

Kinetics and Mechanism—A Games Approach

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The basic questions in chemical kinetics are two:

How do the concentrations of the reactants, intermediates, and products of a chemical reaction change quantitatively with time?

Which events at the molecular level are responsible for these changes of concentrations?

The first question is answered experimentally by measuring the concentrations at various times, the temperature usually being held constant throughout the course of the reaction. The second question is answered theoretically by postulating a sequence of elementary reactions that are in accordance with the stoichiometric and energetic requisites for the overall reaction and that explain the observed kinetic behavior.

However, the stoichiometric equation, which summarizes the elementary reactions, itself contains very poor information about the types and sequences of these reactions. For example, $A = B$, while it specifically excludes mechanisms such as $A \rightarrow 2B$, could stand for many other mechanisms, a few of which are shown in Figure 1.

The standard procedure for elucidating the mechanism of an experimentally studied chemical reaction is to postulate mechanisms, to write down the rate laws for all mechanisms and substances (in Fig. 1 this has been done only for A), to integrate the rate laws in order to get the time laws and to compare these with the experimental data. If it turns out that the experimental concentration versus time curves are in accordance with one of the theoretical time laws (for properly chosen values of the rate constants k), the mechanism in question is said to be possible; otherwise it is definitively wrong.

Chemical kinetics can never provide sufficient conditions for a definitive positive proof of a unique mechanism. This is so because the number of intermediates (the concentrations of which may be too low to be detected) is quite unlimited. Thus, the proof of a mechanism is a difficult job.

Students' problems in understanding how mechanisms are elucidated by chemical kinetics arise from the fact that mechanisms (which tell individual molecular events) and experimental data (which tell the kinetic behavior of macroscopic samples containing a huge number of molecules) are correlated only in a coded way by means of a mathematical construct (rate laws and time laws). If the mathematical competences of the students are poor, students have no chance of bridging the gap between the submicroscopic level of mechanisms and the macroscopic level of concentrations versus time curves. Even if they are well acquainted with integral calculus they often make use of it quite formally and do not realize that these deterministic equations are the consequences of statistical laws governing molecular random events.

Statistical Games for Simulating Chemical Kinetics

I propose an approach to chemical kinetics and mechanism using statistical games, the prototype of which was originally developed by the well-known physicists Paul and Tatiana Ehrenfest (1). The Ehrenfests used it for illustrating Boltzmann's H-Theorem. Although this context seems to be far removed from chemical kinetics at first glance, the Ehrenfests' model has the same mathematical structure as the simple racemization reaction $A \rightleftharpoons B$ of optical antipodes. This

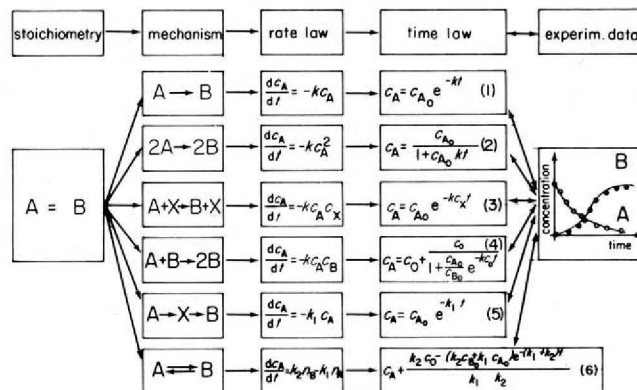


Figure 1. Methodological scheme correlating the macroscopic kinetic behavior of a reaction whose stoichiometric equation is $A = B$, with some microscopic mechanisms compatible with the fixed stoichiometry.

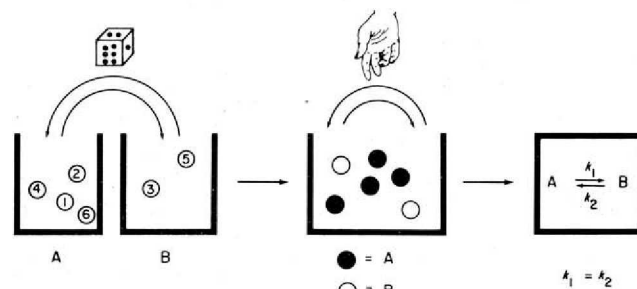


Figure 2. Mental reorganization of Ehrenfest's two-container model in order to show its close congeniality with a monomolecular racemization between $A \rightleftharpoons B$ of optical antipodes.

