Spontaneous formation of chemical motors in simple inorganic systems

JERZY MASELKO, POLINA BORISOVA, MATT CARNAHAN, ERIC DREYER, RON DEVON, MANUELA SCHMOLL, DARYL DOUTHAT
Departments of Chemistry, Physics and Astronomy, University of Alaska Anchorage, Anchorage, AK 99504, USA
E-mail: AFJM1@uaa.alaska.edu

In "Living Systems" [1] Miller defines motors as the "subsystem which moves the system or parts of it in relation to part or all of its environment or moves components of its environment in relation to each other." An example of motor that arise in biological systems is the osmotic pump that is capable of transporting nutrient containing fluids.

In most structures, transport of matter is precisely organized in space and time. One example is the formation of Liesegang [2–4] patterns where precipitation-reactions result from the diffusion of chemicals. As a result, precipitation rings are formed which are separated by a pure solution. Other examples are the formation of domes in the precipitation process [5] and the movement of solids on the surface of a solution [6, 7]. In this paper we present six different chemical motors which are involved in the formation of complex structures.

Stock solutions were prepared using double distilled water and reagent grade chemicals. Pellets were prepared with reagent grade chemical. The diameter of pellets was 0.60 cm and had a mass of 0.20 g. Reactions were conducted in a Petri Dish or in a beaker at temperature of 20+-1 °C. In the case of Petri Dish the pellets were immersed in the solution to a depth of 4 mm.

1. The Cu^{2+} - CO_3^{2-} system, pH = 8.0–9.0. A chemical cannon. After immersing a pellet of copper sulfide in a solution of sodium carbonate, a periodic movement of the resulting precipitate to the surface of the solution was observed. The chemical process may be described by the following set of equations:

$$Cu^{2+} + CO_3^{2-} + 2H_2O \rightarrow Cu_2(OH)_2CO_3 + 2H^+ \quad (a)$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2 \quad (b)$$

During formation of the $Cu_2(OH)_2CO_3$ precipitate, the CO_2 produced in reaction (b) is incorporated into the precipitating compound, thereby forming blobs of inorganic foam. Its density is less than the density of the solution whereas the density of the precipitate without carbon dioxide is 4.4 g/cm^3. The movement of inorganic foam above a pellet is shown in Fig. 1. The process of blob formation is periodic as is shown in Fig. 2 and the period is a simple function of carbonate ion concentration (Fig. 3). As may be expected, the period decreases with increasing carbonate ion concentration.

2. The Cu^{2+} - H_2O system. The copper ions from the $CuSO_4 \times 5H_2O$ pellet dissolve in water, forming copper sulfate solution around the pellet. Due to the increased density, the copper solution moves to the bottom exposing a new portion of the pellet to the fresh solution. Convection of solution occurs away from the pellet and, as observed from above, a blue disk of copper ion solution spreads on the bottom. The velocity of the movement is a function of the distance from the pellet. Since the rate of the dissolution is nearly constant, the rate at which the radius increases is proportional to $1/r$, where r is the radius. This process repeats itself until the pellet is dissolved. Even though this system is unusually simple, it still fulfills Miller's definition of a chemical motor.

3. The Ca^{2+} - $C_2O_4{}^{2-}$ system. Concentration of oxalate 0.08 M. Following the submersion of a pellet of $CaCl_2 \times 2H_2O$ in a saturated solution of sodium oxalate, white clouds of solid are observed rising vertically from the pellet. After reaching the top of the solution, the precipitate spreads along the surface and eventually moves downward and away from the pellet. The mechanism is as follows:

$CaCl_2 \times 2H_2O$ dissolves according to the following reaction:

$$CaCl_2 \times 2H_2O + nH_2O \rightarrow Ca^{2+}\ (aq) + 2Cl^-\ (aq)$$

This reaction is slightly endothermic.

$$Ca^{2+}(aq) + C_2O_4^{2-}(aq) + 3H_2O \rightarrow CaC_2O_4(s) \Delta H = 32.1\ \mathrm{kJ/mol}^8$$

