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WHICH LABORATORY ACTIVITY BEST SIMULATES THE FIRST-ORDER KINETICS OF RADIOACTIVE DECAY?

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ABSTRACT—A review of the literature indicates that many different types of activities have been used in undergraduate science laboratories to illustrate the concept of half-life. The choice of a specific activity will depend on the desired educational outcomes, the sophistication of the students, and the cost of materials. In this paper, I compare and contrast four half-life experiments that have been used in undergraduate science laboratory and lecture courses. The experiment giving the best verification results, based on agreement between experimentally determined values and theoretical values, was the decreasing volume model.

In undergraduate chemistry or general education science courses, students commonly perform an experiment investigating radioactive decay. The experiment usually involves a relatively simple, single decay process, such as $^{14}C \rightarrow ^{14}N + \beta^-$, and illustrates the important concepts of reaction kinetics and half-life. For legal and financial reasons, undergraduate students will probably not use radioactive isotopes. Instead, an experiment simulating the mathematical characteristics of radioactive decay will often be substituted.

A search of the *Journal of Chemical Education* online index for the topic "kinetics" produced 639 papers. These papers included chemical experiments to measure kinetics in the undergraduate laboratory, half-life experiments using various radioactive isotopes, computer programs to simulate kinetics, calculation methods, classroom activities, and various physical simulations.

Some of the physical simulations that obey first-order kinetics include the flow of gas through an orifice (Coffin, 1948; Kahn, 1957) or the flow of liquids through capillaries (Lemlich, 1954; Davenport, 1975; Erwin, 1992). Other methods take a games approach (Harsch, 1984) and include such activities as flipping coins (Sanger et al., 2002; Sanger, 2003) or dice shaking (Schultz, 1997). Others involve the transfer of water using dippers of various shapes (Burk and Gunter, 1977), or the cooling of hot water (Birk, 1976).

With all of these choices, one is bound to ask "Which is the best simulation for my students?" The answer to this question depends on several factors. Is the experiment intended as a simple verification experiment, or is it intended to be a guided discovery experiment? How sophisticated are the students conducting the experiment? How complicated is the experimental procedure? Does the experiment require extensive preparation and expensive materials?

All of the above simulations use relatively inexpensive materials. The experimental procedures given are clear and straightforward. Neither the preparation time for the experiment, nor the laboratory time required to conduct the experiment are excessive. In selecting the simulation to be used, one important choice for the instructor is "Will the students have to measure elapsed time?" In many of the simulations described above, such as flipping coins, shaking dice, or dipping water, iteration can be substituted for elapsed time. For students having little practical laboratory experience, this may be a desirable simplification.

Another critically important question for the instructor is "Is this a simple verification experiment or a guided discovery experiment?" Verification experiments are important exercises, allowing students to develop and gain confidence in their laboratory skills. Guided discovery experiments are significantly different from verification experiments, providing students the opportunity to experience the "full" scientific process: observation, hypothesis, experiment to test hypothesis, revision of hypothesis. A verification experiment may not be useful as a guided discovery experiment, and vice versa. While it is impossible to eliminate all experimental error, a properly designed verification experiment should minimize experimental errors. This is especially important for students with little or no laboratory experience. Such students typically interpret normal, random variations as mistakes and conclude that either 1) they aren't any good at science or 2) the experiment is wrong.

In this paper, four experiments of first order kinetics were compared for accuracy and precision of results, with the goal of identifying the "best" verification experiment. The experiments evaluated were the coin-toss model, the dice roll model, the replacement model and the decreasing volume model. These experiments were chosen based on their simplicity of design and ease of conceptualization.

EXPERIMENTAL

Coin-toss model—The coin-toss model uses a number of objects such as coins, M&Ms™, playing cards, or other similar two-sided objects (Sanger, 2003). The objects are placed into a container, thoroughly mixed, and then poured onto a table. All objects displaying a designated side are removed from the pile. The remaining objects are returned to the container and re-mixed. The procedure is repeated until some fixed number of objects is left. In this experiment, 100 quarters were used, and the designated side for removal was "heads". The experiment was continued until six or fewer coins were left. Five replicates of this experiment were performed.

