

On the Kinetics of Consecutive, Bimolecular Reactions

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Abstract

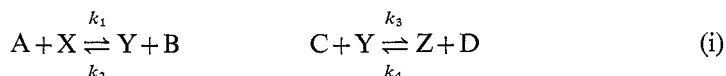
It is shown that the differential equations governing the kinetics of consecutive, bimolecular reactions can be reduced to an Abel equation.

It does not appear to be generally known that chemical processes involving two consecutive, reversible reactions with at least one elementary step of second order^{1,2} are described by an Abel's differential equation.³ This is an equation of the form

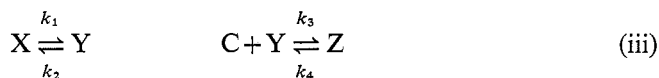
$$dw/dx = \sum_{n=0}^{n=3} f_n(x)w^n \quad (1)$$

In the context of bimolecular chemical kinetics, the functions $f_i(x)$ ($i = 0, 1, 2, 3$) are rational functions of the independent variable x , the elements of the quotients being at most quartic in x .

To justify this conclusion, it is necessary to show only that an equation of the form (1) describes the general process involving four second-order steps:



as well as the simplest processes with only one second-order step



The terms k_i ($i = 1, 2, 3, 4$) denote the velocity constants of the elementary steps. In all cases the time rates of change of the concentrations A , X , B , etc. of the compounds occurring in the reactions are obtained through the Principle of Mass

¹ Benson, S. W., 'The Foundations of Chemical Kinetics' pp. 42-55 (McGraw-Hill: New York 1960).

² Frost, A. A., and Pearson, R. G., 'Kinetics and Mechanism' 2nd Edn, pp. 177-84 (John Wiley: New York 1961).

³ Murphy, G. M., 'Ordinary Differential Equations and Their Solutions' pp. 23-7 (Van Nostrand: New York 1960).

Action.⁴ With the help of the conservation relations involving the initial concentrations of the substances present, which can be derived by inspecting the resulting differential equations, we immediately find that, for the schemes (i), (ii) and (iii)

$$\ddot{X} = F_1(X)\dot{X}^2 + F_2(X)\dot{X} + F_3(X) \quad (2)$$

Dots denote derivatives with respect to the time t , and the F_i terms are rational functions of X . Setting

$$\dot{X} = 1/W \quad \ddot{X} = -\dot{W}/W^2 = -W^{-3}dW/dX \quad (3)$$

we obtain an equation of the form (1), with $f_0 = 0$.

It is clear that reactions involving two and three second-order steps will be likewise described by Abel's differential equations with the functional coefficients of complexity intermediate to the above. The same is true when some of the components are identical. For example, if $A \equiv X$ in the scheme (i), we obtain equation (2) with k_2 , k_3 and k_4 replaced by $k_2/4$, $k_3/2$, $k_4/2$, and the concentrations of all the components other than X replaced by twice their concentrations, respectively.

Some care must be exercised in deriving the appropriate Abel equation when various components are identified with others. Thus, if $C \equiv A$ in the scheme (i) we obtain an Abel equation with X as an independent variable but not if the elimination between the pair A and Y is attempted.

Abel's equation is integrable in terms of elementary functions only in a very few special cases. In fact, it can be shown³ that equation (1) can be reduced to the general form

$$dw/dx = 1 + f(x)w^3 \quad (4)$$

unless, of course, it becomes a linear, Bernoulli or Riccati equation. Equation (4) is immediately integrable only if either

$$f(x) = \text{constant} \quad \text{or} \quad f(x)x^3 = \text{constant} \quad (5)$$

On the other hand, if a solution is found for some reaction scheme, the time-dependence of all the concentrations involved can be found with just one additional integration.

Examples of the schemes (i), (ii) and (iii) are perhaps not easily found among inorganic reactions. An exception may be acid-base reactions when ionic concentrations are taken into account. It should be pointed out, however, that Abel's equation occurs also, when, for example, the second step in scheme (i) is irreversible. Cases conforming to our result are, on the other hand, common in organic reactions, and in biochemistry. Thus we may quote the Mannich reaction on aminoalkylation of cyclohexanone⁵ or enzyme reactions, which originally led to the present investigations.⁶

In all these cases study of Abel's equation is indispensable to a comprehensive survey of the situation as soon as results are required for the transient phase of the reaction and not just for the steady state.

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⁴ Frost, A. A., *J. Chem. Educ.*, 1941, **18**, 272.

⁵ Gutsche, C. P., and Pasto, P. J., 'Fundamentals of Organic Chemistry' pp. 712-3 (Prentice-Hall: Englewood Cliffs, New Jersey, 1975).

⁶ Darvey, I. G., Klotz, A. H., and Ritter, M., *Bull. Math. Biol.*, in press.