

2. Write a program to solve numerically the rate equations given by (4). A simple Euler algorithm is sufficient. Your program should input the initial values of X and Y and the fixed concentrations A and B, and plot X versus Y as the reactions evolve.

3. Systematically vary the initial values of X and Y for given values of A and B. Are their steady state behaviours independent of the initial conditions?