Since there are two possible outcomes of equal probability for each coin, the experiment can be easily modeled. The expected number of coins remaining is

$$x = Np_{tail}$$

where N is the number of coins in the container and p_{tail} is the probability of getting a tail (Taylor, 1982). The expected standard deviation is determined by

$$\sigma = \sqrt{Np_{tail}p_{head}}$$

Dice roll model—The dice roll model is a variation of the coin-toss model. A number of dice are placed into a container, thoroughly shaken, and poured onto a surface (Shultz, 1997). Dice showing a given number, or range of numbers, are removed, and the remaining dice are re-rolled. In this experiment, 50 dice of identical size were used. Dice showing "1" were removed, and the remaining dice were re-rolled until either six or fewer dice remained, or 12 iterations were completed. Five repetitions of each experiment were performed. Theoretical results for this experiment were calculated as in the coin-toss model with substitution of the appropriate probability values.

Replacement model—In the replacement model, objects with one particular feature are replaced by similar objects having a different, distinctive feature (Harsch, 1984). The most commonly used feature is color. A relatively large number of white objects, such as beads, will be combined with a smaller number of black beads. The beads are thoroughly mixed and without looking into the container, a fixed number of beads are removed and examined. Any black beads are returned to the container, while all white beads that were removed are replaced with an equal number of black beads. The number of white beads remaining is determined by subtraction and the procedure is repeated until ten or fewer white beads remain in the container, or until a total of 20 iterations have been performed.

This experiment began with 90 white beads and 10 black beads. For each sampling interval, ten beads were removed and examined. Since the students would be able to feel differences in size or texture, it is extremely important that all objects be indistinguishable by touch. Five repetitions of the experiment were performed.

This experiment can be readily modeled, but the calculations are more complicated due to the changing probabilities of selecting white beads. For the first selection of ten beads, the probability that a white bead will be chosen is 0.90. For the second selection of ten beads, the probability that a white bead will be chosen is 0.81. Nevertheless, the expected number of white beads remaining and the standard deviation can be calculated as above.

Decreasing volume model—In the decreasing volume model (Harsch, 1984), a suitable container such as a 25 mL graduated cylinder is filled with water, and the initial volume recorded. A glass tube or other suitable "straw" is dipped into the graduated cylinder until the bottom of the tube touches the bottom of the cylinder. The open end of the tube is covered with a finger, and the tube is removed, taking care that the portion of water inside the tube does not drip out of the end of the tube. The new volume in the graduated cylinder is recorded and the procedure repeated. This procedure can be continued until almost all of the water has been removed. In our experiment, 19 aliquots were removed for a total of 20 volume measurements. Five repetitions were conducted.

Theoretical calculations for this model are the most complex of the four models investigated. Accurate dimensions of the graduated cylinder and the glass tube are required. The inside height of the 25.0 mL mark was measured at different locations using a steel ruler calibrated in millimeters. The average height was found to be 90.25 mm. The cylinder was filled with water to the 25.0 mL mark, and the mass of water contained by the cylinder determined. The temperature of the water was measured, and from the density of water at the recorded temperature, the volume of water was determined. Assuming the graduated cylinder to be a uniform cylinder, these measurements gave an average internal radius of 0.943 cm.

The outside diameter of the glass tube was measured to the nearest 0.1 mm at several locations along its length, and produced an average value of 0.60 cm. To determine the average internal radius, one end of the tube was sealed with Parafilm™, and the tube filled with water. The mass of water was measured to within 0.01 grams, and the volume calculated as described above. The length of the tube was 19.3 cm, and the average internal radius was determined to be 0.193 cm. The difference between the internal and external radius allowed calculation of the volume of glass per unit length of the tube.

Since the glass tubing will displace a finite volume of water, it is necessary to account for the corresponding increase in water level. The volume of glass submerged at the 25.0 mL mark was calculated, and this volume was added to the calculated volume of the graduated cylinder at the 25.0 mL mark. From this calculated volume, the new water level in the graduated cylinder was calculated, and a new volume of submerged glass determined. These calculations were continued until two consecutive volumes, representing the total of the water volume and submerged glass volume and agreeing within 0.1 mL were obtained. From the final calculated volume, the final height of the water was determined, and the volume of water inside the glass tube was calculated and subtracted from the original theoretical volume of the graduated cylinder. No attempt was made to correct for the additional volume in the tube due to capillary action.

