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Minimal Permanganate Oscillator: The Guyard Reaction in a CSTR[1]

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The concept[2] of a minimal oscillator within a family of oscillating chemical reactions has been extremely useful in guiding the design of new chemical oscillators. Both the minimal bromate[3] and the minimal chlorite–iodide systems[4] have led to the discovery and categorization of families of related oscillating reactions.[5,6]

Recently, the first transition metal based oscillator, the $KMnO_4$–H_2O_2–H_3PO_4 reaction, was found,[7] and this has been followed by reports of two other permanganate oscillators.[8,9] We have discovered oscillatory behavior in a large number of other permanganate oxidation reactions in a flow reactor (CSTR). From these systems, we have been able to construct the simplest version of a permanganate oscillator, in which only manganese species play principal roles. This reaction, the venerable Guyard reaction[10] between permanganate and manganese(II) ions in a CSTR, may be regarded as a core system from which many other oscillators may be built, since other oscillatory permanganate reactions generate Mn(II).

We report here the most important results on the minimal permanganate oscillator. Further details as well as a characterization of several new oscillators derived from this system will appear elsewhere.

The experiments were carried out at 25.0 °C in a 20.5-cm^3 glass CSTR equipped with a magnetic stirrer and Pt and glass electrodes. The four feed streams from the peristaltic pump contained $KMnO_4$, $MnSO_4$, KH_2PO_4, and NaOH. In Figure 1, we show typical oscillations observed in the Pt electrode potential. The pH remains constant during the oscillations at a value between 6 and 7, depending on the input concentrations. The solution is yellow-brown during the oscillations, which are accompanied by periodic precipitation of MnO_2.

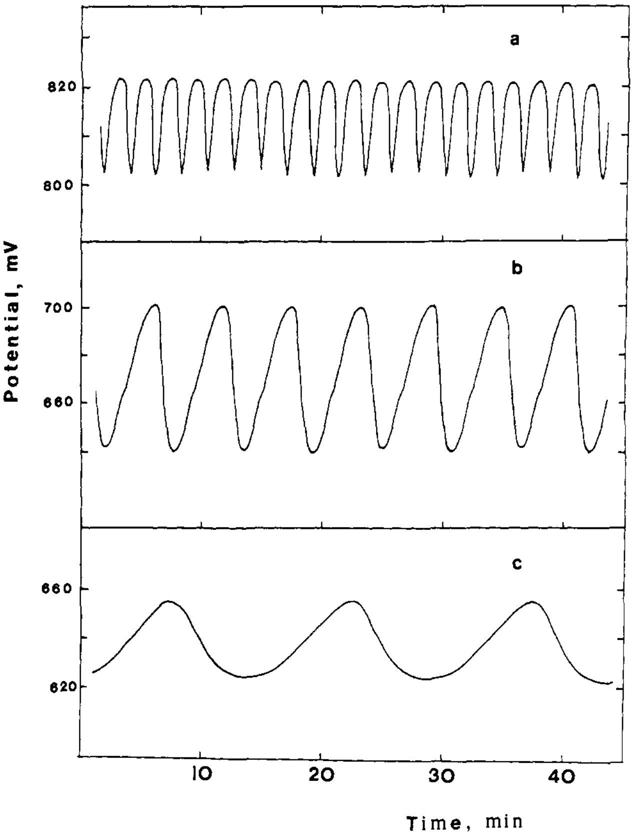

Figure 1. Oscillations in the potential of a Pt electrode with $[KMnO_4]_0 = 9 \times 10^{-5}$, $[MnSO_4]_0 = 2.5 \times 10^{-4}$, $[KH_2PO_4]_0 = 1.5 \times 10^{-3}$, and $[NaOH]_0 = 1.0 \times 10^{-3}$ M. Flow rates: (a) 0.048, (b) 0.019, and (c) 0.0085 s^{-1}.

