

Mathematical basis of the integral formalism of chemical kinetics. Compact representation of the general solution of the first-order linear differential equation

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Abstract The standard approach in chemical and photochemical kinetics is to proceed from the kinetic scheme to the corresponding system of first-order differential equations, and then to integrate it, analytically or numerically. An equivalent integral formulation circumventing such system was recently developed on the basis of physical arguments. The mathematical basis of this *ansatz* is discussed here. A compact representation of the general solution of the linear first-order differential equation is also obtained.

Keywords Ordinary differential equations · Chemical kinetics · First-order linear differential equation

1 Introduction

The standard approach in formal chemical and photochemical kinetics is to proceed from the kinetic scheme to the corresponding system of first-order differential equations, and then to integrate this system, analytically or numerically, in order to obtain the concentrations of selected species as a function of time, which is the main goal [1,2].

When the species of interest decay solely via unimolecular or pseudo-unimolecular steps, it is nevertheless possible to sidestep the system of differential equations. In fact, the evolution equations can be directly written in integral form by application of the convolution method (CM) [3–6]. The equations are in general coupled, but the explicit solutions can be obtained in most cases by repeated substitution or by appli-

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cation of Laplace transforms. Specific applications are given in [7–10]. The CM is nevertheless not applicable if at least one of the species of interest decays by one or more bimolecular processes [6].

The CM was recently extended by developing a completely general integral formulation of chemical and photochemical kinetics [11]. The results obtained were derived on the basis of physical reasoning. In this work, a connection is made with standard mathematical methods for solving ODEs, and the mathematical basis of the *ansatz* established. A compact representation of the general solution of the first-order linear differential equation is also obtained as a side result.

2 Physical approach

The central quantity in the CM is the survival probability of a given species X_i ($i = 1, 2, \dots$) after delta (instantaneous) production [3–6]:

$$X_{i\delta}(t) = \exp(-k_i t) \quad (1)$$

where for simplicity X_i stands also for the concentration of species X_i . The survival probability function is assumed to be the same, whatever the time at which production takes place. This means in particular that the decay of species X_i is not dependent on the concentration of other species, hence it must be unimolecular (or pseudo-unimolecular at most). The response to other types of stimuli, be they reactants or other production modes (e.g. light absorption that generates an excited state) is written as

$$X_i(t) = P_i \otimes X_{i\delta}(t) = P_i \otimes \exp(-k_i t) \quad (2)$$

where \otimes stands for the convolution between two functions, $f \otimes g = \int_0^t f(u)g(t-u) du$. This results from an assumption of linearity [3–6].

Equation (1) is now generalized in order to include cases where X_i decays by bimolecular processes. If X_i is generated at time t_0 , then the respective survival probability is [11]

$$X_{i\delta}(t|t_0) = \exp\left(-\int_{t_0}^t k_i(u) du\right) \quad (3)$$

where $k_i(t)$ is an appropriate time-dependent rate coefficient. The time dependence may arise from a concentration dependence, if the respective disappearance step is bimolecular, with $k_i(t) = k_{ij}X_j(t)$, but also from the temperature dependence of a unimolecular rate constant, if the reaction is not isothermal. In both cases the delta response is neither independent of the production time nor of the subsequent system's evolution (unlike the cases previously considered in the so-called transient kinetics [3,4] where the same time-dependent rate coefficient is valid for impulses occurring at different times). The time evolution of a species is linked to the rest of the system not only by the production, but also by the disappearance rate. Instead of Eq. (2), the response to a general (non-delta) production is now given by [11]

$$X_i(t) = \int_0^t P_i(v) X_{i\delta}(t|v) dv \quad (4)$$

This is the main result of the integral formulation of chemical kinetics [11], and represents a complete generalization of the CM. An assumption of linearity is still implicit, which is consistent with the usual differential equation formalism. Indeed, differentiation of Eq. (4) with respect to time gives

$$\frac{dX_i}{dt} = P_i(t) - k_i(t)X_i(t) \quad (5)$$

This result demonstrates the equivalence of the two approaches. The differential and integral kinetic formalisms are thus strictly equivalent.