RESULTS

Coin-toss model—A plot of ln(coins remaining) versus iteration for five replicates, where iteration represents elapsed time, is shown in Fig. 1. For any reaction exhibiting first order kinetics, the slope of the line is used to calculate the half-life of the reaction using the relationship $t_{1/2} = 0.693/\text{slope}$. The total number of objects at the start of the experiment, called A_o, can be found from the formula $A_o = e^{\text{intercept}}$. Table 1 summarizes the linear regression values for the five experimental replicates and for the theoretical values. The half-life and A_o values were calculated using the equations described above. Since all of the slopes calculated were negative, the absolute value of the slope was used to determine half-life.

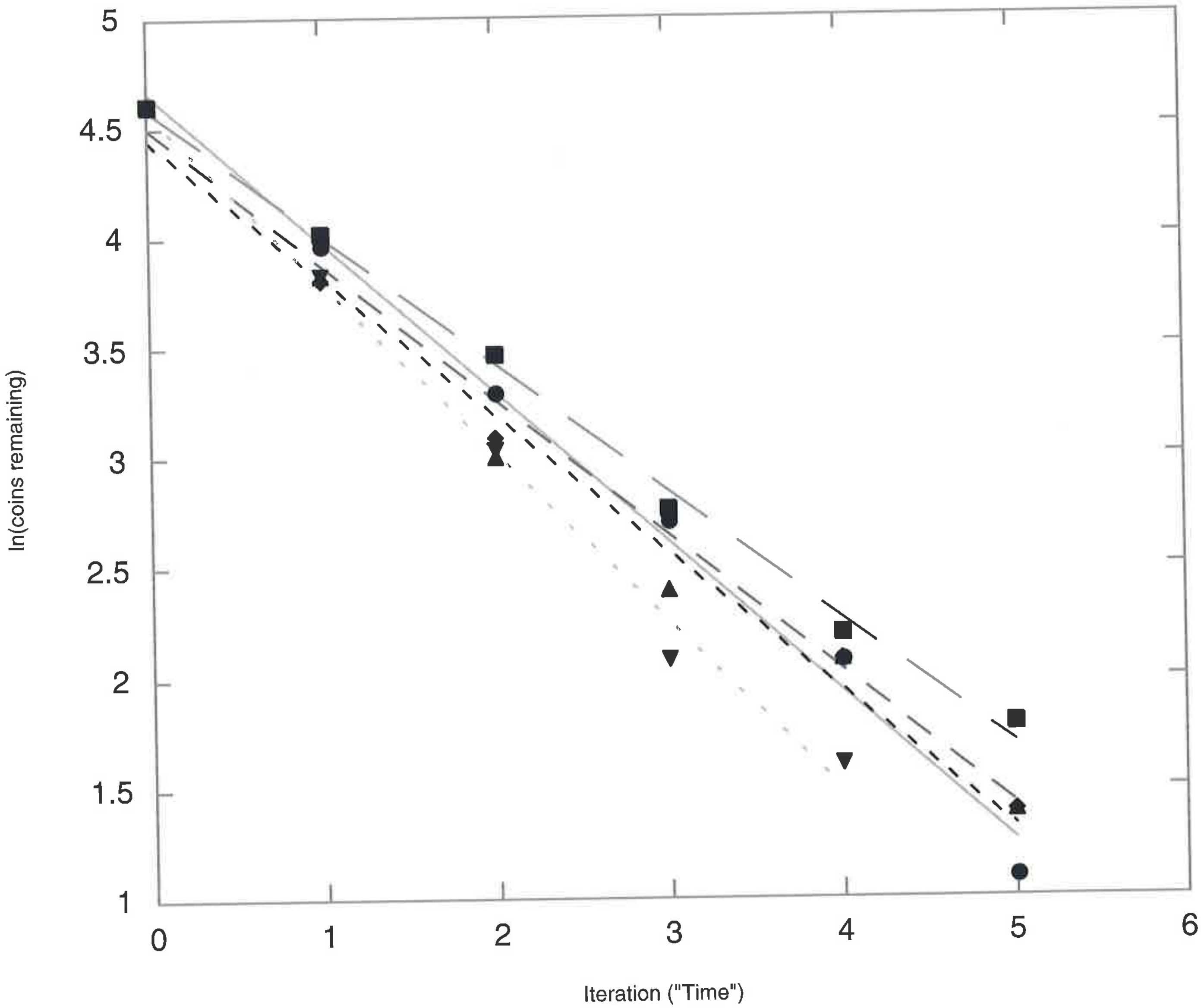

FIG. 1. Plot of ln(coins remaining) versus iteration for the coin-toss model. Results of five replicates presented.

TABLE 1. Linear regression, half-life, and total number of objects at the start of the experiment (A_0) values for the coin-toss model.

Trial	Slope	Intercept	R	Half-life	A_o
1	−0.680	4.660	0.99653	1.0	106
2	−0.578	4.588	0.99803	1.2	98
3	−0.617	4.500	0.99516	1.1	90
4	−0.626	4.450	0.99168	1.1	86
5	−0.774	4.581	0.99595	0.9	98
			Mean	1.1	96
			Sx	0.1	8
Theoretical	−0.693	4.605	1.0	1.0	100

The individual half-life values appear reasonable and give an average value of 1.1 ± 0.1. These half-lives correspond closely with the theoretical value of 1.0. The estimate for the number of coins initially present fluctuates over a large range (−14% to 6%), giving an average value of 96 ± 8 coins.

Dice-roll model—A plot of ln(dice remaining) vs. iteration for the five replicates is shown in Fig. 2. Table 2 summarizes the linear regression values for the five experimental replicates and the theoretical values. There is more variation in the individual half-life values than was observed in the coin-toss model, with an average half-life value of 3.4 ± 0.8, corresponding favorably with the theoretical value of 3.8. The estimate for the number of dice originally present gives an average value of 51 ± 5 dice.

Replacement model—The ln(white beads remaining) vs. iteration for the five replicates is shown in Fig. 3. Table 3 summarizes the linear regression values for five replicates and the theoretical values. The average half-life value was 5.9 ± 1.0, which compares favorably with the theoretical value of 6.6. The

