

Chemical reaction rate determination II. numerical PIPD integral method

Christopher Gunaseelan Jesudason

*Department of Chemistry and Centre for Theoretical and Computational Physics,
Science Faculty, University of Malaya, 50603 Kuala Lumpur, Malaysia*

Summary. In this second sequel, the integrated rate law expression is the basis for a new method of projecting all its parameters to be determined as function of one primary varying parameter -in this case the rate constant- by utilizing the experimental data points to construct the functional dependency where this method is called the principle of induced parameter dependence (PIPD). Such a technique avoids problems associated with multiple minima and maxima because of the possibly large number of parameters. The method is applied to first and second order reactions based on published data where the results accord very well with standard treatments. The PIPD and its method could be a promising optimization technique for a large class of phenomena that have a large number of parameters that need to be determined without leading to "unphysical" and anomalous parameter values.

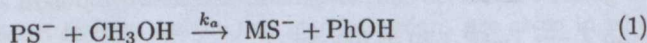
1 INTRODUCTION

The PIPD application is tested against the same first order reaction (i) as in sequel I involving the methanolysis of ionized phenyl salicylate with data derived from the literature [1, Table 7.1,p.381]

and a second order reaction (ii) the details being

(ii) the reaction between plutonium(VI) and iron(II) according to the data in [2, Table II p.1427] and [3, Table 2-4, p.25].

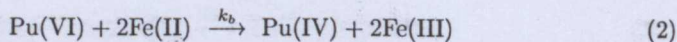
Reaction (i) may be written



where for the rate law is pseudo first-order expressed as

$$\text{rate} = k_b[\text{PS}]^- = k_c[\text{CH}_3\text{OH}][\text{PS}^-].$$

Reaction (ii) was studied by Newton et al. [2, eqns. (8,9),p.1429] and may be written as



whose rate ξ is given by $\xi = k_0[\text{PuO}_2^{2+}][\text{Fe}^{2+}]$ where k_0 is relative to the constancy of other ions in solution such as H^+ . The equations are very different in form to the first-order expressions and serves to confirm the viability of the current method. We use their data [2, TABLE II,p.1427] to verify the principles presented here. Espenson had also used the same data as we have to derive the rate constant and other parameters [3, pp.25-26] and we refer to his values for the final concentration parameter and rate constant to check on the accuracy of our methodology.

2 PIPD introduction

Deterministic laws of nature arefor the simplest examples written in the form

$$Y_{law} = Y_{law}(\mathbf{P}, k, t) \quad (3)$$

linking the variable Y_{law} to the experimental series of measurements of physical variable t (which in this case involves time). The components of \mathbf{P} , $P_i (i = 1, 2, \dots, N_p)$ and k are parameters. Verification of a law of form (3) relies on an experimental dataset $\{(Y_{exp}(t_i), t_i), i = 1, 2, \dots, N\}$. Several methods [4, 5, 6, 7, etc.] have been devised to determine the optimal \mathbf{P}, k parameters, but these methods consider the (\mathbf{P}, k) parameters as autonomous and independent (e.g. [5]) subjected to free and independent variation during the optimization process. On the other hand, if one considers the interplay between the experimental data and Y_{law} one can derive certain parameters like the final concentration terms (e.g. λ_∞ and Y_∞ in what follows in Sec.(4)) if k , the rate constant is known. To preserve the viewpoint of interdependency, we devise a scheme that relates \mathbf{P} to k for all P_i via the set $\{Y_{exp}(t_i), t_i\}$, and optimize the fit over k -space only. i.e. there is induced a $P_i(k)$ dependency on k via the the experimental set $\{Y_{exp}(t_i), t_i\}$. The advantages of the present method is that the optimization is over 1D k space, leading to a unique determination of \mathbf{P} with respect to k , whereas if all \mathbf{P} are considered equally free, the optimization could lead to many different local solutions for each of the $\{P_i\}$, some of which would be considered erroneous on physical grounds. The rate constant is considered constant over all measurements, although this assumption is not strictly correct [8].

