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# Chemical Kinetics without Calculus

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# Chemical Kinetics without Calculus

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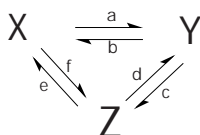
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Chemical kinetics is a fundamental part of every undergraduate physical chemistry course. However, students often fail to appreciate that specific chemical reaction schemes are special cases of general mathematical entities called networks. The networks have wide applicability in physics, engineering, and mathematical modeling, as well as chemistry (1). This question has the aim of helping students understand basic chemical kinetics by examining the variation of concentrations of reaction species with time. The approach is less artificial than the conventional one, because it investigates the variation of concentrations with time before any mechanisms or equations are postulated. Furthermore, it demonstrates that a variety of reaction types can be generated and analyzed qualitatively on the basis of a single reaction scheme (network).

The question is suitable for beginners in undergraduate physical chemistry courses since solving it does not require the use of calculus.

## Question

Consider the following general reaction scheme (network):



where  $\{a-f\} \geq 0$  are rate constants describing interconversion of reacting species X, Y, and Z. The initial concentrations for all reactions are  $[X] = 10$ ,  $[Y] = 0$ ,  $[Z] = 0$  at  $t = 0$ . The changes of  $[X]$ ,  $[Y]$ , and  $[Z]$  with time have been determined and are shown in Figures 1–6. In these figures,  $[X]$  is represented by the thick line,  $[Y]$  by the thin line, and  $[Z]$  by the broken line. The task is to extract from the general scheme given above the reaction(s) needed to explain data in each of the Figures 1–6. For every reaction, write down the simplest reaction scheme, estimate relative magnitudes of rate constants, and deduce how many (if any) independent equilibria have been established upon completion of a particular reaction.

## Acceptable Solution

### Figure 1

The presence of three curves in Figure 1 indicates that 3 species are present, two of which decay to zero within reaction life-span.

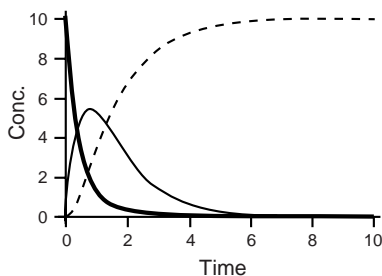


Figure 1

Therefore, no equilibria are established and the possible scheme which fits the observation corresponds to a consecutive reaction:



where  $a > c$ . The reason for the  $a > c$  deduction is that the  $[X]$  decays to zero quicker than  $[Y]$ . EXAMPLE: *nuclear decay along radioactive series*

### Figure 2

The presence of 3 curves in Figure 2 indicates presence of three species, X, Y, Z. The  $[X]$  curve decays to zero while the other two converge to constant values.

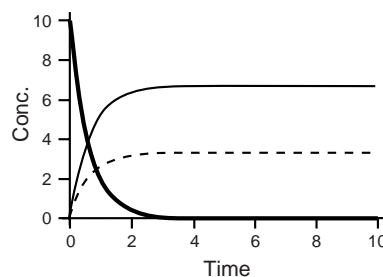
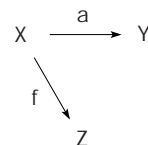


Figure 2

The possible solution is a parallel reaction:



with two rate constants ( $a, f$ ). Because  $[Y]$  and  $[Z]$  curves level off at different values,  $a > f$ . No equilibria are established. EXAMPLE: *hydrolysis of alkyl halides in basic media*.

### Figures 3–5

The presence in Figures 3–5 of two curves which are parallel at large  $t$  values and do not converge to zero indicates that only two species participate in each reaction and a single equilibrium is established upon completion of the reaction (between  $[X]$  and a single product).

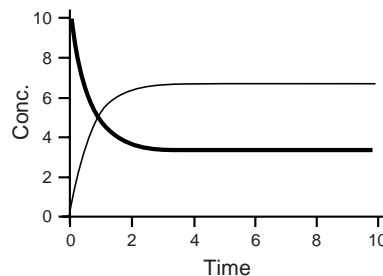


Figure 3

Figure 4

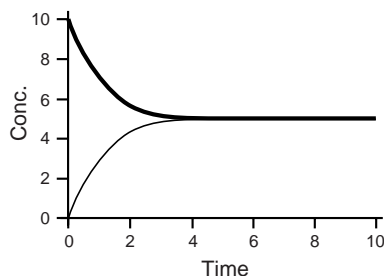
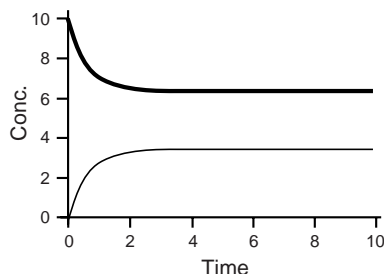
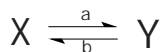


Figure 5



The reactions are of opposing type with two rate constants:  $a$ ,  $b$ :

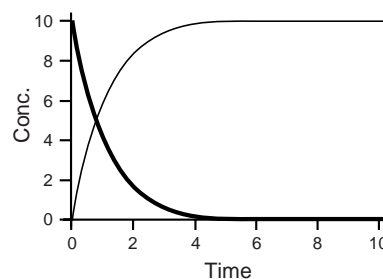


The differences between the reactions illustrated in Figures 3–5 are shown by the relative positions of the  $[X]$  and  $[Y]$  curves. When the two curves intersect (Fig. 3),  $a > b$ ; when they merge (Fig. 4),  $a = b$ ; and when they do not intersect (Fig. 5),  $a < b$ . EXAMPLE: *racemization reactions*.

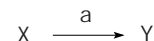
Figure 6

The presence of only two curves indicates that only two species participate. Furthermore, no equilibria are established, since  $[X]$  decays to zero and the product reaches a constant, nonzero value.

Figure 6



The reaction is an elementary 1st-order reaction with a single rate constant.



### Literature Cited

1. Temkin, O. N.; Zeigarnik, A. V.; Bonchev, D. *Chemical Reaction Networks: A Graph Theoretical Approach*; CRC: Boca Raton, FL, 1996.

### Appendix

Figures 1–6 were derived from the system of three ordinary linear differential equations:

$$d[X]/dt = b[Y] + e[Z] - a[X] - f[X]$$

$$d[Y]/dt = a[X] + d[Z] - b[Y] - c[Y]$$

$$d[Z]/dt = f[X] + c[Y] - e[Z] - d[Z]$$

The equations can be solved and graphs plotted by using computer algebra software (e.g., Mathematica, Maple, MathCad, Matlab). The nonvanishing rate constants used in the plots are:

Fig. 1:  $a = 2$ ,  $c = 0.8$

Fig. 4:  $a = b = 0.5$

Fig. 2:  $a = 1$ ,  $f = 0.5$

Fig. 5:  $a = 0.6$ ,  $b = 1.1$

Fig. 3:  $a = 1$ ,  $b = 0.5$

Fig. 6:  $a = 1$