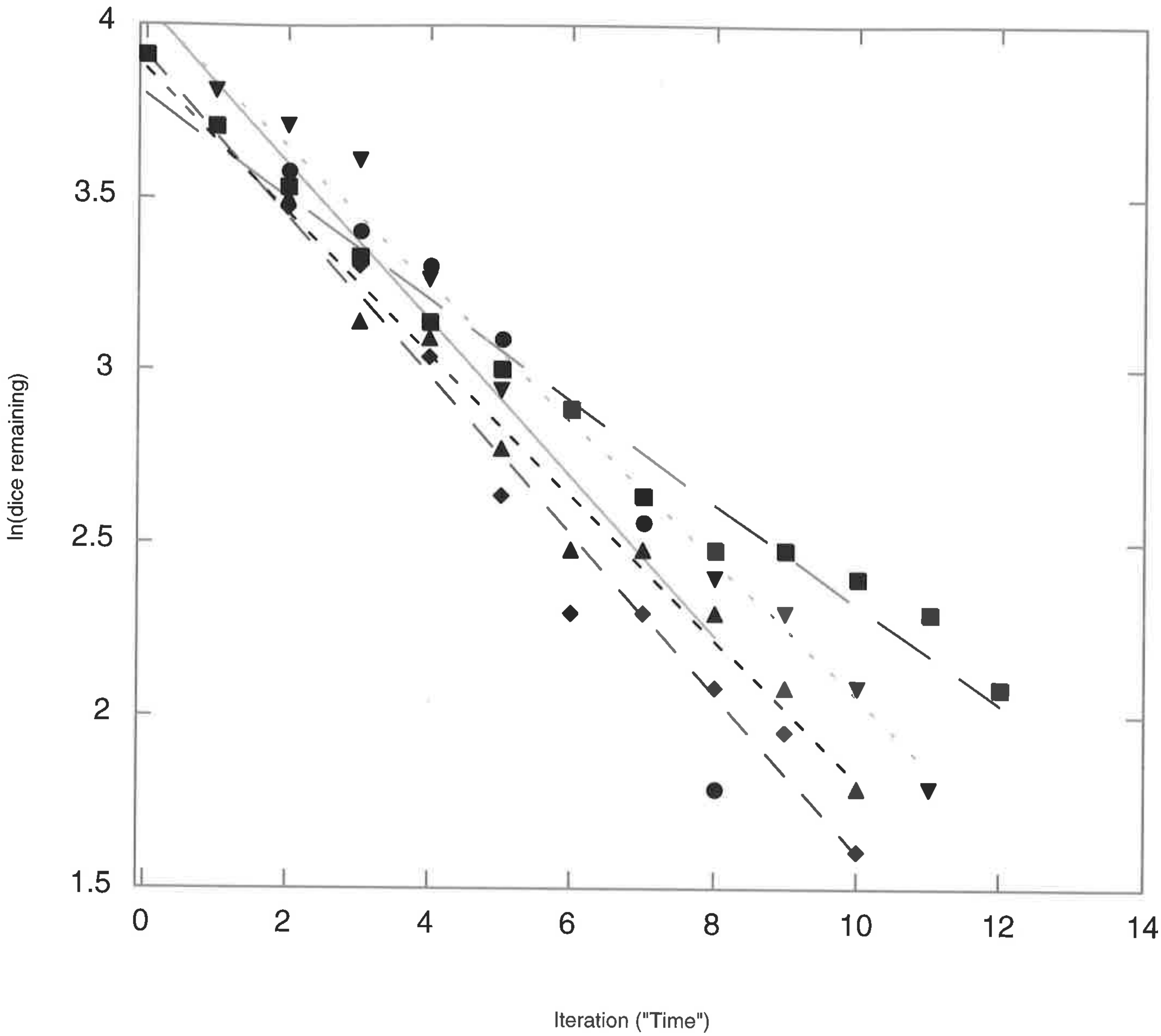

FIG. 2. Plot of ln(dice remaining) versus iteration for the coin-toss model. Results of five replicates presented.

TABLE 2. Linear regression, half-life, and total number of objects at the start of the experiment (A_0) values for the dice-roll model.

Trial	Slope	Intercept	R	Half-life	A_o
1	−0.277	4.045	0.94963	2.5	57
2	−0.147	3.798	0.98936	4.7	45
3	−0.231	3.912	0.99250	3.0	50
4	−0.206	3.870	0.99343	3.4	48
5	−0.198	4.036	0.99364	3.5	57
			Mean	3.4	51
			Sx	0.8	5
Theoretical	−0.182	3.912	1.0	3.8	50

estimate for the number of white beads originally present fluctuates from 88 to 102, with an average value of 97 ± 6.

Decreasing volume model—The ln(mL of water remaining) vs. iteration for the five replicates is shown in Fig. 4. Table 4 summarizes the linear regression values for this experiment. The average half-life was 13.0 ± 0.1, compared to a theoretical value of 15.2. The estimate for the initial volume of water present gave an average value of 24.9 ± 0.1 mL.

DISCUSSION

The coin-toss, dice-roll and replacement models allow relatively simple predictions of $t_{1/2}$ and A_o, and their theoretical behavior can be readily modeled. While these experiments are simple, they all suffer from the same basic problem: the number of items being manipulated is statistically small. Normal, random variations produce results with