This process begins with a precipitate forming at the interface of the pellet and the solution. Some of the precipitate spreads radially on the bottom of the container and some is transported upward above the pellet. Then it spreads on the surface, and descends in the convection currents that form as a consequence of local heating of the solution. During the process of dissolution, heat is released which increases the temperature of the solution near the pellet. Due to the consequent buoyancy of this heated solution, it rises and carries with it the precipitate of calcium oxalate that is forming. The convection current cell includes a plume that rises above

0022-2461

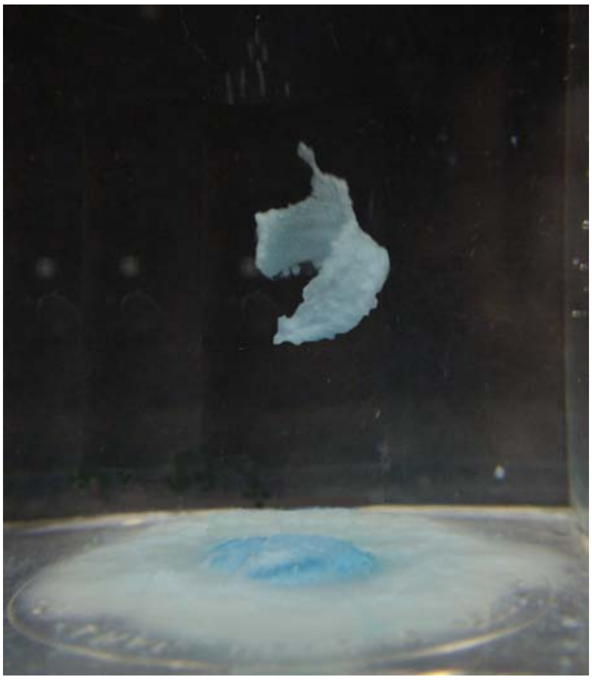

Figure 1 The Chemical Canon. The flake moves above the rest of the pellet. 0.10M Na_2CO_3. Pellet: $CuSO_4 \times 5H_2O$.

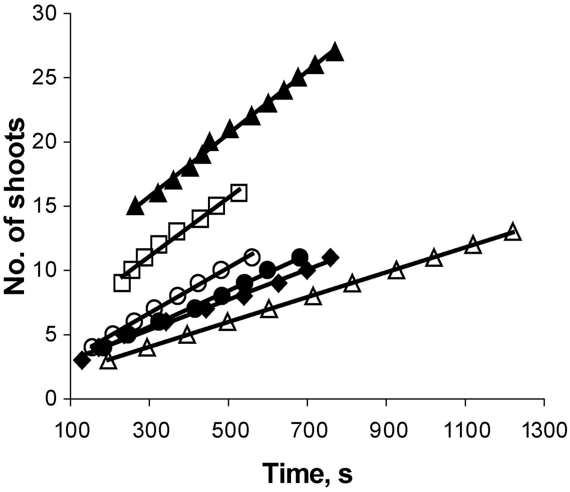

Figure 2 Shoots vs. time (seconds) for different concentrations of Na_2CO_3 (in mol/L). The shoots are defined as release of an inorganic foam above the pellet ▲ 0.16 M, ☐ 0.13 M, ◯ 0.11 M, • 0.09 M, ◇ 0.07 M, △ 0.06 M. The transient behaviors are not shown.

