

Kinetics of Consecutive Reactions: First Reaction, First-Order; Second Reaction, Zeroth-Order

David W. Ball

Department of Chemistry, Cleveland State University, Cleveland, OH 44115

In the kinetics portion of many physical chemistry texts (1a–k), a discussion of integrated rate laws includes as an example the so-called *sequential* or *consecutive reactions*, namely:



in which an initial reactant A reacts to make some intermediate B, which then reacts to make a final product C. Furthermore, it is commonly presumed that each step is first-order with respect to the reactant:

$$\text{rate (reaction 1)} = k_1[A] \quad (2)$$

$$\text{rate (reaction 2)} = k_2[B] \quad (3)$$

By setting up differential forms for the change in concentrations of A, B, and C, these differential forms can be manipulated and ultimately integrated to get expressions for three time-dependent concentrations. These expressions are

$$[A]_t = [A]_0 e^{-k_1 t} \quad (4)$$

$$[B]_t = \frac{k_1[A]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right) \quad (5)$$

$$[C]_t = [A]_0 \left[1 + \frac{1}{k_1 - k_2} \left(k_2 e^{-k_1 t} - k_1 e^{-k_2 t} \right) \right] \quad (6)$$

Since natural radioactive decay processes are all first order, they are commonly used as examples of consecutive reactions in physical chemistry texts. (Of the texts that I surveyed, only two [2, 3] do not consider consecutive first-order reactions.)

No physical chemistry text surveyed considers an even simpler set of consecutive reactions: one first-order reaction followed by a *zerath*-order reaction. That is, rather than eqs 2 and 3 for the kinetics of each step, we consider

$$\text{rate (reaction 1)} = k_1[A] \quad (7)$$

$$\text{rate (reaction 2)} = k_2 \quad (8)$$

for the rate laws of each reaction.

Why would we even want to consider such a scheme? It turns out that a very common set of consecutive reactions follows these steps, but I have never seen it illustrated. It is the behavior of alcohol absorption by our bodies (the first step, which follows first-order kinetics) followed by the metabolic oxidation of ethanol by LADH (liver alcohol dehydrogenase, sometimes also abbreviated LAD) in the liver (the second step, which over the course of most of the reaction follows *zerath*-order kinetics) (1g). Let us, then, consider this scheme of consecutive reactions.

If we use the reaction scheme in eq 1, the differential forms for the rates of change of each species are

$$\frac{d[A]}{dt} = -k_1[A]_t \quad (9)$$

$$\frac{d[B]}{dt} = +k_1[A]_t - k_2 \quad (10)$$

$$\frac{d[C]}{dt} = +k_2 \quad (11)$$

The integrated form of eq 9 is the same as eq 4. To determine an integrated rate law for species B, the tactic in the textbooks is to substitute for $[A]_t$ from eq 4, assume a product form for $[B]_t$ as $f \cdot e^{-k_1 t}$ (where f is some undetermined function), differentiate the product solution, substitute, then separate the differentials and integrate. We do not need to be so arduous here; substituting for $[A]_t$ into eq 10 yields

$$\frac{\partial[B]}{\partial t} = \left(+k_1[A]_0 \cdot e^{-k_1 t} \right) - k_2 \quad (12)$$

Substituting, rearranging, etc., are unnecessary in this case because $[B]$ already appears on only one side of the equation! We can separate the differentials by bringing the dt to the right side and write:

$$d[B] = \left[\left(+k_1[A]_0 \cdot e^{-k_1 t} \right) - k_2 \right] dt \quad (13)$$

Now, we distribute the dt through the brackets on the right side and integrate both sides. The limits are 0 to t for time and 0 to $[B]_t$ for concentration of B (remember that we start the consecutive reactions with only species A present):

$$d[B] = \left(+k_1[A]_0 \cdot e^{-k_1 t} \right) dt - k_2 dt \quad (14)$$

$$\int_{[B]=0}^{[B]_t} d[B] = \int_{\text{time}=0}^t +k_1[A]_0 \cdot e^{-k_1 t} dt - \int_{\text{time}=0}^t k_2 dt \quad (15)$$