is shown in Figure 2. The left part represents the Ehrenfest's model: There are two containers A and B holding n numbered notes (lottery tickets). Random numbers z in the range $1 \leq z \leq n$ are produced, once every 10 s. The ticket whose number is generated immediately jumps from one container into the other. This is of course a prototype for demonstrating mass action and equilibrium, but it is interesting to note that neither the Ehrenfests nor Kohlrausch and Schrödinger (2), who analyzed the mathematical structure of this model 19 years later, mentioned the analogy to chemical kinetics. The only hint for interpreting the Ehrenfest model in a context other than Boltzmann's H-Theorem is given by Kohlrausch and Schrödinger at the end of page 309, where their calculations arrived at a differential equation that they recognized as being equivalent to Smoluchowski's well-known equation that governs the diffusion of a Brownian particle under the influence of an elastic force pulling it into an equilibrium position. The analogy to chemical kinetics is better seen if we rearrange Ehrenfest's model as shown in Figure 2:

- Instead of numbered tickets we take equal-sized balls without numbers.
- Instead of two containers A and B we only use one (reaction vessel) and store the information A or B ("state" of the original tickets) as colors (A = black, B = white) of the balls.

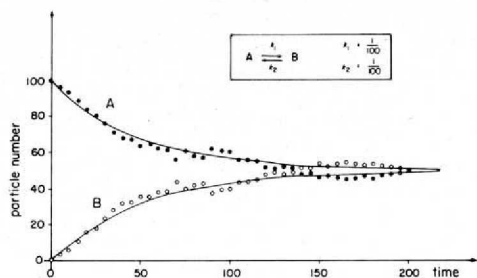


Figure 3. Kinetics of Ehrenfest's two-container model. The points were obtained by the physicists Kohlrausch and Schrödinger (1926). The curves were calculated using eqn. (6) in Figure 1.

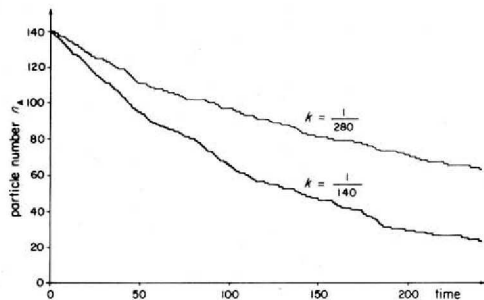


Figure 4. Kinetics of $A \rightarrow B$ for the A-balls. All tries were recorded. The curve with $k = 1/140$ is related to the basis set of rules. The curve with $k = 1/280$ requires a modified "reaction rule" for drawn A-balls, reducing the probability of reaction by a factor of 0.5.

- Instead of generating random numbers we put our hand into the container and draw single balls blindly and successively. Every selected ball is identified visually as an A-ball or a B-ball.
- Instead of jumping from one container to another, every drawn ball is replaced by a ball of the opposite color taken from stock and mixed with the others in the container before the next ball is drawn. In effect, the ball "changes color."
- Instead of one jump per 10 s (absolute time counting) we specify that each try—independent of its result and its real period and frequency—will represent 1 unit of time (relative time counting).

The last rule is permissible because in chemical systems (under constant ambient conditions) the number of collisions between the particles per second is huge and constant, say, for example 10^{30} s^{-1} . Therefore, we can always find a minute time unit (here 10^{-30} s) within which just 1 collision occurs (on the average). If we identify 1 collision = 1 activation event (reality) with 1 activation event (model) = 1 try, we see at once that the time rule is justified by kinetic gas theory. The model time (number of tries) is a relative time which is proportional to the real time, provided that the total number of balls does not change during the reaction (which is equivalent to constant volume conditions).

It is also clear that the mathematical structure of the Ehrenfest model has not been changed by this mental rearrangement. Therefore, we need not play this game in order to get data but can just take the original data generated by Kohlrausch and Schrödinger according to the Ehrenfest's lotto rules. We see (Fig. 3) that their results (points) are in accordance with the integrals of the kinetic rate laws for an equilibrium reaction $A \rightleftharpoons B$ (see eqn. (6) in Fig. 1). With $n_{A0} = 100$, $n_{B0} = 0$, and $k_1 = k_2 = 1/100$, we obtain the theoretical curves and recognize at once the obvious meaning of the rate constants k_1 and k_2 : they measure the chance for any individual ball to be drawn in any one try—that is, the activation probability of an individual molecule per unit of time.

