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**A CONVOLUTION APPROACH TO THE KINETICS OF CHEMICAL
AND PHOTOCHEMICAL REACTIONS**

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A new method for writing kinetic equations directly in the integrated form is presented. This method applies to any species that is consumed solely through first order steps, regardless of the complexity of its formation pathways.

INTRODUCTION

Macroscopic chemical kinetics is based on differential equations of the type

$$\frac{dX_i}{dt} = \left(\frac{dX_i}{dt}\right)_{in} + \left(\frac{dX_i}{dt}\right)_{out} + \left(\frac{dX_i}{dt}\right)_{pro} + \left(\frac{dX_i}{dt}\right)_{con} \quad (1)$$

which are simple balances for the amount of species X_i ($i=1, \dots, n$) within the system, in standing for input, out for output, pro for internal production and con for internal consumption, the first two processes being relevant for open systems and the last two being associated with chemical reactions occurring in the system.

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Comparison with experimental data is usually done in the integrated form, that is, the system of differential equations (1) is integrated, analytically or numerically, and the resulting time functions $X_i(t)$ then compared with the experimental ones, in order to extract rate constants or even to test the proposed mechanism/kinetic scheme.

The opposite procedure is also possible, *i.e.*, numerical differentiation of experimental data followed by direct comparison with the system of differential equations (1) (e. g. method of the initial rates). For a number of reasons, which include the amplification of experimental error, this is a much less common procedure. A general discussion of the advantages and limitations of the differential and integral methods is given by Laidler [1]. More recently, Steel and Razi Naqvi [2] addressed the differential method in detail.

The integration of system (1) can be made using several mathematical techniques, including matrix methods [3-5]. However, when all the consumption rates (*i.e.* the second and fourth terms in eq. 1 are first order (or pseudo-first order), there is a straightforward way to write down the balances directly in the integrated form. The method, based on the concept of convolution, has been used in photochemical kinetics [6]. In this letter, we summarize the approach and apply it to two cases.

CONVOLUTION APPROACH

Suppose that a reactive chemical species X_i can be instantaneously produced at unit concentration at time $t=0$: ignoring the possibility of reformation of X_i via closed loops (e.g. a reversible step), its time evolution will be given by a certain function $X_{i\delta}(t)$. This function is the response to a unit input of X_i at time zero, that is, to a Dirac's delta function $\delta(t)$, and reflects all possible disappearance routes for X_i . It is in general a function of the concentration of X_i and of the concentration of the other species X_j ($j \neq i$).

However, under first order or pseudo first order conditions, this function is independent of all concentrations,

$$X_{i\delta}(t) = \exp\left(-\sum_j k_{ij}t\right) \quad (2)$$

where k_{ij} are strict or pseudo first order rate constants of the elementary steps by which X_i disappears. Now the general time evolution for X_i is given by the convolution integral

$$X_i(t) = \int_0^t P_i(\theta) X_{i\delta}(t-\theta) d\theta = P_i \otimes X_{i\delta} \quad (3)$$

where $P_i(t)$ is the rate of production of X_i . This production rate includes all steps that generate X_i , either internal or external, and arising or not from closed loops. Equation 3 is the fundamental equation of the convolution approach and can be understood on the basis of the following: the total concentration of X_i at a given instant t will be the sum of all delta responses $X_{i\delta}$ weighed by the respective initial amount produced $P_i(\theta)$ and taking into account that a time lapse $t-\theta$ has passed since that particular creation process.

Taking the time derivative of eq. 3 yields [6] of course the usual differential balance

$$\frac{dX_i}{dt} = P_i - \left(\sum_j k_{ij}\right) X_i \quad (4)$$

this being the proof of the equivalence of the differential and convolution (integral) approaches.

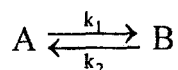
For a given kinetic problem, the full solution in terms of the convolution approach is obtained in four steps:

- (1) Identification of the delta responses $X_{i\delta}(t)$;
- (2) Identification of the production terms $P_i(t)$;
- (3) Writing of

the system of coupled (through the P_i 's) integral equations $X_i = P_i \otimes X_i \delta$ ($i=1,2,\dots$); (4) Solution of the system of coupled equations, e.g. by the use of Laplace transformation theory. Two cases will now be discussed.