The range of input concentrations and flow rates in which the system oscillates is quite narrow, as seen in Figure 2. Above the oscillatory region in the figure, the solution is dark brown, while below it the solution is pinkish brown. In contrast to other minimal oscillators,[3,4] no bistability was observed under any conditions. The amplitude of the oscillations increases with the input $KMnO_4$ and Mn(II) concentrations, reaching a maximum of about 100 mV. Increasing the flow rate through its oscillatory range of $(5–20) \times 10^{-3}$ s^{-1} decreases the oscillation period from about 30 to about 2 min, while the amplitude increases to a maximum and then decreases. The inputs of KH_2PO_4 and NaOH must also be kept within relatively narrow limits, about $(1.2–3.0) \times 10^{-3}$ and 5×10^{-4} to 1×10^{-3} M, respectively.

At the pH of the minimal manganese oscillator, the stable oxidation states of manganese are +2, +4, and +7, and the overall reaction is

$$2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2 + 4H^+ \qquad (1)$$

The rate of this reaction, important in the permanganometric determination of Mn(II), increases with pH. Reaction 1 is autocatalytic,[11,12] being accelerated by Mn(IV), which can precipitate as solid brown MnO_2 or can remain in solution in a soluble yellow form. The stability of the yellow solution to flocculation is greatly enhanced by phosphate ions, and the soluble form may be regarded as colloidal MnO_2 stabilized by phosphate[13] or as a hydroxo-bridged binuclear phosphatomanganese(IV) complex.[14-16]

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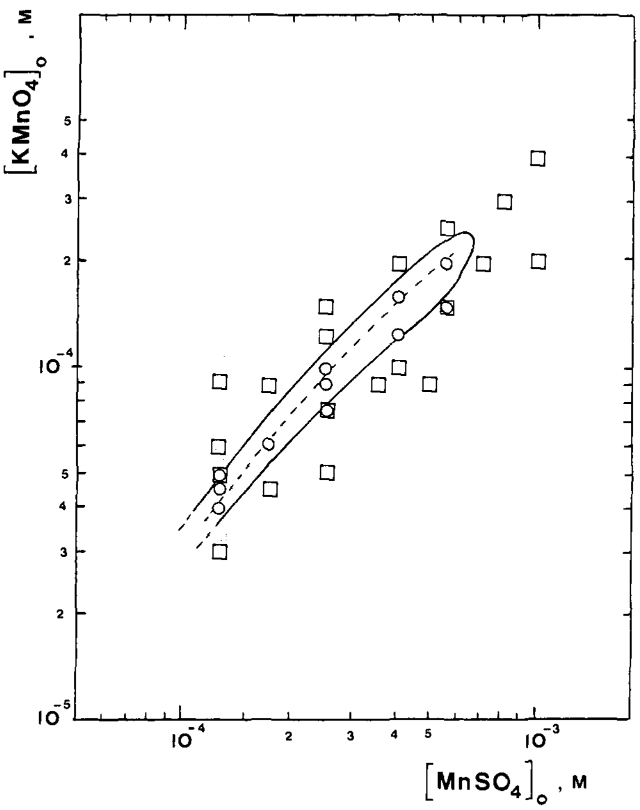

Figure 2. Phase diagram in the input $[KMnO_4]_0$ – $[MnSO_4]_0$ plane showing the oscillatory domain at fixed inputs $[KH_2PO_4]_0 = 1.6 \times 10^{-3}$ M and $[NaOH]_0 = 1 \times 10^{-3}$ M. Along the broken line within the oscillatory region, the reciprocal residence time k_0 can be varied from 0.005 to 0.020 s^{-1}. At other points, oscillation occurs only for k_0 between 0.005 and 0.010 s^{-1}. Symbols: ○, sustained oscillations; ⊡, damped oscillations; ☐, nonoscillatory steady state.

Phosphate ion (as $H_2PO_4^-$) appears to be essential for the minimal manganese oscillator. Efforts to replace this species with others known to form stable complexes with manganese intermediates ($P_2O_7^{4-}$, F^-) were unsuccessful. We believe the phosphate plays *two* key roles. First, it influences the formation of soluble Mn(IV) and its rate of flocculation to solid MnO_2, which serves as the autocatalyst, apparently via a surface effect. Equally important, because the rate of the Guyard reaction is extremely pH-dependent, the added KH_2PO_4 serves as a buffer, capturing the H^+ formed in reaction 1 and maintaining the pH of the system close to 7.

