

Excel Simulations of Games: An Introduction to Kinetics and Equilibrium Concepts

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Abstract: Basic concepts relating to rate, rate constant, and equilibrium can be taught using games. One drawback in using such games with student-acquired data is the time consumed in performing the game activity. Excel programs using Excel's random number capabilities can produce game results in the few seconds it takes to scroll through the data for a view of the averaged results, graphs and empirical equations describing some aspect of the game. Four games are described. Excel programs used to simulate the four games are provided in the supporting material.

Introduction

Chemical kinetics and equilibrium concepts play important roles in physical chemistry. It does not seem that many chemical demonstrations are available as lecture demonstrations (apart from those that refer to catalysis). There is a sound reason for the above: a chemical demonstration should, in principle, be as short as possible (~ 5 min).

Student-conducted activities, games, have been used to help students form concepts relating to rate, rate constant, order of a reaction and integrated rate plots [1–3].

Student-conducted activities have also been used to introduce equilibrium concepts [4, 5].

The instructional potential of such games may not have been utilized because of a reluctance to use laboratory time that has been reserved for other purposes. Usually, the game is analyzed in terms of its averaged outcome after each play.

With a small number of game pieces, a rate or equilibrium game involving stochastic processes requires a correspondingly large number of repetitions of the game. A computer simulation allows for the use of as many as 1000 or as few as 3 game pieces. The simulations have user option for the number of game pieces and other parameters. The game simulations are Excel files available in the supporting material. Four games are considered in the present contribution. With the exception of the quasi-second-order game, the games described have been used as student activities in which the data is student acquired in laboratory or classroom situation. A description of each game follows [6].

A Zero Order Rate Game [7]

- Students measure and record the mass of an empty, plastic disposable coffee cup. A small handful of beans is added to the cup and the mass of the cup and contents is measured.
- One bean at a time is removed from the cup and the mass of the cup and its contents is recorded. A total of ten beans are removed from the cup.

From their measurements, students are asked to estimate the number of beans placed in the cup at the start of the exercise. Figure 1 and the empirical equation that describes the graph are used.

A First Order Rate Game [8]

- N sugar cubes are marked with a felt-tipped marker on $n < 6$ faces.
- The marked cubes are tossed as dice are tossed and cubes landing so as to display a marked face are replaced with an unmarked cube [9]. The number of marked cubes remaining after each of 10 throws is recorded.

Quasi Second Order Game [10]

Twelve black beans are placed in a cup. Two beans are drawn from the cup. The beans chosen are, of course, black beans. The two black beans are replaced by two white beans and returned to the cup. Initially the cup contains ten black beans and two white beans.

- Successive attempts are made to reduce the number of black beans in the cup by drawing two beans.
- If both beans drawn are black beans, the two black beans are replaced by two white beans and returned to the cup.
- If the beans drawn are not both black beans, the beans drawn from the cup are returned to the cup.
- The cup is shaken to mix the beans after each draw and possible replacement of black beans by white beans.
- The number of black beans remaining in the cup is recorded after each draw.

The averaged outcome for a large number of repetitions of the game can be used to produce the integrated rate plot shown in Figure 3.

An Equilibrium Game

Sugar cubes are used as game pieces. The reactant (R) game pieces are marked on n_R faces while the product game

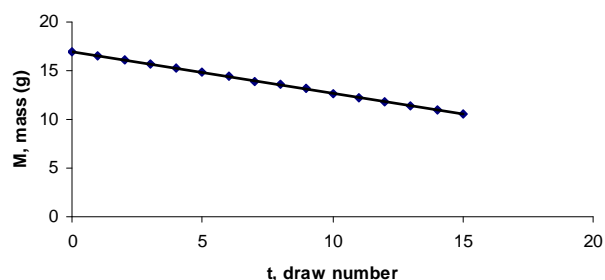


Figure 1. Mass of cup and contents as a function of draw number.

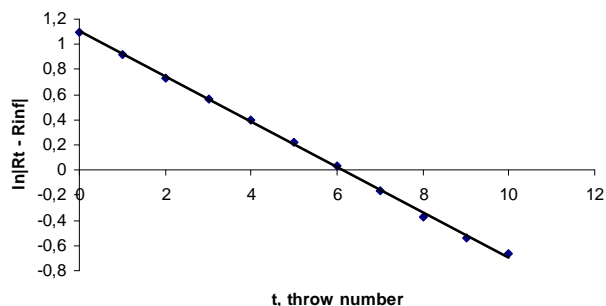


Figure 2. Progress of first-order game taken from Excel simulation "Order1" (R_{inf} is the limiting value for R_t as $t \rightarrow$ infinity. For a rate game, $R_{inf} = 0$ and the absolute value sign is unnecessary).

