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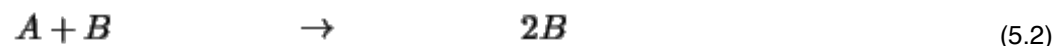
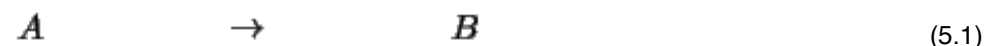
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The Belousov-Zhabotinski Reaction

For most chemical reactions, a state of homogeneity and equilibrium is quickly reached. The Belousov-Zhabotinski reaction is a remarkable chemical reaction that maintains a prolonged state of non-equilibrium leading to macroscopic temporal oscillations and spatial pattern formation that is very life-like. Many different preparations can be used to illustrate the BZ reaction. One typical combination consists of sulphuric acid in which is dissolved: cerium sulfate $\text{Ce}_2(\text{SO}_4)_3$, malonic acid $\text{CH}_2(\text{COOH})_2$, and potassium bromate KBrO_3 . If the reactants are well-stirred in a beaker, then for the right initial concentrations one observes oscillations

(lasting minutes) in the system, with the system changing alternately between a yellow colour and colourless. The yellow is due to the preponderance of Ce^{4+} ions while the colourless state is due to the Ce^{3+} ions. This behaviour of the system is in the literature called a chemical clock, and is often studied as a prototype of a simple biological system. Note that in this case there is spatial homogeneity (symmetry) but temporal variation caused by the non-equilibrium, in contrast to the Benard cell example which displayed spatial inhomogeneity. What is the cause of the chemical oscillations? The actual reaction is very complicated and involves many steps but the key features can be illustrated by a highly simplified model as discussed by Ball [2]. Let the first step be the conversion of material A into B , followed by a second *autocatalytic* reaction:



In reaction (5.2), the substance B is acting as a catalyst since each molecule of B on the left-hand-side reappears on the right-hand-side. However notice that more of the catalyst B is produced than one started out with. Thus the rate of reaction (5.2) depends on the product formed and consequently speeds up because of the positive feedback. Let us now assume that there is a second competing branch in which two processes take place :



Step (5.4) is an autocatalytic reaction that tends to reduce the amount of substance B , in opposition to step (5.2) that increased it. Now let us suppose that there is an indicator included in the reactions that turns red in the presence of B and blue in the presence of C . If the reaction is started with A and some C , then step (5.2) would dominate over step (5.4) because initially there is much more A than C (recall that reaction rates are proportional to concentrations of reactants). Thus there will be a rapid increase in the concentration of B , until the amount of C increases to a point where the second autocatalytic process takes over to reduce the concentration of B . Thus there will be a colour change from red to blue. Step (5.4) consumes C however and eventually the amount of C present will diminish as its production from step (5.4) has also been reduced (because of the low concentration of B). Hence step (5.2) regains its dominance and one sees a switch from blue to red. These oscillations will continue as for some time until the supply of A is used up or until the waste product D clogs up the system.

Therefore continued oscillations are possible only if there is an influx of A and a removal of D . In other words, inflow and dissipation processes are crucial in maintaining the system far from equilibrium and the resulting formation of a temporal dissipative structure. A number of *quantitative* models have been developed in the literature to study the BZ reaction. One of them is the "Oregonator" model which is discussed in the exercises below. The BZ reaction can also display spatial inhomogeneity if the ingredients are combined in a shallow dish without stirring. Then because of the autocatalytic reactions, small random differences in concentration are amplified leading to propagating wave fronts of chemicals (think of the water wave fronts in a pond when it is disturbed by a stone thrown in it).

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