

What Happens When an Equilibrium Becomes Unstable? An Introduction to Linear Stability Analysis *

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Abstract

The microscopic concept of "statistical averaging" allows us to describe the complicated behaviour of all the atoms and molecules in a chemical reaction by the macroscopic concept of the rate equation. We can examine our reaction on a higher level and do not have to pay attention to what is going on on the lower one. However there is a "gray" area between these two levels since the microscopic processes permanently produce small perturbations of the macroscopic levels.

If an equilibrium state is perturbed, the perturbation can damp out and we have a stable state, or it can increase and create a new stable state. Below, we discuss in detail what can happen when an equilibrium state experiences small perturbations.

Stability

A chemist is accustomed to having all his reactions approach some equilibrium smoothly. These reactions can be described by appropriate potentials such as the entropy, Gibbs free energy etc., according to the boundary conditions. It is quite exciting when one finds reactions like the *Belusov-Zhabotinsky* reaction [6-9] that do not care about this "law of nature" and are able to oscillate or to produce a pattern in space. The underlying laws of these reactions are not restricted to chemistry. Some of

the best known examples are from biology [2, 3], electroengineering (e. g. oscillators) etc. We shall now look at what sort of different behaviors are possible and how we can determine the circumstances under which they emerge.

In chemistry reactions are normally described in terms of concentrations $c_j(\vec{r}, t)$ *, which are thought of as smoothly varying functions of time. The progress of the reaction can then be described by a differential equation, the rate equation, in the form given below:

$$dc_i/dt = f(c_j, t)$$

From this, together with the initial concentrations, we are able to evaluate the concentrations at any time t (see appendix 1).

The first step is to realize that on a microscopic level there is no such thing as "smoothly varying". There are atoms and molecules bouncing around and reacting in a stochastic manner. Only by averaging in space and/or time can we get rid of the fast statistical fluctuations. This is exactly what happens when we make measurements with any instrument. The microscopic fluctuations, however, are still present! Every density or concentration in a

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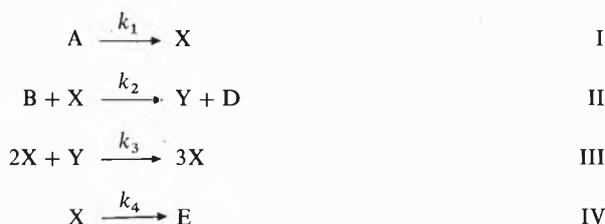
* \vec{r} is a vector that indicates a point in space: (x, y, z)

solution is always fluctuating slightly. For this reason we should not only ask:

Given the concentrations, what are the rates of change? but also:

How does a slight perturbation influence the rates and the evolution of the reaction?

If a small change in the initial concentrations has a small effect at any time of our experiment then the system is termed stable. Otherwise, if a microscopic disturbance has a macroscopic effect, the system is termed unstable. To become more concrete we shall look at an example. Real reactions which intimate most of the important phenomena like the *Belusov-Zhabotinsky* reaction are complicated and hard to analyze, so we shall look at a theoretical example from *Prigogine* [1] which better fits our needs:



Back reactions are not allowed in our model (e.g. we may eliminate D and E and set $k_{-1} = k_{-3} = 0$).

We now define equilibrium as a state where there are no changes in time (i.e. $dc/dt = 0$) and where all the reagents are distributed homogeneously: $\nabla c = 0$ (which implies: $\nabla^2 c = 0$)*.

Furthermore, we make the following simplifications:

– [A], [B] are held constant (from the outside, by excess ...)

and

– We examine only small deviations around the equilibrium.

(later we shall put:

– $\nabla c(\text{wall})$ is parallel to the wall)

In the following we abbreviate [A] by A, [B] by B, etc.

We begin by stating the rate equations, where we assume, as we usually do in chemistry, that a product «ANSATZ» will describe our system sufficiently.

The concentration at point r and time t can vary due to reactions or due to diffusion (see appendix 2):

$$dX/dt = k_1A - k_2BX + k_3X^2Y - k_4X + D_x \nabla^2 X$$

$$dY/dt = k_2BX - k_3X^2Y + D_y \nabla^2 Y$$

Next we simplify our equations by choosing appropriately convenient units given below.

* ∇c means the gradient of c : (dc/dx , dc/dy , dc/dz), the 3-dimensional derivative.

$\nabla^2 c$ means $d^2c/dx^2 + d^2c/dy^2 + d^2c/dz^2$.

$$t: 1/k_4, x: \sqrt{k_4/k_3}, y: \sqrt{k_4/k_3}$$

$$A: 1/\sqrt{k_1^2 k_3/k_4^3}, B: k_4/k_2, D: k_4$$

(e.g. we have to replace t by t/k_4 etc).