This model may be further developed in order to cover more complex kinetics (including oscillations, instabilities in open

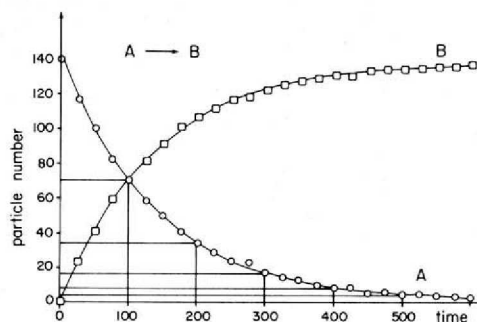


Figure 5. Kinetics of $A \rightarrow B$ (basic version). The points represent the average results of five students. The curves were calculated using eqn. (1) in Figure 1. Note the constant half-life $t_{1/2} = 100$ time units.

systems, etc.). In all cases that I have studied in detail (3) the results of the games were in full accordance with the known analytical solutions of the kinetic rate laws.

The following six examples demonstrate the simplicity and validity of the games' approach, which it is hoped will reduce the problems in teaching and learning chemical kinetics since it uses as little mathematics as possible.

Six Examples

Example 1: The Monomolecular Reaction $A \rightarrow B$

- Put 140 (black) balls A into an urn.
- Pull out successively and blindly single balls and determine after each try which sort of ball you have drawn.
- If you have drawn an A-ball, change its color to a (white) B-ball and mix this product particle back into the container.
- If you have drawn a B-ball, mix this useless activated particle back into the container without changing its color.
- Each try (independent from its result) is counted as one unit of time.

The result of this game is shown in Figure 4 (lower curve). Every single try was recorded. The above rules apply for $k = 1/140$. This value of the rate constant may be diminished to $k = 1/2 \times 1/140 = 1/280$ by specifying a new "reaction rule" for A: If you have drawn an A-ball, flip a coin; if it is "heads," mix A back in without changing its color, otherwise change it into a B-ball as usual.

The kinetic curve of A now falls more slowly than in the former case, but the type of analytical function $n_A = f(t)$ is the same in both cases. In order to show this it is convenient to average the results of, say, five students (Fig. 5) so that statistical fluctuations nearly disappear. It is clearly seen that the half-life is constant throughout the course of the reaction and is equal to 100 units of time. It is not necessary for the general intended arguments to identify this criterion with the exponential function. However, if students are familiar with it they may calculate the rate constant from $t_{1/2}$ according to $k = \ln 2/t_{1/2} = 0.0069$, which corresponds quite well with the theoretical value $1/140$ and they may also use the logarithmic form of eqn. (1) (Fig. 1) to find the rate constant from the slope of the straight lines in the usual manner.

A general method for quantifying the results without using higher mathematics analyzes the rate law by means of defining an average rate $(\bar{v}_A - \Delta n_A/\Delta t)$. Taking, for example, $\Delta t = 40$, the corresponding values of Δn_A (loss of A-balls) and \bar{n}_A (average number of A-balls) within each of these intervals may be picked out of the results, and if these pairs of values are represented in a diagram $\bar{v}_A = f(\bar{n}_A)$, a straight line results (Fig. 6) indicating that the kinetics of the game $A \rightarrow B$ follows the rate law $\bar{v}_A = -k \cdot \bar{n}_A$. The rate constant k may be read from the slope of the line.

Example 2: The Bimolecular Reaction $2A \rightarrow 2B$

The rules of this game are altered (in comparison to example 1) in the following way:

- Pairs of balls are drawn simultaneously.
- If a drawn pair consists of two A-balls, then these change their colors and are remixed as two B-balls. (If one wishes to alter the rate constant, a coin decision may be made here.)

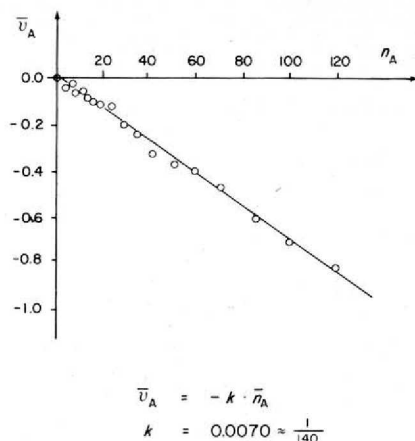


Figure 6. Numerical approach for getting the rate law of the container game $A \rightarrow B$ and for evaluating the rate constant. The rates correspond to intervals $\Delta t = 50$.