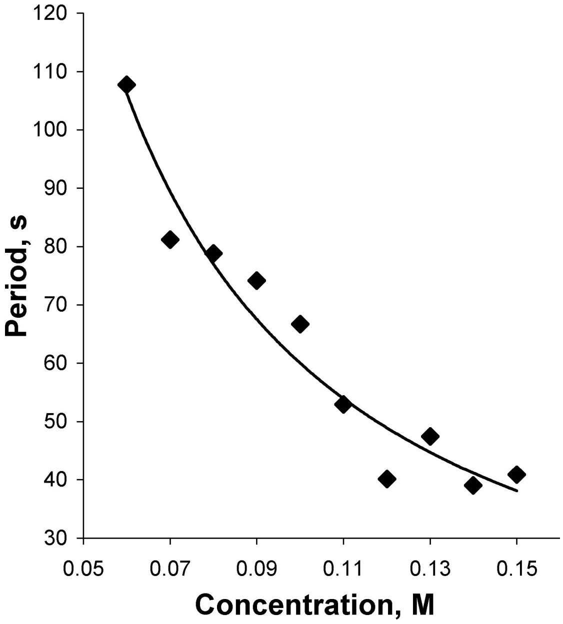

Figure 3 Period vs. concentration of Na_2CO_3 in mol/L. The period was determined from a linear regression of the shoots vs. time.

the center of the pellet, spreads radially upon reaching the surface, and then descends. Simultaneously, a thin disc made of precipitate forms on the bottom of the container.

4. The $Cu^{2+} \pm PO_4^{3-}$: dome formation. Concentration of phosphate below 0.06 M. In addition to the formation of the disc that is described above in the Cu^{2+} - H_2O system, the precipitation of copper phosphate is observed [5]. Directly above the pellet, an elastic semi-permeable membrane is formed. Farther from the pellet, a solid precipitate is formed above the copper solution in the shape of a dome that stops the movement of the solution. The concentration of copper ion inside the dome is different from that on the outside. This concentration difference causes water to diffuse through the membrane into the dome. The subsequent increase of hydraulic pressure causes upward movement of the dome. This process repeats itself until the pellet is dissolved.

5. The Ca^{2+} - CO_3^{2-} system. Concentration of carbonate 1.5 M. The basic structure observed in the “silicate garden” [9–12] consists of vertical pipes which transport the solution. A crystal of salt is immersed in a solution of silicate or carbonate that will react with the metal in the crystal to form a membrane. The solution inside the membrane has a lower density than the anion solution outside. Due to its buoyancy it pushes the membrane up. The membrane bursts at the top. The two reactants meet and produce precipitate on the edge of the pipe. As the solution inside continues to be pushed through the pipe, the process of pipe building continues. The pipes may be smooth or have a periodic structure [9].

In another modification of this pump, the membrane forms a cell. This cell may form daughter cells that break from the mother cell and migrate to the surface transporting the inside solution as is shown in Fig. 4. A similar phenomena of cell formation was reported in the Cu^{2+}-silicate [11] system, but in this case the copper solution was pumped from a dish instead of a pellet. The periodic formation of cells carrying the solution to the top was discovered

6. The Cu^{2+} - PO_4^{3-}: vertical and horizontal pipes formation. Phosphate solution 0.4 M. In this system the most complex mechanism has been observed. A pellet of copper sulfate was immersed in a solution of tri-sodium phosphate. In this case, the copper dissolves forming a solution that is more dense that the Na_3PO_4 solution. This solution moves along the bottom forming horizontal pipes. These pipes may be as long as 25 cm. In our experiments, during the formation of the pellets the air was captured inside the pellet and was not further removed. Therefore the copper solution which includes air bubbles migrates to the end of the pipe. On the end of the horizontal pipes the membranes are more elastic and as the bubbles push up, formation of the

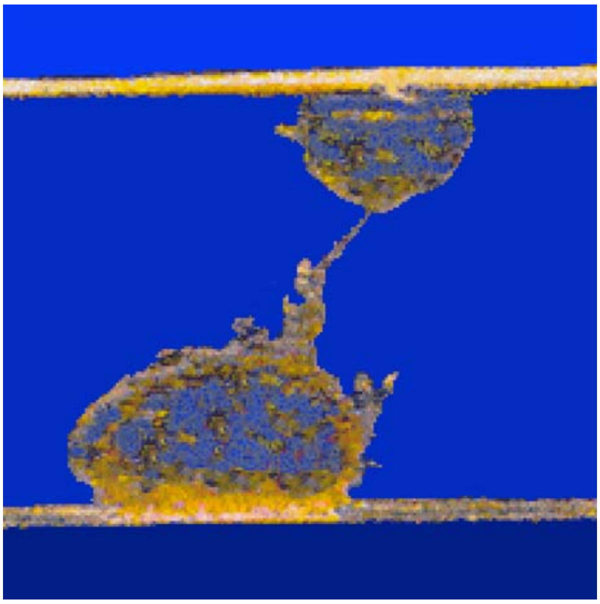

Figure 4 The other kind of chemical motor in the Ca^{2+} - $CO_3{}^{2-}$ system. The balloon transports a solution to the surface. The concentration of CO_3^{2-} is 0.15 M.