The above equations can now be expressed as:

$$dX/dt = A - (B + 1)X + X^2Y + D_x \nabla^2 X$$

$$dY/dt = BX - X^2Y + D_y \nabla^2 Y \quad \text{V}$$

As the temporal evolution of our reaction depends crucially on what is going on at the boundaries of our system (e.g. the vessel wall), we have to specify some boundary conditions. If we imagine that our reactants are enclosed in a vessel, we may specify that there is no mass transfer through the vessel wall. This implies that we do not have any diffusion-flux across the wall:

$$\nabla c(\text{wall}) \text{ is parallel to the wall} \quad \text{VI}$$

We look now for the equilibrium:

$$\nabla X = \nabla Y = 0 \text{ implies } dX/dt = A - (B + 1)X + X^2Y \\ dY/dt = BX - X^2Y$$

together with $dX/dt = dY/dt = 0$ gives for equilibrium

$$X_e = A \text{ and } Y_e = B/A$$

We now ask: What will the system do if we slightly perturb the equilibrium state at $t = 0$. In mathematical notation:

$$\text{Let } X(\vec{r}, t) = X_e + x(\vec{r}, t), Y(\vec{r}, t) = Y_e + y(\vec{r}, t)$$

$$\text{Given } x(\vec{r}, t = 0), y(\vec{r}, t = 0) \text{ with } x(\vec{r}, 0), y(\vec{r}, 0) \ll X_e, Y_e,$$

what are:

$$x(\vec{r}, t), y(\vec{r}, t)?$$

We shall now show that the answer depends on A and B. We profit from the assumption that the perturbations x, y are small: $x, y \ll X_e, Y_e$ and this allows us to neglect all higher powers of x, y compared with x, y (e.g. x^2, xy, y^2, \dots compared with x, y). As a result we get linear equations in x, y which are simple to treat. This is why this method is called «linear stability analysis».

With $X_e = A, Y_e = B/A$ and V we get:

$$\begin{aligned} dx/dt &= (B - 1)x + A^2y + D_x \nabla^2 x \\ &\text{or } \begin{pmatrix} x \\ y \end{pmatrix} = M \begin{pmatrix} x \\ y \end{pmatrix} \quad \text{VII} \\ dy/dt &= -Bx - A^2y + D_y \nabla^2 y \end{aligned}$$

$$\text{Where } M = \begin{pmatrix} B - 1 + D_x \nabla^2 & A^2 \\ -B & -A^2 + D_y \nabla^2 \end{pmatrix}$$

We now try to decompose the solution into easily treatable and interpretable summands. First we look for a form in which the temporal derivative is easy to manipulate:

$$\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} \sum_m a_m(\vec{r}) \exp(w_m t) \\ \sum_m b_m(\vec{r}) \exp(w_m t) \end{pmatrix} = \sum_m \exp(w_m t) \begin{pmatrix} a_m(\vec{r}) \\ b_m(\vec{r}) \end{pmatrix}$$

where w may be complex. (Although we are looking for

real solutions, taking complex functions makes it easier). We shall see, that w will be fixed by A and B.

With the above decomposition, the temporal derivative is easily done. (The question does arise whether every solution can be decomposed in this manner. Not going into details here, we only state that if at the end we are able to give a solution for every initial value, we have completed our job.)

In the next step we try to decompose similarly every space dependent term a and b so that it is easy to operate with ∇^2 on each summand and the solution is consistent with the boundary condition VI. For this purpose we have to specify the boundary explicitly. For simplicity, we choose a one dimensional vessel of length l (or a parallelepiped with homogeneous conditions along two axes). The boundary conditions then are:

$$dc/dr(r=0) = dc/dr(r=l) = 0$$

and a decomposition into cosine functions will fit our needs. This is given below:

$$a(r) = \sum_n c_{a,n} \cos\left(\frac{\pi n}{l} r\right)$$

$$b(r) = \sum_n c_{b,n} \cos\left(\frac{\pi n}{l} r\right)$$

The constants c will be given by the initial values of x, y . We conclude, that we have to look for a «fundamental» solution of the form:

$$\exp(wt) \cdot \cos\left(\frac{\pi n}{l} r\right) \begin{pmatrix} c_a \\ c_b \end{pmatrix} \text{ where } c = \text{constant} \quad \text{VIII}$$

placing eqn VIII in eqn VII and dividing by $\cos\left(\frac{\pi n}{l} r\right)$

gives:

$$w \begin{pmatrix} c_a \\ c_b \end{pmatrix} = \begin{pmatrix} B-1-D_x n'^2 & A^2 \\ -B & -A^2-D_y n'^2 \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix}$$

where we let $n' = \pi n/l$

We have now found the familiar «eigenvalue» problem. If we rewrite:

$$\begin{pmatrix} B-1-D_x n'^2 - w & A^2 \\ -B & -A^2-D_y n'^2 - w \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0$$

we see that for c not equal 0 the determinant must vanish. This results in the following quadratic equation in w :

$$w^2 + \alpha w + \beta = 0$$

$$\text{where } \alpha = A^2 - B + 1 + n'^2(D_x + D_y)$$

$$\beta = A^2 + [A^2 D_x - (B-1)D_y]n'^2 + D_x D_y n'^4$$

$$\text{and } w_{+/-} = -\alpha/2 \pm \sqrt{(\alpha/2)^2 - \beta}$$

The solution will be a linear combination of the form:

$$c_a = a_+ \exp(w_+ t) + a_- \exp(w_- t)$$

$$c_b = b_+ \exp(w_+ t) + b_- \exp(w_- t)$$

$a_{+,-}$ and $b_{+,-}$ will be determined by the initial values

for x, y , and the requirement of real solutions. See Fig. 1 and Fig. 2.

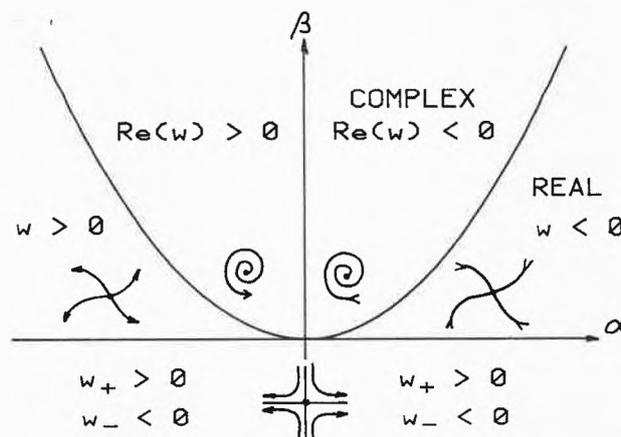


Fig. 1: Types of solutions

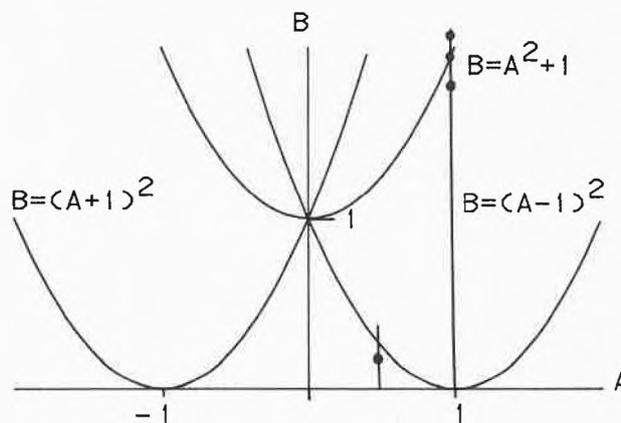


Fig. 2

The temporal behaviour of the solution depends crucially on whether w is real or complex. If the real part of w is negative the perturbation will die out asymptotically, and if it is positive the perturbation will drive the system further and further away from equilibrium. We now look at the different types of solutions in detail.

1) Periodic solution

If w is imaginary, the deviation from the equilibrium (x, y) will harmonically oscillate about that equilibrium. (Real part of $\exp[i \cdot \text{abs}(w) \cdot t]$).

For w to be imaginary we must have:

$$\alpha = 0, \beta > 0 \text{ (Fig. 1)}$$

$$\alpha = A^2 - B + 1 + n'^2(D_x + D_y) = 0$$

$$\beta = A^2 + [A^2 D_x - (B-1)D_y]n'^2 + D_x D_y n'^4 > 0$$

For example: Let $n = n' = 0$ (homogeneous)

$$A^2 - B + 1 = 0$$

$$A^2 > 0 \text{ e.g. } A=1, B=2$$

For a test we can put these values in V with $n' = 0$ and simulate V numerically (see appendix 1).