- In all other events (AB or BB) the wrong pair is remixed without changing the colors.
- Each try of a pair, independent from its result, is counted as one unit of time.

The result is shown in Figure 7. Unlike Figure 5 the half-life is not constant, indicating that the rate law of this reaction differs from that which was found in the first example. It is not difficult to find by trial and error that the generated rates follow the rate law $\bar{v}_A = -k \bar{n}_A^2$, using the same procedure described above. The experimental rate constant (read from a typical slope) fits the theoretical value $k = 2 \cdot 1/140 \cdot 1/139$ very well. This value may be taken to represent the chance that a certain (numbered) A-ball and another numbered A-ball will be drawn together. The pair drawing may be split mentally into two consecutive drawings of single balls (without remixing the first ball before the second drawing). As the two numbered pairs $A_i A_k$ and $A_k A_i$ represent the same physical situation, the factor 2 becomes understandable as a statistical weight. Note that pairs $A_i A_i$ or $A_k A_k$ are physically nonsensical because an individual particle cannot be present twice in a bimolecular activated complex. Both the pair drawing and the (mental) consecutive drawing of two single balls (without remixing the first) guarantee that this nonsensical situation cannot occur.

Example 3: The "Catalytic" Reaction $A + X \rightarrow B + X$

The rules are very similar to that given for $2A \rightarrow 2B$:

- Whenever a pair AX is drawn, it is changed to BX and then remixed (that is, the A-ball changes its color, the X-ball is not altered).
- All others pairs (AA, BB, BX) are fruitless.

Because of the high number of fruitless pairs that will be drawn, it is advisable to play only with 110 balls. As X is not changed by the reaction and A cannot be converted into B without being simultaneously activated together with an X-ball, X may be interpreted as a primitive catalyst ("contact"), i.e., no intermediate product of A and X has been taken into account. This is certainly a restricting idealization. Note that X may be a solvent or even the wall of a reaction vessel. Starting with 70 A and 40 X, the results (Fig. 8) show that the rate law must be the same as that found for $A \rightarrow B$, because the half-life is constant. It may be found by the same procedures discussed in example 1, that $\bar{v}_A = -k \cdot \bar{n}_A$ holds and that k has (incidentally!) a similar numerical value $k = 0.0069$, but this value must be interpreted theoretically in a completely new manner according to $k = 2 \cdot 1/110 \cdot 35/110$, which may be explained as the chance for simultaneous "activation" of a certain (numbered) A-ball together with any of the 40 X-balls by a pair try, and that both $A_i X$ and $X A_i$ contribute equally to this event. The factor $40/110$ shows that the rate constant depends on the amount of the "catalyst" X. Indeed, if the game is played with 35 A and 70 X (instead of 70 A and 40 X) the students may find that the rate constant's value is increased according to $k = 2 \cdot 1/110 \cdot 70/110$ and that the half-life is shortened to $t_{1/2} = 60$.

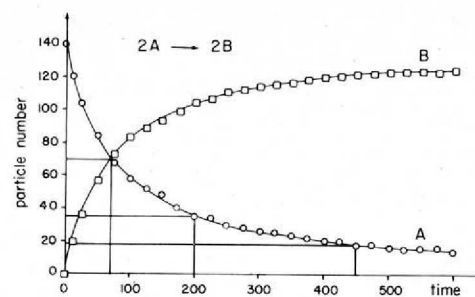


Figure 7. Kinetics of $2A \rightarrow 2B$. The points represent the average results of five students. The curves were calculated from eqn. (2) in Figure 1. Note that the half-life is not constant.

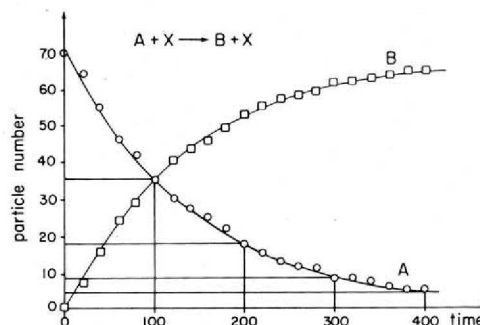


Figure 8. The bimolecular reaction $A + X \rightarrow B + X$ produces kinetic curves which are indistinguishable from $A \rightarrow B$. This may be recognized by the half-life criterion.

