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AN INTERESTING CASE OF CONSECUTIVE REACTIONS

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ABSTRACT

This paper deals with a special case of two consecutive first order reactions where the two rate constants are equal. This peculiar situation, that may not exist in real systems, has an interesting mathematical solution.

RESUMO

Este trabalho trata do caso especial de duas reações consecutivas de primeira ordem quando as duas constantes de velocidade são iguais. Nesta situação peculiar, que pode não existir em sistema reais, a solução matemática é muito interessante.

Considering a system of first order consecutive reactions of the type

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \tag{1}$$

and starting with pure A it is possible to solve a set of three differential equations finding the temporal dependence of the concentrations of A, R and S[1].

$$C_A = (C_A)_o \exp(-k_1 t) \tag{2}$$

$$C_R = \frac{k_1 (C_A)_o}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] \tag{3}$$

$$C_S = (C_A)_o + \frac{(C_A)_o}{k_2 - k_1}\left[k_1 \exp(-k_2 t) - k_2 \exp(-k_1 t)\right] \tag{4}$$

boundary conditions being at t=0, $C_A = (C_A)_o$, $(C_R)_o = (C_S)_o = 0$

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Equations (3) and (4) may be used whenever $k_1 \neq k_2$ but not in the particular case when $k_1 = k_2$. A closer look at this very peculiar situation becomes a quite interesting kinetic exercise although it may not have real existence.

Supposing $k_1 = k_2 = k$ in system (1) we may write, in differential form

$$-\frac{dC_A}{dt} = kC_A \tag{5}$$

$$\frac{dC_R}{dt} = kC_A - kC_R \tag{6}$$

Equation (5) integrates to the usual first order decay expression $C_A = (C_A)_o \exp(-kt)$. On the other hand, eq.(6) may be written

$$\frac{dC_R}{dt} + kC_R = k(C_A)_o \exp(-kt) \tag{7}$$

Solving eq.(7) for boundary conditions $t=0$, $(C_R)_o = 0$, the time dependence of C_R is given by

$$C_R = k(C_A)_o t \exp(-kt) \tag{8}$$

The maximum concentration of R in the system and the time necessary to reach it can be calculated by equating to zero the time derivative of eq.(8).

$$(C_A)_o t^2 \exp(-kt) = 0 \tag{9}$$

which gives

$$t_{max} = 1/k \tag{10}$$

$$(C_R)_{max} = (C_A)_o \exp(-1) \tag{11}$$

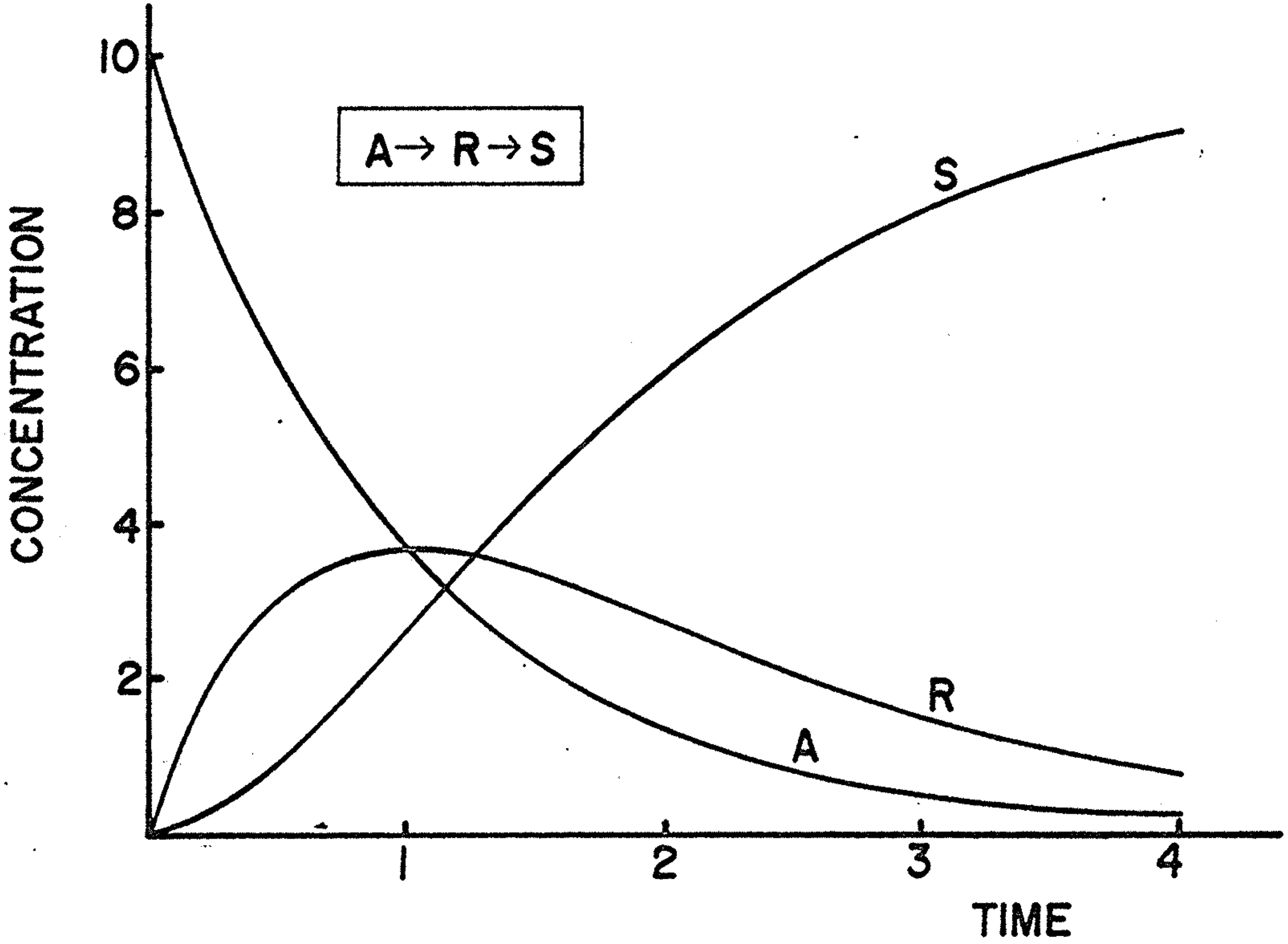

FIGURE 1. CONCENTRATION VERSUS TIME CURVES FOR THE FIRST ORDER SYTEM A →R →S, WITH IDENTICAL RATE CONSTANTS, STARTING WITH PURE A. ARBITRAY UNITS WERE USED FOR CONCENTRATION AND TIME.

Equations (10) and (11) show that t_{max} is the mean life of A and the maximum value of C_R is 1/e or about 37% of the initial amount of A present in the system.

Figure 1 is a graphical representation of the case in study. Concentrations of A, R and S can be easily calculated with the help of a pocket calculator and the curves may be either drawn by hand or displayed in a microcomputer making use of a quite simple BASIC program.

Note that, according to the derived equations, the maximum of the curve which gives C_R coincides with the curve C_A in the point where the concentration of A is reduced to 1/e or 37% (see Fig. 1).

REFERENCES

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