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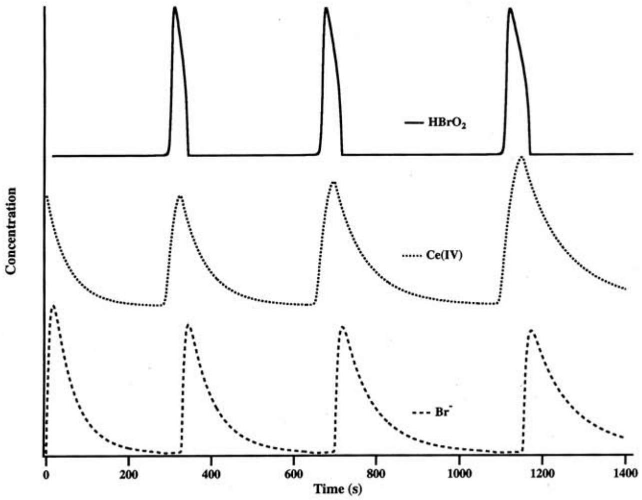

Figure 4. Chemical oscillations generated by the Oregonator model of the Belousov–Zhabotinskii reaction.

of chemical kinetics. Students really enjoy building reaction models and comparing results as they change initial parameters; Stella can be programmed to adjust parameters automatically on multiple runs. Perhaps most significantly, using software like Stella enables them to study complex kinetic phenomena that they would not have even considered before. We encourage students to explore a large number of "what if?" scenarios for a wide variety of reactions in classroom presentations and on problem sets. In the process teaching and learning kinetics becomes not a tedious exercise but an enjoyable and beneficial experience. We will be happy to provide supplementary information to interested readers.

Acknowledgment

We would like to acknowledge NSF-ILI grant USE-915353 which was used to develop the chemistry department computer laboratory. In addition, we are indebted to our colleagues, W. R. Winchester and N. S. Mills, for insightful discussions and critical reading of the manuscript. We thank our many wonderful students who have made teaching chemistry fun. LKS would like to thank the Camille and Henry Dreyfus Foundation for their generous support.

Spreadsheet Simulation of a Simple Kinetic System

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Kinetics and equilibrium are important and conceptually difficult topics in the introductory as well as the advanced chemistry curriculum. This article describes a spreadsheet simulation of a first-order intramolecular rearrangement reaction that has been quite effective in illustrating the concepts of kinetics and equilibrium to both general chemistry and physical chemistry students. Cis–trans and keto–enol isomerizations are examples of such reversible processes. In order to make the problem more concrete, the flipping of pennies can be used as a effective teaching analogy to such problems. The simulation can be readily done by students with only a very basic knowledge of Lotus 1-2-3, Excel or other spreadsheet software.

Construction of the Spreadsheet

The construction of the spreadsheet for this problem is quite simple. Begin with a column of times with a range between 0 and 100 s as an example. The associated population of the heads and tails will be in the two adjacent columns. The important input parameters are the initial population of heads, the initial population of tails, the rate constant for the heads to tails reaction, k_f, and the rate constant for the tails to heads reaction, k_r. These values will be assigned to specific cells on the spreadsheet.

The initial population values are assigned to the cell locations corresponding to zero time. The coins are assumed to be on a tray that is agitated once each second. The number of heads that change to tails in a given second will be equal to the rate constant for the heads to tails reaction, k_f, multiplied by the number of heads prior to the agitation. The number of coins that change from tails to heads can be calculated in an analogous way. To get the population of heads after one second, take the initial number of heads, subtract the number of coins that flipped from heads to tails, and add the number that flipped from tails to heads. Calculate the number of tails after one second in an analogous way. The formulas for these calculations can be copied to the remaining cell locations, and the graph feature of the spreadsheet can be used to give plots of the head and tail populations vs time.