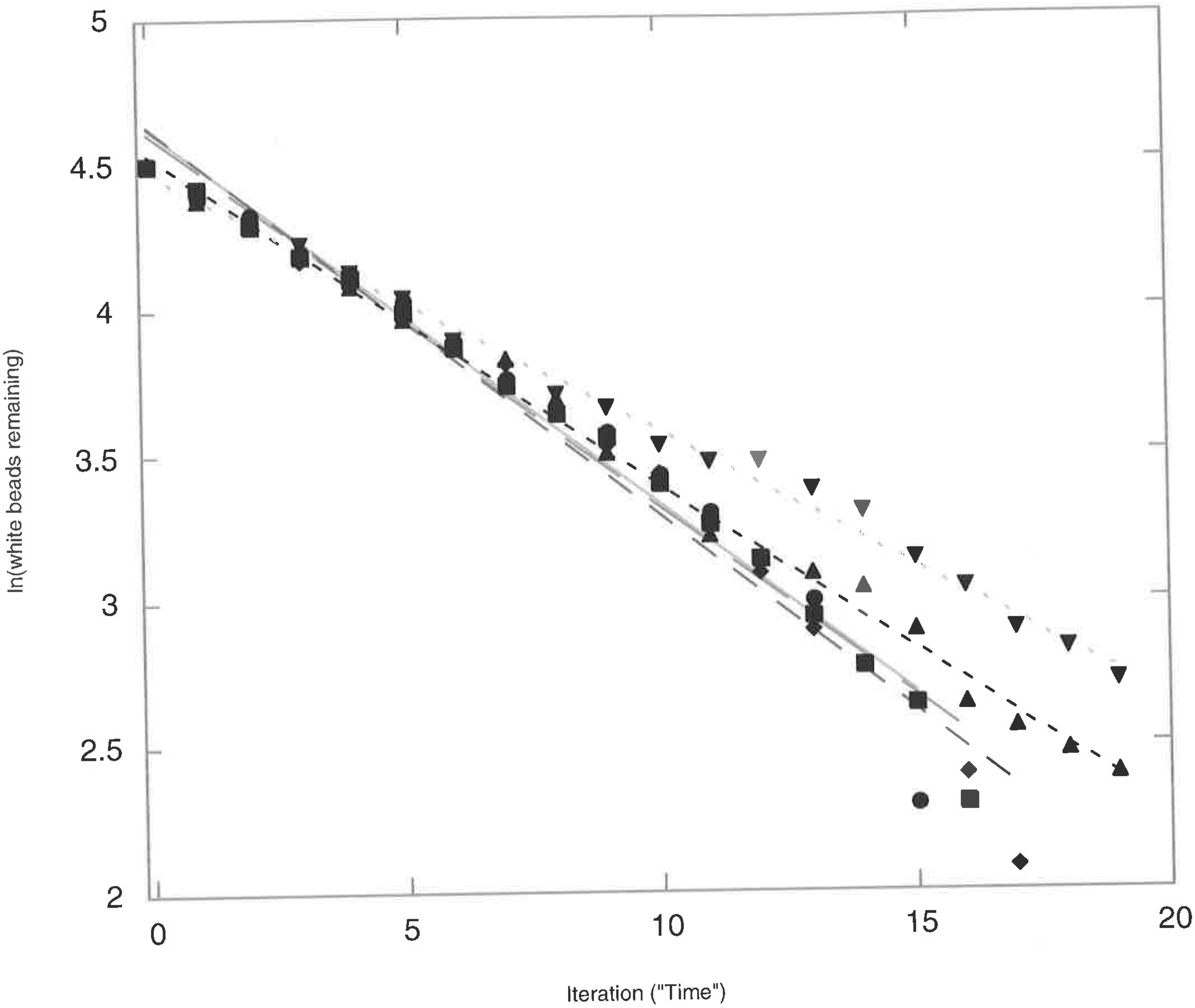

FIG. 3. Plot of ln(white beads remaining) versus iteration for the coin-toss model. Results of five replicates presented.

TABLE 3. Linear regression, half-life, and total number of objects at the start of the experiment (A_0) values for the replacement model.

Trial	Slope	Intercept	R	Half-life	A_o
1	−0.130	4.622	0.98028	5.3	102
2	−0.129	4.606	0.99128	5.4	100
3	−0.134	4.630	0.98918	5.2	102
4	−0.113	4.533	0.99742	6.1	93
5	−0.0909	4.481	0.99610	7.6	88
			Mean	5.9	97
			Sx	1.0	6
Theoretical	−0.105	4.500	1.0	6.6	90

significant deviations from both the predicted values and the mean values. Of the first three simulations, the replacement model produces the lowest relative standard deviation (measured by %RSD), although above 6 iterations significant divergence of replicate experiments is observed (Fig. 3).

