GRAPHICAL SOLUTIONS FOR THE CONSTANTS IN THE FIRST ORDER AUTOCATALYTIC REACTION VELOCITY EQUATION

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Introduction

The velocity of a first order autocatalytic reaction is expressed by the differential equation

$$\frac{dx}{dt} = k(b+x)\ (1-x)$$

where **x** is the amount of product formed in time **t**

b is the initial catalytic influence which **must** be present to start the reaction, since a truly "autocatalytic" reaction could never start.

k is the reaction velocity constant

and the concentrations of the reactant and product of the reaction are expressed in arbitrary units, so that the initial concentration of the reactant and the final concentration of the product of the reaction are equal to unity.

On integration, the equation takes the form

$$k = \frac{2.303}{t\ (1+b)} \log \frac{b+x}{b\ (1-x)}$$

which does not afford a simple solution for the constants, **k** and **b**. An algebraic solution of limited applicability has been presented by the author[1].

1. Graphical Solution by Means of the Flex-Point Ordinate

Gann[2] has presented a graphical solution for **b** based on the flex-point ordinate, x_m, which can be obtained by inspection of the curve, and which is related to b mathematically as follows:

At the flex-point, the slope of the curve (plotted with **x** as the ordinate and **t** as the abscissa) passes through a maximum, so that the second derivative of the equation equals zero at this point.

$$\frac{d_2x}{dt} = 1 - 2x_m - b = 0$$

$$\text{whence,} \quad b = 1 - 2x_m$$

While Gann's solution is mathematically sound, it is limited in its applicability by the difficulty of accurately determining the flex-point ordinate from the curve of experimental data. The results of an attempt to apply this method to the plots of ideal curves is shown in Table I.

2. Graphical Solution by Means of the Ratio of the Slopes of the Curve at Fixed Points

Graphical solution of the first order autocatalytic equation is theoretically possible on the basis of the ratio of the slopes at fixed points when the curve is plotted with **x** as the ordinate and **t** as the abscissa. The slope of the curve at any point is given by the differential equation

$$\frac{dx}{dt} = k\ (b+x)\ (1-x)$$

For practical reasons, the points selected for measurement of the slopes should not be near the beginning or end of the curve, and should be far enough apart so that the slope change is significant. The example is carried out with the slope at the point, x = 0.333, and the slope at the point, x = 0.667. The ratio of the two slopes leads to a relatively simple expression in **b**, so that the method can be considered a graphical solution for the constant **b**. Substituting the values of **x** selected above, we have,

$$\frac{\left\{\frac{dx}{dt}\right\}_{0.333}}{\left\{\frac{dx}{dt}\right\}_{0.667}} = \frac{k\ (0.333+b)\ (0.667)}{k\ (0.667+b)\ (0.333)} = \frac{1+3b}{1+1.5b} = R$$

$$b = \frac{R-1}{3-1.5R}$$

[1] H. W. Carhart and E. H. Shaw, Jr., Proc. So. Dak. Acad. Sci., 15, 48 (1935).
[2] J. Gann, Koll. Beih., 8, 64 (1916).

The practical limitations of this method of graphical solution are shown in Table I, where the results obtained by the application of this method to ideal curves are given.

3. Graphical Solution Based on the Common Asymptote to the Plots, log $\frac{x}{1-x}$ vs t, and log $\frac{1}{1-x}$ vs t

The first order autocatalytic equation

$$k = \frac{2.303}{t\,(1+b)} \log \frac{b+x}{b\,(1-x)}$$

may be converted algebraically to the form

$$t \cdot \frac{k\,(1+b)}{2.303} = \log \left\{ \frac{x}{1-x} \cdot \frac{1+b}{b} + 1 \right\}$$

which approaches asymptotically the simpler expression

$$t \cdot \frac{k\,(1+b)}{2.303} = \log \frac{x}{1-x} + \log \frac{1+b}{b}$$

a straight line in the variables **t** and **log** $\frac{x}{1-x}$. This asymptote is readily drawn to the curve obtained by plotting from the data, log $\frac{x}{1-x}$ vs **t**. At the upper values of **x**, and in those cases where **b** is less than 0.3, the coincidence between the curve and the asymptote is almost complete. The intercept on the log $\frac{x}{1-x}$ axis equals log $\frac{b}{1+b}$. The slope, $\frac{d \log \frac{x}{1-x}}{dt}$ equals $\frac{k\,(1+b)}{2.303}$. In those cases where **b** is 0.3 or greater, the location of the asymptote is facilitated by plotting, in addition to log $\frac{x}{1-x}$ vs **t**, the curve log $\frac{1}{1-x}$ vs **t**, since the two curves have a common straight line as asymptote. The first order autocatlytic equation

$$t \cdot \frac{k\,(1+b)}{2.303} = \log \frac{b+x}{b\,(1-x)} = \log \frac{b+x}{b} + \log \frac{1}{1-x}$$

takes the form, in the limiting case when **x** approaches unity, of

$$t \cdot \frac{k\,(1+b)}{2.303} = \log \frac{1+b}{b} + \log \frac{1}{1-x}$$

which, except for the change in the ordinate to log $\frac{1}{1-x}$, is identical with the equation for the asymptote given above, and leads to the same solution.

This graphical solution yields values for both **b** and **k**. The value of **k** is dependent on **b**, however. The results of the practical application of this method of graphical solution to ideal curves are given in Table I. It will be noted that they are very much more satisfactory than the values obtained from the flex-point and the ratio of the slopes, both of which methods have the additional disadvantage of yielding no direct solution for **k**.

Table I

Results of the Practical Application of Graphical Solutions to a Series of Ideal First Order Autocatalytic Curves

Known Values		Values Obtained from the Graphical Solutions			
		Flex-point	Ratio of Slopes	Common Asymptote	
b	k	b	b	b	k
1.0	0.1373	0.9–1.0	1.233	0.9690	0.1397
0.3	0.3220	0.2–0.6	0.2643	0.2877	0.3265
0.1	0.5648	0 –0.4	0.1452	0.1039	0.5587
0.02	0.9676	0 –0.2	0.06202	0.02084	0.9612
0.001	1.726	0 –0.2	negative	0.001048	1.718

Table I shows the obvious superiority of the method of the Common Asymptote as a means of graphical solution for the constants, **b** and **k**, in the first order autocatalytic reaction velocity equation.