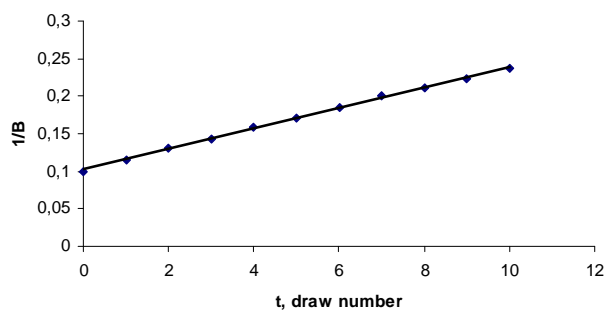


Figure 3. Integrated rate plot taken from Excel simulation "Order2" (B is the number of black beans in the cup).

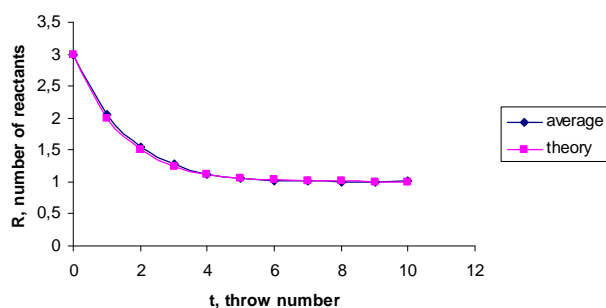


Figure 4. Simulation of the equilibrium game for $N = 21$, $n_R = 2$, $n_P = 1$, $R_{equi} = 7$.

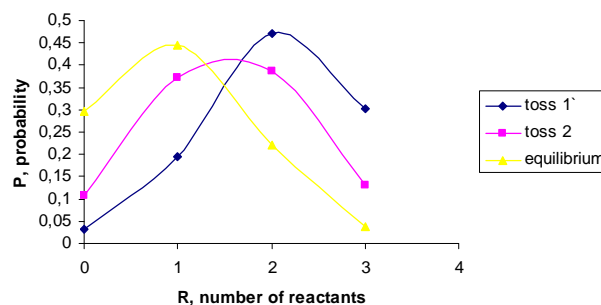


Figure 5. Theoretical probabilities for $N = 3$, $n_R = 2$, $n_P = 1$, $R_{equi} = 1$ calculated using Excel simulation "Matrix."

pieces are each marked on n_P faces, $n_R > n_P > 0$. The mark(s) on product cubes are made with one color and the mark(s) on reactant cubes are made with a different color. The initial conditions for the game involve R reactant cubes and P product cubes for a total of $N = R + P$ cubes [11]. The number of cubes, N , does not change during the course of the game.

R cubes that display a marked face are replaced with P cubes, and P cubes displaying a marked face are replaced with R cubes. After each throw, t , and $R \rightarrow P$ and $R \leftarrow P$ conversions have been accomplished, the number of reactant cubes remaining in the collection is recorded.

Figure 4 displays an outcome for a simulation of the game.

Let P_{kt} represent the probability that k reactant cubes remain after t^{th} toss and Φ_t represents the column vector with entries $p_{0t}, p_{1t}, \dots, p_{N,t}$. Theoretical probabilities can be calculated for each toss by repeated use of $M \Phi_t = \Phi_{t+1}$ starting with the initial condition, (Φ_0) . Excel performs the matrix multiplication. The matrix M is somewhat tedious to construct. Only the case for $N = 3$ is given in the supporting material. For each Φ_t , an expectation value, $\langle n_t \rangle$ is calculated. A graph of $\langle n_t \rangle$ as a function of t very closely follows the graph produced by the simulation program. Two probability distributions are shown in Figure 5.