Each integral can be evaluated analytically and the expressions evaluated at the limits. We get

$$[B]_t = [A]_0 - [A]_0 e^{-k_1 t} - k_2 t \quad (16)$$

for the time dependence of $[B]$. The expression for $[C]_t$ can be determined either by integrating eq 11 or by considering the concentration balance from the reaction stoichiometries, that is,

$$[A]_t + [B]_t + [C]_t = [A]_0 \quad (17)$$

Either way, we can arrive at

$$[C]_t = k_2 t \quad (18)$$

for the time dependence of $[C]$. Equations 4, 16, and 18 therefore represent the changes of concentrations for a first-order/*zeroth* order set of consecutive reactions.

Equation 18 is problematic because it implies that $[C]_t$ increases without limit. This of course cannot happen, since the amount of original reactant, ethanol, is limited. In any discussion of consecutive reactions, the presumption of *initial* rates of reactions is made, although usually implicitly. For large values of time, individual reactions do not follow their initial rate laws, and ultimately thermodynamics takes control in determining the concentrations $[A]_{t \rightarrow \infty}$, $[B]_{t \rightarrow \infty}$, and $[C]_{t \rightarrow \infty}$ (4). Although equations 4, 16, and 18 are not applicable for all values of t , we are mostly interested (as are many textbook examples) in the concentration behavior at relatively short values of t . In this specific example, the concentrations of A and B approach zero at large t , whereas the specific concentration of C depends on the kinetics of metabolism of acetaldehyde in the body. (See ref 1*g* or 5 for additional information on the metabolism process.)

While initial rate constants for the absorption and metabolism of alcohol are very subject dependent, Tinoco et al. (1*g*) give values of k_1 and k_2 as $2.89 \times 10^{-3} \text{ s}^{-1}$ and $4.44 \times 10^{-5} \text{ mol s}^{-1}$. Plots of $[A]_t$, $[B]_t$, and $[C]_t$ are shown in Figure 1 using these numbers. For 1 mol of alcohol (which corresponds roughly to one serving of an alcoholic beverage), the maximum amount of absorption and concentration in the body appears in about 20 minutes. This peak is followed by a near-linear decline until $[B]_t$ reaches zero and the last product—ethanol metabolized into acetaldehyde—is the sole remaining chemical species. (Of course, in the body the process continues, but here we are focusing on the first two steps.) Because we are mixing first- and *zeroth*-order kinetics, the shapes of the plots and the relative positions of the maxima will depend on the initial amount as well as the exact value of the rate constants (which again are highly subject dependent).

The combination of first-order and *zeroth*-order reactions does make an interesting exercise, and its solution is in fact easier than the consecutive reactions usually considered in texts. Students and teachers are urged to use this, since it does pertain to a very well known phenomenon. And as a variation, what would be different if the *first* step were the *zeroth*-order reaction?

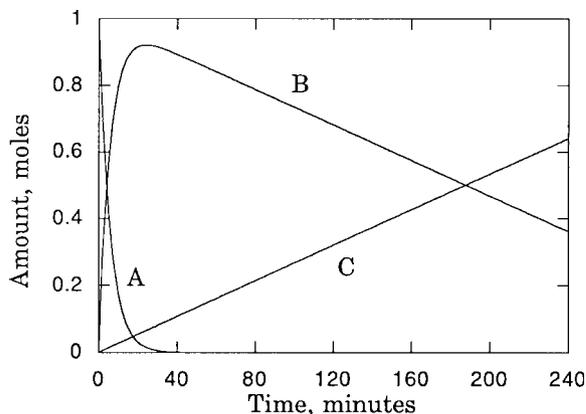


Figure 1. Amounts of A (unabsorbed ethanol), B (absorbed ethanol) and C (ethanol oxidized by LADH) according to the integrated rate laws for the first-order/*zeroth*-order consecutive reactions. The initial amount of A was 1 mol; $k_1 = 0.00289 \text{ s}^{-1}$; and $k_2 = 0.0000444 \text{ mol} \cdot \text{s}^{-1}$.

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