Statistical variation is greater in smaller populations than in larger populations, so the results obtained for the coin-toss, dice-roll, and replacement models are not surprising. However, the average first year science student, or the average general science student, may not have the necessary mathematical background to distinguish random, normal variations from flaws in experimental design or mistakes in experimental technique.

There can be little doubt that from a conceptual standpoint, the simplest of the four experiments is the coin-toss. Nevertheless, what may appear to be a "reasonable" outcome from this experiment might not be reasonable in practice. Ordinary probability would indicate that the most probable sequence would be 100 → 50 → 25 → 12 → 6. We

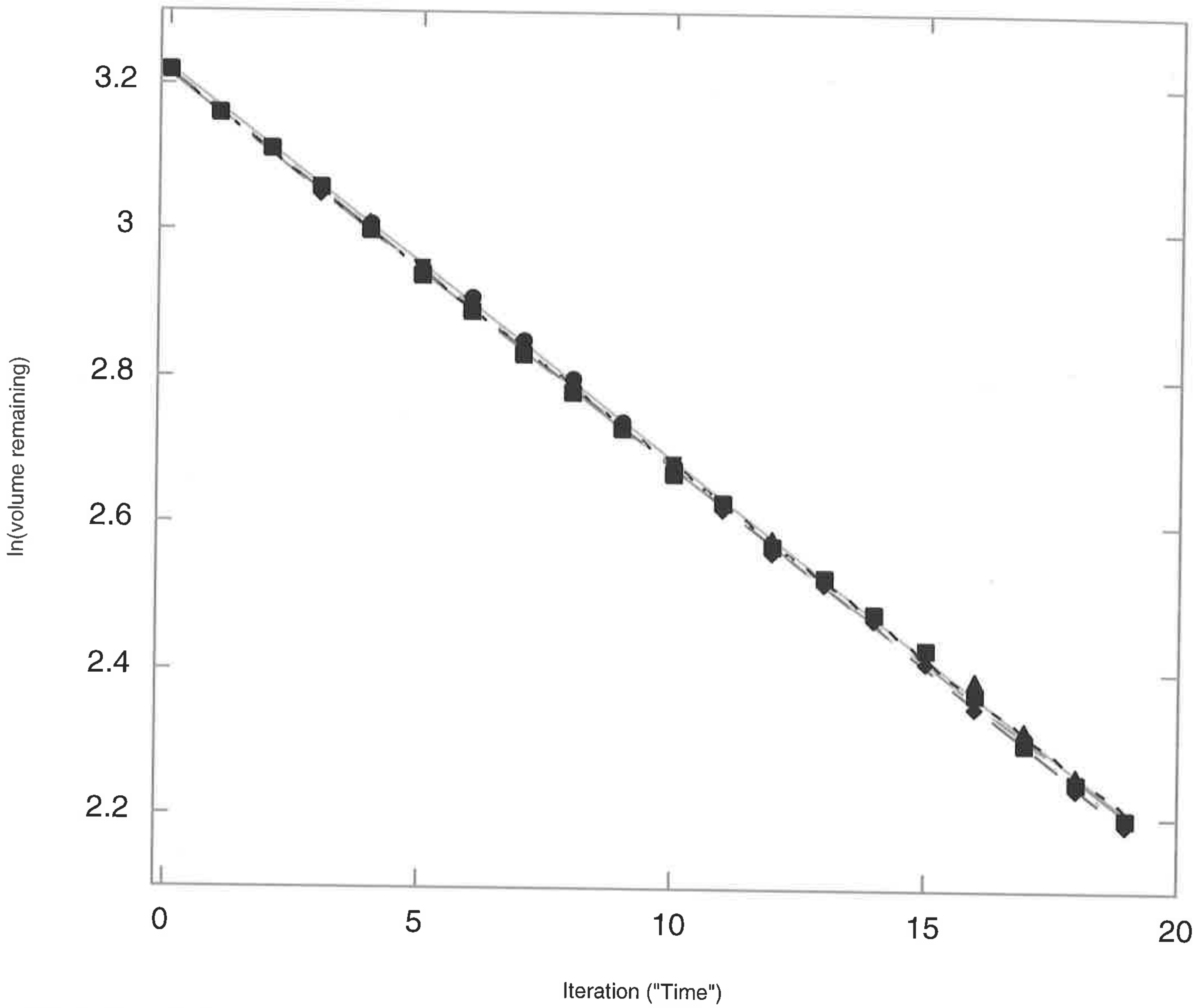

FIG. 4. Plot of ln(water remaining) versus iteration for the decreasing volume model. Results of five replicates presented.