The experimental probability functions produced by the simulation using the same game parameters ($N = 3$, $R_{initial} = 3$, $n_R = 2$, $n_P = 1$) is also in agreement with Figure 5. Φ_t rapidly converges to $\Phi_{equilibrium}$ as t becomes larger. $R_{equilibrium}$ is the expectation value associated with $\Phi_{equilibrium}$, that is, $M \Phi_{equilibrium} = \Phi_{equilibrium}$. In the case considered, M has an eigenvalue $\lambda = 1$ and $\Phi_{equilibrium}$ is the eigenvector associated with eigenvalue $\lambda = 1$. This aspect of the equilibrium game, describing an equilibrium situation as a probability distribution, may be useful in helping students form concepts relating to wave functions. While not really probability functions, wave functions are eigenfunctions and as such are independent of time. Throw number plays the role of time for Φ_t but $\Phi_{equilibrium}$ is time independent.

Conclusion

The games offered might be useful to supplement lectures and laboratories. Given the corresponding Excel files, students can "experiment" for hours, varying the initial conditions (number of cubes, draws etc.). Basically, the response of students has been positive. Some students at the university level have said that the task suggested in the "Order0" game is a bit too simple. One of us (D. Lewis) taught for a number of

years at the high school level. The “too simple complaint” was not voiced.

Supporting Material. The four Excel files referring to each of the games discussed are included as supporting material (<http://dx.doi.org/10.1333/s00897092183a>). The files are as follows: Order0: This simulation is useful only for the zero-order rate game. Order1: This simulation may be used either for the first-order rate game or for the equilibrium game. Order2: This game produces data and graphs related to the quasi second-order game. Matrix: This file constructs the transition probability matrix for either the first-order rate game or for the equilibrium game. In either situation, the total number of cubes is three. If one uses the simulation “Order1” to compare results from “Matrix,” the total number of cubes chosen in “Order1” should also be three.

References and Notes

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 - To start a game, just double click the corresponding Excel icon and inspect the results in the file (for the latter “macros” must be enabled). Note that the use of the random number generator may provide slightly different results for each run even if the same initial conditions are used (this is particularly true for the “Order0” game).
 - The simulation is based on measurements of mass for 100 beans. The simulation uses the average mass of a bean, the standard deviation in the mass of a bean and, the average mass of the container used. The initial mass of the container and contents is derived from a random assignment of the initial number of bean in the cup ($20 < N_0 < 35$).
- Mass changes after each withdrawal reflect random departures of magnitude $\sigma/2$ from the average mass of a bean. Particularly at the high school level, this activity has instructional value as an example of a situation illustrating that “How much?” can mean “How many?”—a notion critical to the development of the mole concept. By entering the mass of the cup, the initial mass of the container and contents and the measured mass after each removal of a bean, the simulation can serve as a template for producing a graph and empirical equation for student collected data.
- For cubic dice, if $n = 0$ there is no game. If $n = 6$, all of the reactant cubes become products after the very first toss.
 - Replacement of marked cubes by unmarked cubes is not really necessary since unmarked cubes would not effect changes in the number of marked cubes. The simulation may produce an integrated rate graph and an empirical equation from which a rate constant can be assigned. Students may intuitively feel that if say two faces are marked on each reactant cube then on the average, $1/3$ of the number of reactants present at the beginning of each throw would be removed. However, using $n = 2$, $N = 20$ in the simulation might result in a slope of the graph = -0.404 , quite different from the student’s expectation, -0.333 . This situation arises because the average behavior of the system is described by a difference equation, $\Delta R_{\text{avg}}(t) = (1/3) R_{\text{avg}}(t)$. For t an integer the equation has the solution $R_{\text{avg}}(t) = N(1-1/3)^t$. The integrated rate plot suggests that $R_{\text{avg}}(t) = Ne^{-0.404t}$. The apparent disagreement is resolved in the simulation by evaluating $e^{-0.404} = 0.666$ (approximately $2/3$).
 - The game described is not really a second-order game. It is impossible to contrive a game with discrete game pieces, no matter how many game pieces are involved in which the behavior of the game is described by a second-order rate expression. The simulation displays integrated rate plots assuming zero, first- and second-order kinetics. The second-order description seems to best describe the outcome. In the simulation, the total number of beans can be changed from the default value 12. Even changing 12 to 14, results in drastically altered integrated rate plots.
 - In order to have integer equilibrium values for R_{equil} and P_{equil} , one must use N as an integral multiple of $n_R + n_P$. For example, if $n_R = 6$, and $n_P = 5$ using 33 cubes leads to $R_{\text{equil}} = 15$. This pathological choice for n_R and n_P produces an interesting graph of the system’s approach to equilibrium.