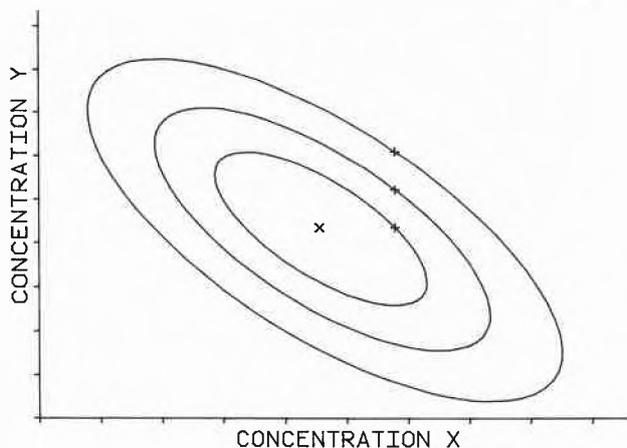


Fig. 3: Periodic solution

$$A = 1, B = 2, X_s = 1.01 \cdot A, Y_s = 1.00 \cdot B/A$$

$$X_s = 1.01 \cdot A, Y_s = 1.005 \cdot B/A$$

$$X_s = 1.01 \cdot A, Y_s = 1.01 \cdot B/A$$

This simulation for three different initial values X_s, Y_s is shown in Fig. 3. We can see, that the oscillatory state depends on the initial value. For stochastic perturbations the behavior can not be predicted exactly. If the perturbations are small, however, we will stay near the equilibrium.

In Fig. 1 we can see that for a periodic solution we have to specify A and B exactly. In practice we always introduce some error, so that we can realize this case only approximately.

2) *Stable Focus*

If both solutions for w are complex and have negative real parts, the deviation of the equilibrium after an initial perturbation will disappear by a damped oscillation:

$$\exp[\text{Re}(w) \cdot t] \cdot \exp[i \cdot \text{Im}(w) \cdot t]$$

damping oscillation

For w in both cases to be complex with negative real parts we must have:

$$\alpha > 0, \beta > \alpha^2/4 \text{ (see Fig. 1)}$$

For example: let $n' = n = 0$

$$A^2 - B + 1 > 0$$

$$A^2 > (A^2 - B + 1)^2/4$$

The last inequality can be rewritten as

$$[B - (A + 1)^2] \cdot [B - (A - 1)^2] < 0$$

e.g. (see Fig. 2): $A = 1, B = 1.9$

Test: Numerical solution of V with the above parameters yields Fig. 4.

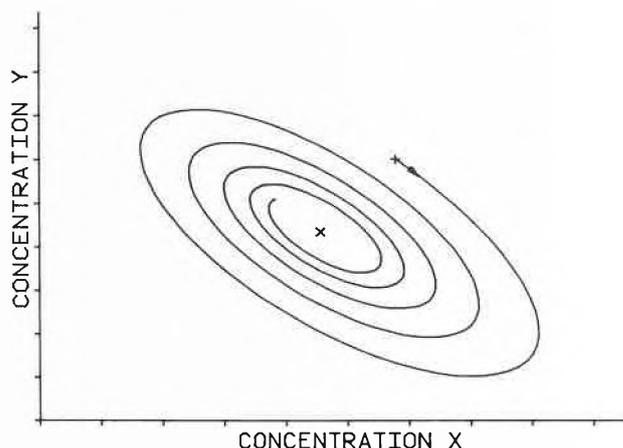


Fig. 4: Stable Focus

$$A = 1, B = 1.9, X_s = 1.01 \cdot A, Y_s = 1.01 \cdot B/A$$

We can see, that every perturbation dies out, hence this system is stable.

3) *Unstable Focus*

If w is complex and has a positive real part, the deviation from equilibrium will oscillate with increasing amplitude. The conditions are:

$$\alpha < 0, \beta > \alpha^2/4 \text{ (see Fig. 1)}$$

For example: $n' = n = 0$:

$$A^2 - B + 1 < 0$$

$$A^2 > (A^2 - B + 1)^2/4 \text{ (see Fig. 2)}$$

e.g. $A = 1, B = 2.2$

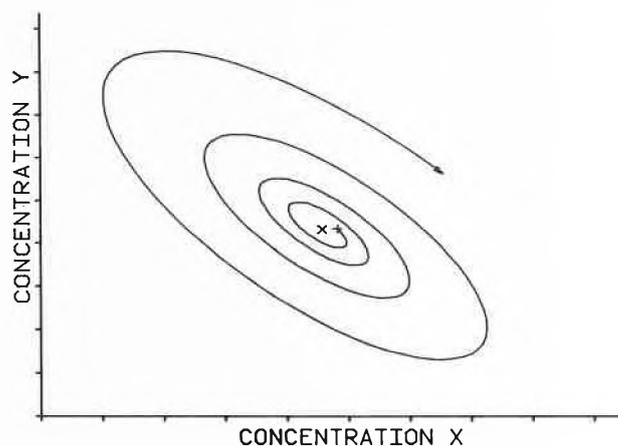


Fig. 5: Unstable Focus

$$A = 1, B = 1.9, X_s = 1.002 \cdot A, Y_s = 1.00 \cdot B/A$$

Test: numerical solution of V yields Fig. 5.