In the CM, the long-time limit of X_i , $X_{i\infty}$, is given by [4]

$$X_{i\infty} = \lim_{t \rightarrow \infty} P_i \otimes X_{i\delta}(t) = P_i(\infty) \int_0^\infty X_{i\delta}(u) du \quad (6)$$

And assumes a simple form if $X_{i\delta}(t)$ is given by Eq. (2).

The more general result in integral kinetics is [11]

$$X_{i\infty} = P_i(\infty) \int_{t_0}^\infty X_{i\delta}^\infty(u|t_0) du \quad (7)$$

where $X_{i\delta}^\infty(u|t_0)$ stands for the limiting form of $X_{i\delta}(u|t_0)$ when t_0 is very large. Eq. (7) is valid only when $P_i(t)$ attains a constant value for $t \rightarrow \infty$.

3 Mathematical basis

Insertion of Eq. (3) in Eq. (4) gives

$$X_i(t) = \int_0^t P_i(v) \exp\left(-\int_v^t k_i(u) du\right) dv \quad (8)$$

This is therefore the full-fledged solution of Eq. (5). On the other hand, the general solution of the first-order linear differential equation

$$y' + P(x)y = Q(x) \quad (9)$$

is [12]

$$f(x) = b \exp[-A(x)] + \exp[-A(x)] \int_a^x Q(t) \exp[A(t)] dt \quad (10)$$

with $b = f(a)$ and

$$A(x) = \int_a^x P(u) du \quad (11)$$

Setting $a = 0$, and changing $P(t)$ into $k_i(t)$ and b into X_{i0} , Eq. (10) becomes

$$X_i(t) = X_{i0} \exp \left[- \int_0^t k_i(u) du \right] + \exp \left[- \int_0^t k_i(u) du \right] \int_0^t Q(v) \exp \left[- \int_0^v k_i(u) du \right] dv \quad (12)$$

Eq. (12) can then be rearranged to give

$$X_i(t) = X_{i0} \exp \left[- \int_0^t k_i(u) du \right] + \int_0^t Q(v) \exp \left[- \int_v^t k_i(u) du \right] dv \quad (13)$$

Eqs. (8) and (13) are thus equivalent only if

$$P_i(t) = X_{i0} \delta(t) + Q(t) \quad (t \geq 0) \quad (14)$$

Indeed, when discussing chemical reactions it is assumed that species X_i is initially present with concentration X_{i0} , and that the reaction begins at time $t = 0$ only (“mixing of the reactants”). Eq. (5) is in fact valid only for $t \geq 0$, and Eqs. (8) and (14) reflect this asymmetry. On the other hand, Eq. (10) is assumed to hold for all values of x . If $P(t) > 0$, then in order for $X_i(0) = X_{i0}$, $Q(t)$ must be nonzero for at least some negative values of t , and can even be a continuous positive function for $t < 0$. There is no need for a delta-type function term, as the action of $Q(t)$ during negative times allows X_i to smoothly approach X_{i0} at $t = 0$, see Eq. (16) below.

The above discussion leads to a compact representation of the general solution of the linear first-order differential equation, valid for any $P(x)$ and $Q(x)$,

$$f(x) = \int_a^x [f(a) \delta(v - a) + Q(v)] \exp \left(- \int_v^x P(u) du \right) dv \quad (15)$$

compare Eq. (10). Although simple, this appears to be a new result.

For $t = 0$ Eq. (15) gives

$$X_{i0} = f(a) \exp \left(- \int_a^0 P(u) du \right) + \int_a^0 Q(v) \exp \left(- \int_v^0 P(u) du \right) dv, \quad (16)$$

and X_{i0} results from the two contributions mentioned above. Eq. (16) encompasses the special case $Q(t) = X_{i0} \delta(t)$ ($t \leq 0$) but shows that allowance for negative times leads to an infinite number of ways of getting X_{i0} at $t = 0$. The $Q(t)$ in Eq. (14) is thus $Q^+(t)$, i.e. for $t > 0$ only, a distinction that is necessary only when a discontinuity is present at $t = 0$.

4 Conclusions

An integral formulation of chemical kinetics was recently developed on the basis of physical arguments. The mathematical basis of this *ansatz* was obtained here, by comparison with the general solution of the linear first-order differential equation. A compact representation of the general solution of the linear first-order differential equation emerged from the discussion.

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