Example 4: The "Autocatalytic" Reaction $A + B \rightarrow 2B$

The rules are analogous to $A + X \rightarrow B + X$, where $X \equiv B$, that is, the catalyst X of the former example is identical with the product B of the reaction. Starting with 139 A-balls and 1 B-ball, sigmoid kinetic curves are obtained (Fig. 9). During the first hundred drawings most pairs are "wrong" pairs AA, and only now and then a fruitful pair AB is drawn. Therefore we observe an induction period. Every fruitful draw lowers the number of A-balls by one unit (which lowers the rate \bar{v}_A) and raises the number of B-balls by one unit (which increases \bar{v}_A). These two countercurrent effects are of different strength as long as the number of A-balls and B-balls are different. For example lowering n_A from 139 to 138 means a loss of less than 1% with respect to the momentary number ("mass") of A, whereas the simultaneous raising of n_B from 1 to 2 means an increase of 100% so the latter effect strongly predominates. The reaction accelerates and reaches its highest rate at the moment when $n_A = n_B$. As soon as $n_A < n_B$, the reduction of A-balls overwhelms the positive effect of the increase of the catalyst so the reaction becomes slower and slower. The correlation between the macroscopic kinetic curves (Fig. 9) and the "microscopic" events producing them may be demonstrated by registering the series of drawn pairs AA, AB, and BB, dividing this list in intervals $\Delta t = 40$ and counting these three types of events within each interval during the course of reaction. If these data were then plotted, the "pair curve" AB, which is a measure of the rate \bar{v}_A , would be bell-shaped with a maximum coinciding in time with the intersection point (turning points) of the kinetic curves in Figure 9. Note that this illustrates the important statistical principle that equal occupation of the two states A and B (that is, $n_A = n_B$) guarantees a maximum number of individual pairs $A_i B_k$ and therefore a maximum chance for drawing any one of them.

Note also that the reaction $A + B \rightarrow 2B$ may be interpreted as some sort of reduplication or strong influence ("B makes A become a B") so that Figure 9 could also describe the propagation of an infection, rumor, idea, etc., provided that all individuals move freely, meet by chance, never change spontaneously from A to B, remain B's forever, and so on. Also, the fission of uranium by neutrons may be illustrated this way. The rate law $\bar{v}_A = -k \cdot \bar{n}_A \cdot \bar{n}_B$ may be found from the game data in the usual way by trial and error. It is possible to promote this result by referring to the rate laws of examples 2 and 3 and by confronting the students with the series of numerical products, say, 9-1, 8-2, 7-3, 6-4, 5-5, 4-6 ... 1-9, which they should be able to relate to their graphs by themselves.

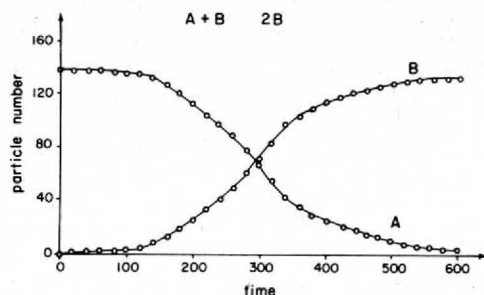


Figure 9. Kinetics of $A + B \rightarrow 2B$, starting with 139 A-balls and 1 B-ball. The duration of the induction period in the early stage of an autocatalytic reaction is subjected to considerable statistical fluctuations. In order to bring the students' averaged results in good agreement with the theoretical curves of maximum probability, some relative shifting parallel to the time axis is usually necessary. The fluctuations are in accordance with Delbrück's theory (4).

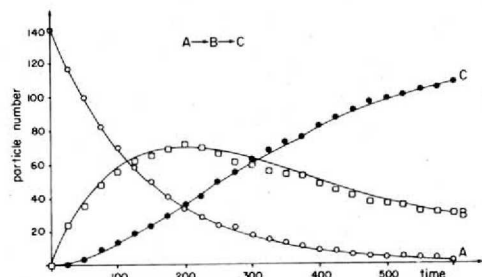


Figure 10. Kinetics of $A \rightarrow X \rightarrow B$ with $k_1 = 1/140$ and $k_2 = 1/280$. The points represent the averaged results obtained by three students. The curves were calculated according to the well-known analytical equations for the mono-molecular consecutive reaction.