If the deviation from the equilibrium gets large, our assumption $x, y \ll X_e, Y_e$ will break down and our calculation is no longer valid. We get deviations of the "unstable focus"-behaviour here and an analytical solution is hard to find.

An easy way around this problem is to simulate numeri-

cally system V for large x, y with some appropriate initial value, see Fig. 6. By this empirical method we see that the system is asymptotically approaching one macroscopic oscillatory state (limit cycle) independent of the special initial values. We may think of this as a type of chemical clock, whose period is independent of the starting kick. The period depends only on A and B.

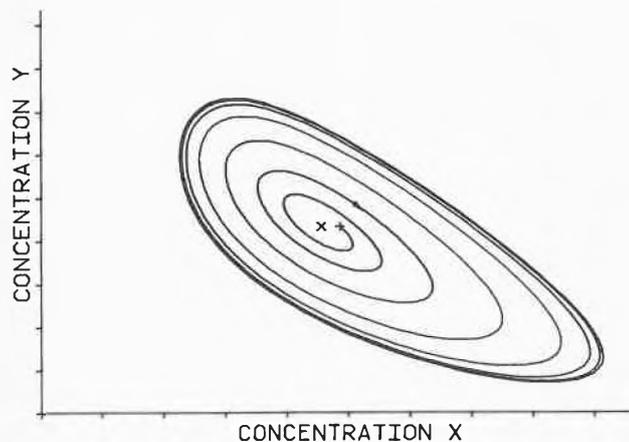


Fig. 6: Unstable Focus, global scale
A = 1, B = 2.2, $X_s = 1.05 \cdot A$, $Y_s = 1.00 \cdot B/A$

A chemical pulse-generator is an interesting variation of this behaviour. In Fig. 7 we have added equidistant time marks to exhibit the temporal behaviour. We see that the concentration of x is low for a long time and suddenly we have a steep increase in x followed by a quick decrease and this behaviour then repeats itself.

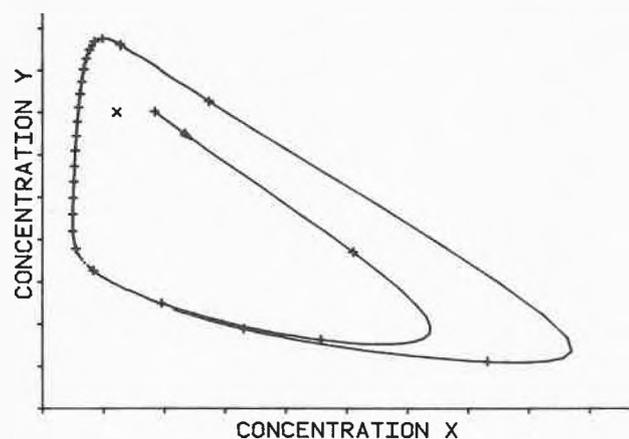


Fig. 7: Pulse generator
A = 0.5, B = 2, $X_s = 1.02 \cdot A$, $Y_s = 1.00 \cdot B/A$

4) Stable node

If w is real and negative, every small disturbance of equilibrium will die out directly without any oscillation, similar to an over-damped pendulum. The system shows its tamest face.

The conditions are:

$$\alpha > 0, \beta > 0, \beta < \alpha^2/4 \quad (\text{see Fig. 1})$$

for example: for $n' = n = 0$:

$$\begin{aligned} A^2 - B + 1 &> 0 \\ A^2 &> 0 \\ A^2 &< (A^2 - B + 1)^2/4 \quad (\text{see Fig. 2}) \\ \text{e. g. } A &= 0.5, B = 0.2 \end{aligned}$$

Test: See Fig. 8 for a numerical solution of V with 4 different initial values. Notice that oscillatory features are already evident.