vertical pipes is observed with an air bubble at the top of each. The movement of the bubble and the growth of the tube are related. The forces that are crucial in the process and act on the bubble are: the buoyancy of the air bubble, the surface tension of the exterior solution that is directed downward, the solution gravitational force directed downward, the surface tension of the solution inside that pushes up. In addition, the osmotic forces and the capillary forces are also pushing up.

In chemical systems, the interaction between diffusion and chemical reactions is the source of chemical waves, chemical fronts, and Turing patterns. The movement of the solution increases the variety of patterns [15–17]. Here we concentrate on the interactions of precipitation patterns and chemical transport. As a result, the self-construction of unusual complex structures is observed in simple chemical systems [5]. These structures are on the scale of centimeters. Following Miller [1], we propose that the process of structure formation is best described by considering simple elements of the systems as motors. These motors may serve new materials science technologies based on mimicking biological processes.

In our experiments the forces that move the matter were:

1. Buoyancy; The buoyancy was caused by chemical dissolution reaction forming solution with bigger density then surrounding solution (case 2), exothermic or endothermic chemical reaction, (case 3) formation of gases by chemical reaction, (case 1), existing gases from initial conditions (case 6),
2. Osmotic pressure that may cause the movement of solutions (case 4) or solids (case 4),
3. Surface tension (capillary effect) (case 5),
4. In few cases we observed interactions of different forces (case 5).

REFERENCES

1. J. B. MILLER, Living Systems (McGraw-HillBook Co.: New York, NY, 1978).
2. R. LIESEGANG, *Naturwiss Wochenschr.* **11** (1896) 353.
3. S. MUELLER, S. KAI and J. ROSS, *J. Phys. Chem.* **86** (1982) 4078.
4. Z. RACZ, *Physica A.* **274** (1999) 50.
5. J. MASELKO, A. GELDENHUYS, J. MILLER and D. ATWOOD, *Chem. Phys. Lett.* **373** (2003) 563.
6. S. NAKATA and Y. HAYASHIMA, *J. Chem. Soc. Faraday Trans.* **94** (1998) 3655.
7. S. NAKATA, H. KOMOTO, K. HAYASHI and M. MENZINGER, *J. Phys. Chem. B* **104** (2000) 3589.
8. E. KONIGSBERGER and L.-C. KONIGSBERGER, *Pure Appl. Chem.* **73** (2001) 785.
9. S. T. LEDUC, The Mechanism of Life; (Rebman Co.: New York, NY, 1911).
10. C. COLLINS, W. ZHOU, A. MCKAY and J. KLINOWSKI, *J. Chem. Phys. Lett.* **286** (1998) 88.
11. R. COATMAN, N. THOMAS, D. DOUBLE, *J. Material Sci.* **15** (1980) 2017.
12. J. CARTWRIGT, J. GARCIA-RUIZ, M. NOVELLA and F. OTALORA, *J. Colloid and Interf. Sci.* **256** (2002) 351.
13. S. THOUVENENEL-ROMANS and O. STEINBOCK, *J. Am. Chem. Soc.***125** (2003) 4338.
14 I. R. EPSTEIN, J. POJMAN, An Introduction to Nonlinear Chemical Dynamics; (Oxford University Press, 1998).
15. M. J. B. HAUSER, R. SIMOYI, *Phys. Lett. A* **191** (1994) 31.
16. *Idem.*, *Chem. Phys. Lett.* **227** (1994) 593.
17. K. MATTHIESSEN and S. C. MULLER, *Phys. Rev. E* **52** (1995) 492.

Received 2 February
and accepted 3 February 2005