Example 5: The Consecutive Reaction $A \rightarrow X \rightarrow B$

Starting with 140 A-balls and drawing single balls, the following reaction rules are followed:

- If an A-ball is drawn, it is changed into an X-ball (which is then remixed).
- If an X-ball is drawn, it is changed into a B-ball (which is then remixed) if, additionally, a tossed coin comes up "heads"; otherwise the X-ball is remixed without changing its color. (The coin rule may be omitted in the simple version.)
- If a B-ball is drawn, it is remixed without changing its color.
- Each try represents one unit of time.

The averaged data produced by three students are shown in Figure 10. The data fit quite well to the theoretical curves. The kinetic curve of A is identical with that found in example 1, which may be recognized by the constant half-life, corresponding to $\bar{v}_A = -k_1 \bar{n}_A$ with $k_1 = 1/140$. This means that the rate of A's decay is independent from the stability or instability of its first decay product (provided the first step is irreversible).

The rate law for the end product B is obtained in the usual way by extracting pairs of values \bar{v}_B and \bar{n}_X (belonging together) from the times and determining their correlation graphically. The straight line, produced should have a slope of 0.0038, supporting the rate law $\bar{v}_B = +k_2 \bar{n}_X$ with $k_2 = 1/280$.

The rate law for the intermediate product X may be found by the rather obvious assumption that the rate \bar{v}_X is just a linear function of the sum $\bar{v}_A + \bar{v}_B$, which is clearly verified when the data are plotted. The strict linear relationship $\bar{v}_X = -1(\bar{v}_A + \bar{v}_B)$ is found and is, of course, a consequence of the stoichiometric equation $\bar{n}_A + \bar{n}_X + \bar{n}_B = N$, from which it may be derived by differentiation. Putting $\bar{v}_A = -k_1 \bar{n}_A$ and $\bar{v}_B = +k_2 \bar{n}_X$ into the linear rate relationship yields $\bar{v}_X = +k_1 \bar{n}_A - k_2 \bar{n}_X$.

Example 6: The Equilibrium Reaction $A \rightleftharpoons B$

The rules already have been discussed in connection with Ehrenfest's two-container model. Starting with 140 A-balls and introducing

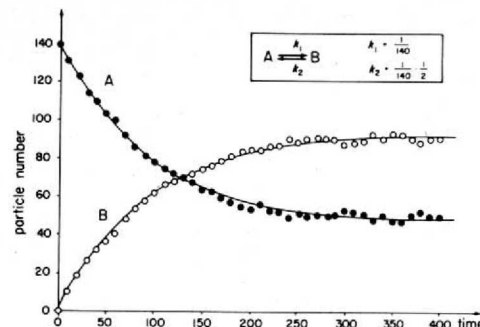


Figure 11. Kinetics of $A \rightleftharpoons B$ with $k_1 = 1/140$ and $k_2 = 1/280$, starting with 140 A-balls. The points represent the averaged results of three students, the theoretical curves were calculated by means of eqn. (6) in Figure 1.

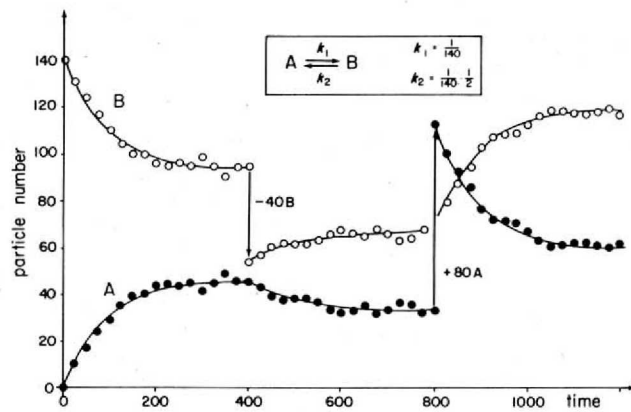


Figure 12. Demonstrating Le Chatelier's principle for the equilibrium reaction $A \rightleftharpoons B$.

the "coin rule" for the back reaction, so that $k_2 = 1/280$ whereas $k_1 = 1/140$, the kinetic curves of Figure 11 are obtained (averaged over three students' runs). The rate equation $\bar{v}_A = -k_1 \bar{n}_A + k_2 \bar{n}_B$ may be obtained by a procedure similar to the one discussed above for consecutive reactions. When the reaction has reached its equilibrium mixture $\bar{n}_{A\infty} = 46.7$ and $\bar{n}_{B\infty} = 93.3$, the equation $k_1 \bar{n}_{A\infty} = k_2 \bar{n}_{B\infty}$, which is well known as the (kinetic) law of mass action, holds. The students easily recognize the dynamic nature of the equilibrium state because further drawings of balls inevitably give rise to color changes (reactions) of balls without changing the equilibrium composition (setting aside statistical fluctuations).