A REVERSIBLE FIRST-ORDER REACTION

Consider the scheme



The δ -production responses are,

$$A_\delta(t) = \exp(-k_1 t) \quad (5)$$

$$B_\delta(t) = \exp(-k_2 t) \quad (6)$$

and the production rates are

$$P_A = A_0 \delta(t) + k_2 B \quad (7)$$

$$P_B = B_0 \delta(t) + k_1 A \quad (8)$$

Combining eqs 5-8 one obtains

$$A = A_0 \exp(-k_1 t) + k_2 B \otimes \exp(-k_1 t) \quad (9)$$

$$B = B_0 \exp(-k_2 t) + k_1 A \otimes \exp(-k_2 t) \quad (10)$$

The time evolutions of A and B are not independent, as eqs 9 and 10 are coupled. Their separation is easily carried out by the use of Laplace transforms. Knowing that the transform of the convolution product $f \otimes g$ is the product of individual transforms, i.e. $f \otimes g = fg$, one gets

$$\bar{A} = \frac{A_0}{s+k_1} + \frac{k_2}{s+k_1} \bar{B} \quad (11)$$

$$\bar{B} = \frac{B_0}{s+k_2} + \frac{k_1}{s+k_2} \bar{A} \quad (12)$$

This algebraic system is easily solved, and after Laplace inversion, one finally obtains

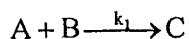
$$A = \frac{A_0}{k} [k_2 + k_1 \exp(-kt)] + B_0 \frac{k_2}{k} [1 - \exp(-kt)] \quad (13)$$

$$B = \frac{B_0}{k} [k_1 + k_2 \exp(-kt)] + A_0 \frac{k_1}{k} [1 - \exp(-kt)] \quad (14)$$

where $k = k_1 + k_2$. Equations 13 and 14 are well known but were now obtained without solving any differential equations.

A MECHANISM WITH BIMOLECULAR STEPS

Complex kinetic schemes frequently contain bimolecular steps. If these cannot be assumed to be first order, the present approach is not applicable to the species that decay by those steps. Even then, the convolution approach may be of some interest. Consider for instance the scheme, whose solutions are already complicated [7],



Species A and B cannot in general be handled by the present approach, as they participate in a bimolecular step. But species C, D and E can still be related with A and B by this approach. From the above enunciated rules, one can write directly the following integral relations between concentrations,

$$C = (k_1 AB) \otimes 1 \quad (15)$$

$$D = (k_2 A) \otimes \exp(-k_3 t) \quad (16)$$

$$E = (k_3 D) \otimes 1 = k_2 k_3 A \otimes \exp(-k_3 t) \otimes 1 \quad (17)$$

Integral relations of this type may be of importance for the experimental determination of rate constants. For example, if all time evolutions are known from experiment, the rate coefficients can be written as

$$k_1 = \frac{C}{(AB) \otimes 1} = \frac{C(t)}{\int_0^t A(u)B(u)du} \quad (18)$$

$$k_3 = \frac{E(t)}{D \otimes 1} = \frac{E(t)}{\int_0^t D(u)du} \quad (19)$$

$$k_2 = \frac{D(t)}{A \otimes \exp(-k_3 t)} = \frac{D(t)}{A \otimes \exp\left[-E(t)t / \int_0^t D(u)du\right]} \quad (20)$$

As far as the authors are aware, this method has never been used for the calculation of rate constants.

DISCUSSION AND CONCLUSIONS

The aim of the present work was to show the interest and range of applicability of the convolution approach. It finds several applications in chemical kinetics, as it allows the writing of the mole balance equations directly in the integrated form, whenever the decay of a species is effectively first order. The first case discussed was a simple kinetic scheme, whose results are well known. It served, however, to introduce the approach and to show its straightforwardness. The final system discussed contained both unimolecular and bimolecular steps. In cases like this, all species disappearing through first order processes can still be handled by the convolution mechanism, and this may allow the direct estimation of rate constants or the comparison between experimental and calculated time evolutions. More complex cases, where the rate coefficients are time-dependent, including excimer formation and radiationless energy transfer can also be treated by the same formalism, nontrivial results being then obtained[6].

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