TABLE 4. Linear regression, half-life, and total volume of water at the start of the experiment (A_0) values for the decreasing volume model.

Trial	Slope	Intercept	R	Half-life	A_o
1	−0.0534	3.221	0.99981	13.0	25.0
2	−0.0532	3.213	0.99970	13.0	24.9
3	−0.0539	3.214	0.99989	12.9	24.9
4	−0.0528	3.215	0.99975	13.1	24.9
5	−0.0537	3.217	0.99983	12.9	25.0
			Mean	13.0	24.9
			Sx	0.1	0.1
Theoretical	−0.0456	3.227	1.0	15.2	25.2

can easily calculate the probability of getting exactly 50 "tails" from flipping 100 coins using the equation

$$P = \frac{n!}{V!\,(n-V)!}\left(\frac{1}{2}\right)^n$$

where P is the probability of having V successes in n trials (Taylor, 1982). From this calculation, we can determine that only about 8% of the time will we get exactly 50 tails from flipping 100 coins. Similar calculations result in 11% to get 25 tails from 50 coins flipped, 15% to get 12 tails from 25 coins flipped and 22% to get 6 tails from 12 coins. The overall probability of getting the sequence described is the product of the individual probabilities, and is approximately 0.03%. This translates into 1 in 3443 trials resulting in this sequence.

It is entirely possible that hundreds of students could perform replicate coin flipping experiments without ever obtaining the most probable outcome. Whether or not the students are able to explain or understand why their experimental data are different from the expected results depends upon their level of mathematical sophistication.

The dice-rolling and bead replacement models are subject to similar random variation. Of course, these topics can and should be covered in either the experimental procedure or during the laboratory briefing. However, if the purpose of the experiment is to demonstrate and verify a first order kinetic process, wouldn't it be more appropriate to use a well-behaved experimental procedure?

The volume reduction model is clearly the most well-behaved of the four models presented. For a given graduated cylinder/straw combination, the maximum variation between replicate volume measurements was 0.4 mL or approximately 4%. Comparison of Fig. 4 with Fig. 1–3 clearly shows that the precision between replicate measurements is much higher for the volume reduction model. The percent average error in A_o, calculated as

$$\left(\frac{A_o theoretical - A_o average}{A_o theoretical}\right) \times 100$$

for the volume reduction model (0.8%) is lower than for the other three models (2–8%). The average error in half-life for the volume reduction model (14%) compares favorably with the other three models (10%).

Refinement of the experiment and the resulting theoretical calculations may result in higher accuracy for half-life measurements. One refinement would be to substitute a thinner walled tube, such as a plastic straw, for the glass tube. This would minimize the displacement of the water level due to the tube. However, careful consideration would have to be given to the materials comprising the tube, since thinner walls can result in the tube becoming distorted during use. Using a tube with a greater internal diameter would eliminate errors associated with the liquid meniscus. Graduated cylinders have rounded bottoms, and this feature was not accounted for in modeling the experiment. Using a different container without the rounded bottom should result in better theoretical calculations.

The volume reduction experiment is not subject to the same kinds of random errors as are the other three experiments. In the volume reduction experiment, the most significant source of error is the accuracy with which the graduated cylinder can be read. It is easy to estimate the volume to within ± 0.1 mL. This relatively small random error remains constant throughout the experiment. Over the range of volumes measured, the relative error amounts to less than 1%. This compares very favorably with the theoretical error ranges for the other experiments evaluated.

Clearly, the volume reduction experiment is the best of the four evaluated. It gives the highest precision for replicate measurements of half-life and A_o. The accuracy of A_o measurements is unsurpassed. The only deficiency in the experiment is the slightly larger error between theoretical and experimental half-lives.

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