As a first example, consider the case in which the pennies are initially all heads up and can flip from heads to tails but not from tails to heads. This corresponds to the irreversible H $\rightarrow$ T reaction. The actual time dependence of the number of heads-up pennies will depend on the rate constant for the heads-to-tails reaction. Figure 5 shows a plot of the number of heads-up and tails-up pennies versus time when the initial number is five million pennies all heads-up and the rate constant is 0.050 s^{-1}, which corresponds to there being a 5.0% probability of a penny flipping from heads to tails in one second. As expected, the number of heads decreases exponentially with the time, a result that can be verified by performing a log plot. The half-life for a first-order reaction is equal to $0.693/k_f$, which is 14 s for this example (7). This value is consistent with the decay curve of Figure 5. Another quantity of interest is the relaxation time, which is the average time that it takes a penny to flip from heads to tails. The relaxation time is equal to the reciprocal of the rate constant and is 20 s for this example (7). Students can "experiment" with this simulation by trying larger and smaller rate constants as well as different initial populations.

After analyzing the irreversible problem, the case of a reversible reaction can be explored. Figure 6 shows a plot

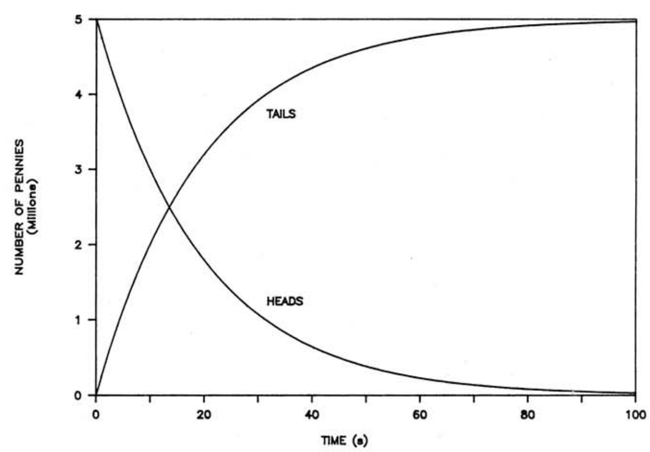

Figure 5. The number of heads and tails versus time for the situation where all coins are heads-up initially and the rate constant for H $\rightarrow$ T, k_f, is 0.050 s^{-1} and that for T $\rightarrow$ H, k_r, is 0.0 s^{-1}.

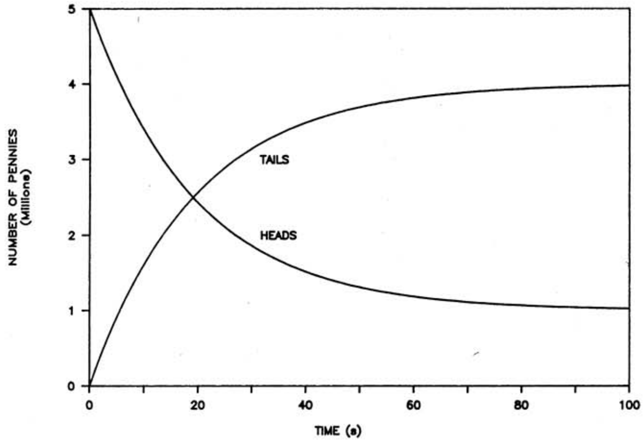

Figure 6. The number of heads and tails versus time for the situation where all coins are heads-up initially and the rate constant for H → T, k_f, is 0.040 s^{-1} and that for T → H, k_r, is 0.010 s^{-1}.

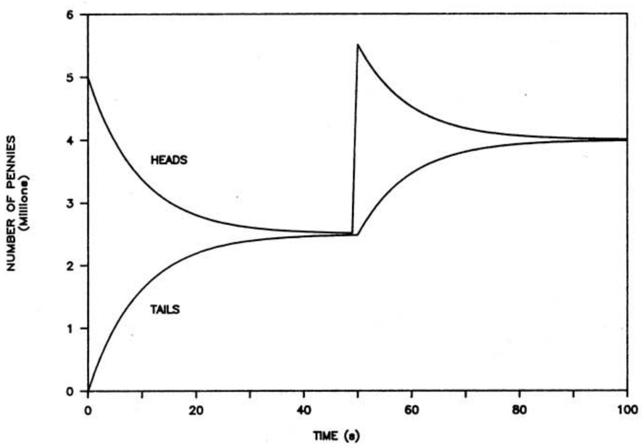

Figure 7. The number of heads and tails vs time for the situation where all coins are heads-up initially and the rate constant for H → T k_f, is 0.050 s^{-1} and that for T → H, k_r, is 0.050 s^{-1}. At t = 50 s, three million additional heads-up coins are suddenly introduced into the sample.