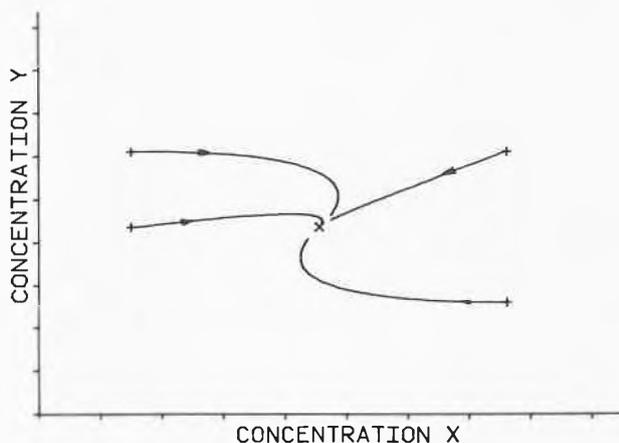


Fig. 8: Stable node
A = 0.5, B = 0.2, $X_s = 1.05 \cdot A$, $Y_s = 1.05 \cdot B/A$
 $X_s = 0.95 \cdot A$, $Y_s = 1.05 \cdot B/A$
 $X_s = 0.95 \cdot A$, $Y_s = 1.00 \cdot B/A$
 $X_s = 1.05 \cdot A$, $Y_s = 0.95 \cdot B/A$

5) Saddle point and unstable node

The case of w real, w_+ positive, and w_- negative is termed saddle point. Theoretically, we can prepare the system so that in the solution $a_+ \exp(w_+ t) + a_- \exp(w_- t)$, a_+ vanishes. This means we retain only the decaying part and we approach equilibrium. In practice, however, we are never able to prepare the initial conditions without error, so that the growing part never completely disappears and we always have a somewhat unstable behaviour. Its importance depends on the time period of our experiment.

If both roots w_+, w_- are positive the solution always drifts away from equilibrium and we have the case of the unstable node.

Neither case is possible for homogeneously distributed reagents (i. e. $n = 0$), because for $n' = n = 0$ we have:

$$\begin{aligned} \text{saddle point: } \beta &= A^2 < 0 \\ \text{unstable node: } \alpha &= A^2 - B + 1 < 0 \quad \text{and} \\ &\beta > 0 \\ &\beta < \alpha^2/4 \rightarrow A^2 < (A^2 - B + 1)^2/4 \\ &(\text{see Fig. 1}) \end{aligned}$$



Fig. 9

Therefore we have to admit some spatial variations in x and y .

Below we give an example taken from [4]. It simplifies the spatial variation by two discrete homogeneous vessels. Imagine two identical vessels, homogeneously filled with our reagents, that are joined by a small tube, see Fig. 9. The diffusion term for the mass transfer between the two vessels ($D_x \nabla^2 x, D_y \nabla^2 y$) can be written as:

$$D_x (x_i - x_j) \text{ and}$$

$$D_y (Y_i - Y_j) \quad (i, j) = (1,2), (2,1)$$

Substituting into V we get:

$$dX_1/dt = A - (B + 1)X_1 + X_1^2 Y_1 + D_x(X_2 - X_1)$$

$$dY_1/dt = BX_1 - X_1^2 Y_1 + D_y(Y_2 - Y_1)$$

and we treat the second vessel analogously.

With $D_x = 1, D_y = 5$ after a linear stability analysis, we get an unstable node when for example $A = 2, B/A = 2.62$. A numerical simulation yields Fig. 10. A small perturbation of one of the two identical vessels results in two completely different vessels.

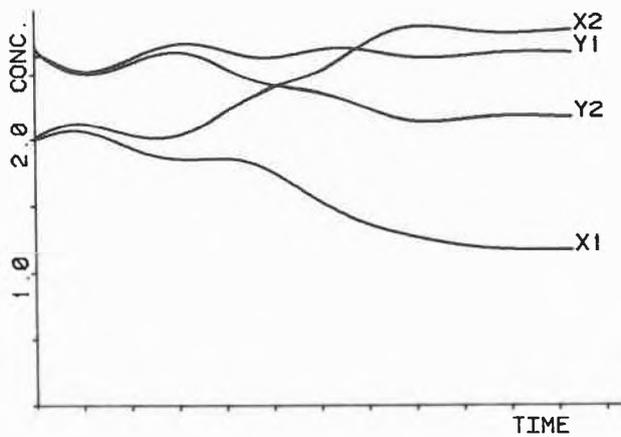


Fig. 10: Emergence of asymmetry in a discrete symmetric system

$$A = 2, B = 5.24, X_{s1} = X_{s2} = 2$$

$$Y_{s1} = 0.5 * B/A, Y_{s2} = 0.5 * B/A + 0.1$$

$$D_x = 1, D_y = 5$$

In general, the condition for a saddle point will be:

$$\beta = A^2 + [A^2 D_x - (B - 1) D_y] n'^2 + D_x D_y n'^4 < 0$$

For example: for $n' = 1$ ($l = \pi, n = 1$) and $D_x = 0.5, D_y = 1, A = 1$ we get $B > 3$ and we may choose $B = 3.05$.

Since x and y increase, we face the same problem as in the case of the unstable node. The simple linear stability analysis does not give us the solution $x(r,t), y(r,t)$ and an analytical solution is hard to find.