Another group of students may find it interesting to start with 140 B-balls, following the same rules. They will obtain the same equilibrium composition showing it is unaffected by the special initial state which was chosen.

It is also interesting to remove from an equilibrium mixture, say, 40 B-balls and to continue the game following the same rules. It is seen then (Fig. 12) that a certain part of the removed B-balls is reproduced by reaction at the expense of A, until the old equilibrium proportion $\bar{n}_{B\infty}:\bar{n}_{A\infty} = 2:1$ is restored. Into this equilibrium mixture are thrown a further 80 A-balls from the store. The A-balls are now represented to a greater extent than allowed by the equilibrium condition, so that their excess is reduced by the following drawings to the benefit of B, until the old proportion 2:1 is once more restored. This is clearly a demonstration of Le Chatelier's principle.

Conclusion

Chemical kinetics correlates the macroscopic and microscopic levels of chemical reactions by means of mathematical constructs, rate laws (differential equations), and concentration-time laws (integrals of differential equations), which are difficult to teach and to understand in introductory courses and which furthermore veil the statistical nature of the processes they describe. It is suggested that the games' approach discussed above may be suited to complement the experimental approach in a satisfactory way especially if the

mathematical knowledge of the students is poor. The games are characterized by the following features:

- The correlation between mechanism and rules is straightforward.
- The connection between mechanism and kinetic curves is a direct result of the game and is independent from any mathematical considerations.
- The connection between mechanism and rate law may be discovered by simple numerical manipulations of the generated data.
- The connection between rate law and time law is arguably dispensable, but it is important to note that the generated data are in full accordance with the analytical equations representing the time laws in chemical kinetics.
- The games provide insight into the nature of the rate constants allowing them to be seen as the chance that an individual molecule or pair of molecules is activated at any particular moment to such a degree that they react within the following time unit.
- It must be admitted that the games are time-expensive. If one makes, say, 10 tries per minute it can be estimated that for each simulation roughly one hour is needed. My own experience with students tells me that only highly motivated students are willing to play six or more games of this length (although I am convinced that this time would be invested quite well). Fortunately several suitable actions may be taken to reduce this problem to a considerable extent.

Two students may work together; one of them makes the tries, the other records the container's composition continually. This reduces the time by as much as half and is, besides, more fun.

The different mechanisms may be assigned to groups of students. Each group simulates a different mechanism, and the groups exchange their results and explain them to one another. This can be interesting and instructive, especially if the groups do not know what mechanisms the others have simulated. It is then possible to let the students make educated guesses about which rules (mechanisms) might have been followed by the playing group to generate the kinetic curves presented. This is a good exercise for divergent thinking (5) and simulates kinetic

analysis, especially if incomplete reporting of information is allowed (not all curves must be shown, only a limited time range is shown, etc.).

The total number of balls may be considerably reduced by averaging ten or more runs. Indeed, in my lectures I prefer games with only 20 balls, and I get good results by averaging. It is convenient to let the students compare the averaged results (say 7 runs with 20 balls) with the unaveraged results (1 run with 140 balls). Although these procedures are not mathematically equivalent, the difference is rather small and may be neglected in practice.

The mechanical algorithms may be transformed very easily into computer programs, and it has been shown (6) that the simplest programmable pocket computers are sufficient for this purpose. It is my philosophy that the computer is an excellent complement but no substitute for the mechanical games. Therefore I use the computer only in the last period of the kinetic course, when the students have gathered enough experience with the mechanical games and when they, of their own initiative, raise the question as to the computability of the games.

The games' approach may be extended to other topics such as Maxwell's and Boltzmann's distribution laws, entropy, diffusion, chromatography, light absorption etc. (7), and to more general topics such as random walks, competition, self-organization and survival of the fittest (8). It is hoped that statistical games are good tools for teaching and learning the use of models in science and science education.

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