of population versus time for the case in which there are initially five million pennies all heads-up and the rate constant for the heads-to-tails reaction is 0.04 s^{-1} while that for the reverse reaction is 0.01 s^{-1}. The heads show an exponential decrease to the equilibrium value of one million, while the tails show an exponential increase to four million. The time for the number of heads to reach three million, which is a value half way between the initial value and the equilibrium value, is equal to $0.693/(k_f + k_r)$ or 14 s (*7*). Another quantity of interest is the relaxation time which is $1/(k_f + k_r)$ or 20 s (*7*). The equilibrium constant for this "reaction" is equal to $k_f/k_r = 4.0$, and this is consistent with the equilibrium concentrations. At equilibrium, the rate at which pennies are changing from heads to tails is equal to the rate at which they are changing from tails to head.

It is instructive for students to verify that the equilibrium state is independent of the initial populations. If the system starts out with all tails or with an equal number of heads and tails, the equilibrium state will still be one in which the ratio of tails to heads is four to one. Students should also experiment with different rate constants in order to appreciate fully the relationship between kinetics and equilibrium.

It is also interesting to investigate the situation where a system at or near equilibrium is disturbed. An example of this is shown in Figure 7. This figure represents the case where $k_f = k_r = 0.050$ s^{-1}. The system begins with five million heads and no tails and is allowed to "react" for 50 s at which point it is near equilibrium. At the 50-s mark, three million pennies, all heads-up, are introduced into the system. This disturbs the equilibrium since it is no longer true that the number of heads equals the number of tails. Thus, the rate at which pennies flip from heads to tails is greater than the rate at which the pennies flip from tails to heads. This causes the number of heads to decrease and the number of tails to increase until the two again become equal, thus illustrating LeChatelier's principle.

This spreadsheet simulation is an effective way for students to learn the relationship between kinetics and equilibrium. They see that the rate constant for a first-order reaction is the probability that a molecule will react in a given time interval, and they understand the relationship between the rate constants and the equilibrium constant. They also see that equilibrium is dynamic since pennies are still flipping from heads to tails and from tails to heads after equilibrium is reached. In addition to this they gain a better appreciation for LeChatelier's principle.

A Simple Method of Digitizing Data Using a Personal Computer and an HP-Compatible Pen Plotter

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Occasionally, a scientist needs to convert graphical data into digital form. There may be a need to reproduce a graph that appears in the published literature, or to obtain digital data from a hardcopy output of an instrument such as a chromatograph, or any of a multitude of spectrometers. Digitized data will allow the scientist to perform a large number of operations with relative ease when using appropriate computer software. Besides comparing published data that may be on different scales, one may wish to integrate peaks, take derivatives, perform a background subtraction, smooth data, take ratios of data sets, or perform numerical and curve-fitting analyses. The conversion to digital data is necessary, since it is the form that a computer can use. There are many devices that can be used for input of graphic information, the most versatile of which are the digitizing tablets and coordinate measuring devices (*8*). Digitizing tablets are versatile devices that can provide a range of features and are commercially available (*9*). The cost of digitizing tablets vary according to performance, averaging about $800. An automated digitizing system that can significantly save time and improve digitizing accuracy, is also commercially available[2]. In this paper, we describe a simple, accurate, and inexpensive way of digitizing data. The only hardware needed is normally available to most scientists and engineers. The performance of the technique is shown by digitizing a quadratic curve.

System Requirements

The program runs on the IBM-PC, XT, AT and PS/2 or compatibles with a minimum of 512K of RAM. It requires a Microsoft-compatible mouse, a color or monochrome monitor, an EGA, VGA, or Hercules card installed, and a Hewlett-Packard 7000-series or compatible pen plotter. An IBM Proprinter or compatible is optional, if a hard copy is desired.

[2]Silk Scientific Corp., Orem, UT 84059.