We may again attempt to find a numerical solution of V for large x, y with the above parameters and several different initial conditions. Six solutions are shown in Fig. 11. Instead of one, we get two stable points! At first

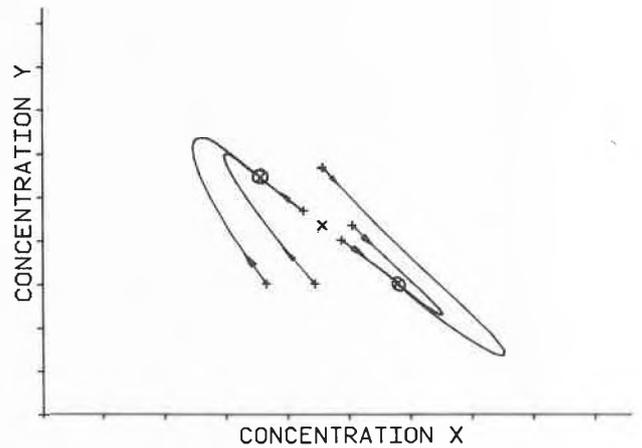


Fig. 11: Bifurcation

$$A = 1, B = 3.05, D_x = 0.5, D_y = 1$$

$$X_s = 1.05 * A, Y_s = 0.975 * B/A$$

$$X_s = 0.95 * A, Y_s = 1.025 * B/A$$

$$X_s = 1.08 * A, Y_s = 1.000 * B/A$$

$$X_s = 1.00 * A, Y_s = 1.100 * B/A$$

$$X_s = 0.98 * A, Y_s = 0.900 * B/A$$

$$X_s = 0.85 * A, Y_s = 0.900 * B/A$$

this looks quite exciting, however this phenomenon is not a rare one (see. e.g. [5]).

The question of how one stable state disappears and creates two new ones, a so called bifurcation, now remains to be answered. We only give a brief outlook and for more detailed description the reader is referred to [1]. Think of any parameter which allows the equilibrium state to be changed continuously across the border between stable and unstable behaviour (e.g. stable node and saddle point). Take B , for example, as a parameter and fix A . We can then try to expand the solution $x(r,t), y(r,t)$ in a power series of B around that value of $B: B_0$ which corresponds to the crossing point. If this analysis is done (see [1]), one finds three different possibilities for a bifurcation from one to two stable points. If we graph some quantity of the system (e.g. x) versus our parameter (e.g. B) we get the following figures for the three possibilities.

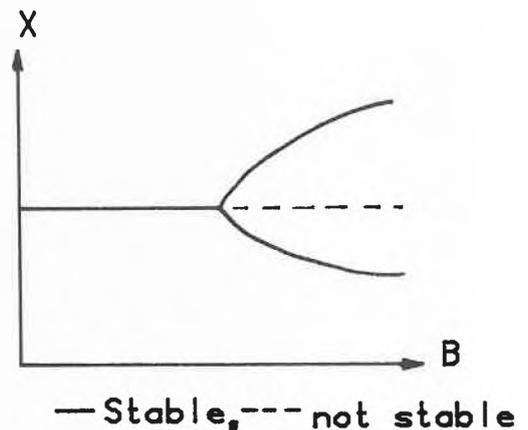


Fig. 12

In Figure 12 we have a smooth change from one stable point to two stable points. Which path the system will take can not be predicted and will be determined by the microscopic fluctuations.

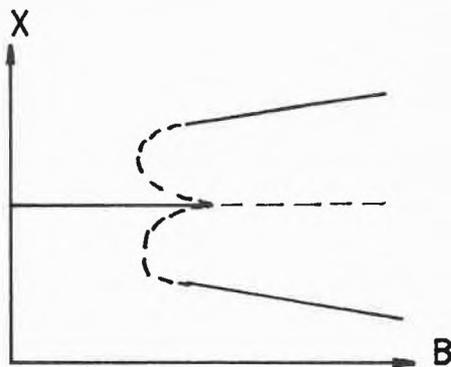


Fig. 13

In Fig. 13 our system jumps when we vary B through B_0 , a so called "catastrophe" occurs. Suddenly the equilibrium loses its stability and the system jumps to one of the stable states. On the way back, the jump will not appear at the same place, which implies that we have hysteresis. Again we can not foresee which path the system will take. The last possibility, Fig. 14, is a mixture of the former two.