Based on our experiments and Tompkins's proposed mechanism[12] for the Guyard reaction, we suggest the following skeleton mechanism to account for the oscillatory behavior:

$$MnO_4^- + Mn^{2+} + H_2O \rightarrow Mn^{3+} + HMnO_4^- + OH^- \quad (M1)$$

$$HMnO_4^- + Mn^{2+} + OH^- \rightarrow 2MnO_2 + H_2O \quad (M2)$$

$$Mn^{3+} + H_2O \rightarrow Mn(OH)^{2+} + H^+ \quad (M3)$$

$$2Mn(OH)^{2+} \rightleftarrows [MnO^{2+}]_{sol} + Mn^{2+} + H_2O \quad (M4)$$

$$[MnO^{2+}]_{sol} + OH^-/H_2O \rightarrow MnO_2 \quad (M5)$$

Steps M2 and M5 are slow, with M2 somewhat slower, so that the main source of MnO_2 precipitate is step M5,[12] the rate of which depends strongly on $[HPO_4^{2-}]$. Step M3 represents the partial hydrolysis of Mn^{3+}, which results in a soluble hydrated oxide that can be present as a dimer or in a polymeric form. The hydrated Mn(III) oxide undergoes disproportionation in step M4 to a soluble Mn(IV) species and Mn^{2+}. The $[Mn(IV)]_{sol}$ first forms a supersaturated solution and then generates MnO_2 precipitate autocatalytically as the result of nucleation and surface effects.[11,13] While using other reducing agents in place of Mn^{2+} can produce oscillators that are more robust in their pH or concentration ranges, they are likely to operate via the same overall dynamics. The key to understanding the behavior of the entire family of manganese oscillators will almost certainly lie in this minimal core system.

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Computer Software Reviews

FitAll. Version 2.04. MTR Software: P.O. Box 902, Station P, Toronto, Ontario M5S 2Z2, Canada. List Price \$40.00 + \$5.00 S&H, no discounts mentioned.

Fitall is a general-purpose, nonlinear, least-squares regression analysis program that can be used to fit a set of experimental data to any one of up to 20 defined functions of your choosing. Two-dimensional graphs of the original data, of the calculated best fit curve, and of the residuals can be displayed on the computer's monitor. It requires an IBM PC/XT/AT or "true" compatible computer with at least 512K RAM, one disk drive, a color graphics adapter, PC/MS DOS 2.0 or later operating system, and TurboPascal v3.0.

The program disk comes with a compiled version of the program that will run without owning TurboPascal v3.0. Nine of the 20 possible functions to choose for fitting are already defined, e.g., $Y + A + BX = C/X^2$ determines A, B, and C for your input set of X,Y data. The program works very well and has easily understood commands in the menus. The compiled version would be an excellent choice for analyzing data in an undergraduate physical chemistry laboratory or for standard fitting of data. A nice feature is the submenu that allows one to modify the data by taking the log, ln, sin, etc. of one or more sets of data. Inverting, scaling, and offsetting are also possible in the modify data submenu.

Data, both input and calculated, are claimed to be capable of being saved to disk in standard ASCII files (checked) or in Lotus 1-2-3 readable files (not checked). This will be an important feature because the autoscaled plots did not place the labels along the axes uniformly with respect to the tic marks. Thus, to prepare plots for publication, the data will have to be exported to a program that will drive a plotter or laserprinter; however, the plots produced by FitAll could be easily redrawn for publication by a draftperson.

The real power and versatility of FitAll is in the ability to input your own special mathematical relationships via the TurboPascal Editor and to fit functions with more than one independent variable. One must use v3.0. A later version did not work. This feature of FitAll allows it to be used in advanced research work where fitting to new relationships would be required. The procedure is relatively painless and is well documented in the usually well written but occasionally incomplete manual (provided on disk).

FitAll v4.0, the most current version of the program is now available in two versions: FitAll Standard v4.0, List price \$50.00 (compiled, no source code), and FitAll Research v4.0, List price \$75.00 (source code, not compiled, requires a high-capacity drive and TurboPascal v4.0 or 5.0).

James C. Howard, *Middle Tennessee State University*