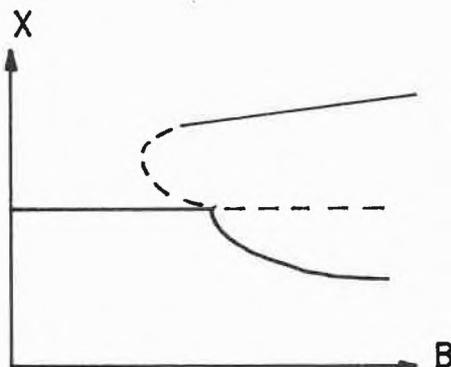


Fig. 14

Conclusions

The stochastic behaviour on the microscopic level permanently creates small perturbations on the macroscopic level. Therefore it is not sufficient to describe reactions in terms of equilibrium and rate equations. We should always consider what happens when the equilibrium or rate equation is slightly perturbed. We saw that a small perturbation can either die out with time, produce some oscillatory behaviour, or grow and drive the system into a new, different state. The behaviour of a system can be controlled by some suitable parameters like A and B.

The author thanks Prof. E. Schumacher for his interest and encouragement during the elaboration of this article.

Appendix 1

Numerical solution of an ordinary differential equation

The following differential equation gives us the rate of change of c with respect to time:

$$dc_{r,t}/dt = f(c,t) \quad \text{where } f \text{ is any function.}$$

With a starting value $c_0(r)$ for $c_{(r,t)}$ at time $t = 0$ we can calculate the rate of change for $t = 0$. If we assume that the rate of change c will stay constant in the lapse of time dt, we can approximately calculate c at the time $t = dt$.

$$c(t = dt) = c_0 + dc/dt(t = 0) \cdot dt$$

Repeating this step with starting value $c(t = dt)$ we get $c(t = 2dt)$ approximately and so on. The smaller we let dt be, the better our approximation.

Advanced methods use better approximations for the variation of c during dt (e. g. Runge-Kutta).

Appendix 2

Diffusion (1 dimensional)

Compare the molecules in a solution with a corral crowded with cattle. If there is a place of higher density, say at the entrance because of a couple of newcomers, the animals will tend to redistribute themselves evenly. The molecules in a solution behave similarly.

If we define the flow I at point x as the number of molecules crossing x (positive from left to right), then there is always a flow in the direction of decreasing concentration proportional to the change of concentration per unit length. Express this as

$$I = -D \cdot dc/dx \quad \text{where } D = \text{diffusion constant}$$

See Fig. 01.

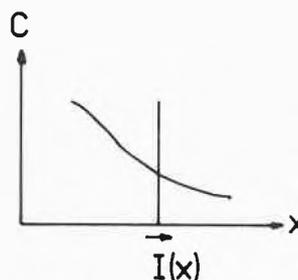


Fig. 01

If we want to calculate the rate of change of the number of molecules in the region dx, we have to take into account the flow of the left side and the right side. If one side brings molecules in and the other side takes molecules out, the situation is analogous to a bath-tub where the water is turned on and the drain is open. To calculate the rate of change we have to consider the total flow (counting the flow toward right as positive).

Change of the number of molecules in dx during dt = $-(I(x+dx) - I(x)) \cdot dt$. See Fig. 02.

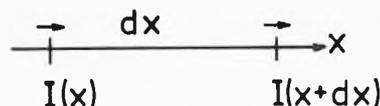


Fig. 02

The concentration c gives the number of molecules per unit length, and dc/dt is the concentration change per unit time so we have to divide the above expression by $dx \cdot dt$:

$$\begin{aligned}dc/dt &= - [I(x + dx) - I(x)]/dx \\ &= D^* [dc/dx(x + dx) - dc/dx(x)]/dx \\ &= D^* d^2c/dx^2\end{aligned}$$

For 3 dimensions we have to replace d/dx by ∇ and d^2/dx^2 by ∇^2 .

Literature

- 1 *I. Prigogine and G. Nicolis: Self organisation in nonequilibrium systems. Wiley Interscience (1977)*
- 2 *V. Volterra: Lecons sur la theorie mathematique de la lutte pour la vie. Gauthier-Villars, Paris (1936).*
- 3 *A. Lotke: Proc. Nat. Acad. Sci. 6, 420 (1920).*
- 4 *I. Prigogine: Vom Sein zum Werden. Piper (1970).*
- 5 *P. Collet and J.P. Eckmann: Iterated maps on the interval. Birkhäuser (1980).*
- 6 *A. T. Winfree: Scientific American, June (1974).*
- 7 *R. J. Field: J. Chem. Educ., 49 (5), p. 308 (1972).*
- 8 *R. J. Field: J. Chem. Phys., 63 (6), p. 2289 (1975).*
- 9 *R. J. Field and R. M. Noyes: J. Chem. Phys., 60 (5), p. 1877 (1974).*