3 Outline of Method

Let N be the number of dataset pairs $\{Y_{exp}(t_i), t_i\}$, N_p the number of components of the \mathbf{P} parameter, and N_s the number of singularities where the use of a particular dataset (Y_{exp}, t) leads to a singularity in the determination of $\bar{P}_i(k)$ as defined below and which must be excluded from being used in the determination of $\bar{P}_i(k)$. Then $(N_p + 1) \leq (N - N_s)$ for the unique determination of $\{\mathbf{P}, k\}$. Define ${}^{N-N_s}C_{N_p} = N_c$ as the total number of combinations of the data-sets $\{Y_{exp}(t_i), t_i\}$ taken N_p at a time that does not lead to singularities in P_i . Write Y_{law} in the form

$$Y_{law}(t, k) = f(\mathbf{P}, t, k). \quad (4)$$

Map $f \rightarrow Y_{th}(\bar{\mathbf{P}}, t, k)$ as follows

$$Y_{th}(t, k) = f(\bar{\mathbf{P}}, t, k) \quad (5)$$

where the term $\bar{\mathbf{P}}$ and its components is defined below and where k is a varying parameter. For any of the $(i_1, i_2, \dots, i_{N_p})$ combinations where $i_j \equiv (Y_{exp}(t_{i_j}), t_{i_j})$ is a particular dataset pair, it is in principle possible to solve for the components of $\bar{\mathbf{P}}$ in terms of k through the following simultaneous equations:

$$\begin{aligned} Y_{exp}(t_{i_1}) &= f(\mathbf{P}, t_{i_1}, k) \\ Y_{exp}(t_{i_2}) &= f(\mathbf{P}, t_{i_2}, k) \\ &\vdots \\ Y_{exp}(t_{i_{N_p}}) &= f(\mathbf{P}, t_{i_{N_p}}, k) \end{aligned} \quad (6)$$

For each P_i , there will be N_c different solutions, $P_i(k, 1), P_i(k, 2), \dots, P_i(k, N_c)$. Define an arithmetic mean for the components of $\bar{\mathbf{P}}$ where

$$\bar{P}_i(k) = \frac{1}{N_c} \sum_{j=1}^{N_c} P_i(k, j). \quad (7)$$

Each $P_i(k, j)$ is a function of k whose derivative are known either analytically or by numerical differentiation. To derive an optimized set, then for the least squares method, define

$$Q(k) = \sum_{i=1}^{N'} (Y_{exp}(t_i) - Y_{th}(k, t_i))^2. \quad (8)$$

Then for an optimized k , we have $Q'(k) = 0$. Defining

$$P_k(k) = \sum_{i=1}^{N'} (Y_{exp}(t_i) - Y_{th}(k, t_i)) \cdot Y'_{th}(k, t_i) \quad (9)$$

the optimized solution of k corresponds to $P_k(k) = 0$. The most stable numerical solution is gotten by the bisection method where a solution is assured if the initial values of k yield opposite signs for $P_k(k)$. Since all $P_i(k)$ functions are known, their values may all be computed for one optimized k value of Q in (8). For a perfect fit of Y_{exp} with Y_{law} , $Q(k') = Q'(k') = 0 \Rightarrow \bar{P}_j \rightarrow P_j (\forall j)$ and so in this sense we define the above algorithm as giving optimized values for all P_i parameters via the k determination. This method is illustrated for the determination of two parameters in chemical reaction rate studies, of 1st and 2nd order respectively using data from the published literature referred to above.

4 Applications in Chemical Kinetics

The first order reaction studied here is reaction (i) and the second order one is reaction (ii) both described above. For both these reactions, we plot the $P_k(k)$ function as in Fig.(1) to test whether the method does in fact yield a unique solution. It can be observed that in both cases, a unique solution exists for $P_k(k) = 0$, and the region about this value of P_k is indicated a line for each of the reaction orders. The graph proves that for these systems a unique solution exists; as to whether this is a reasonable solution can only be deduced by comparison to experimental determinations and the results from other standard techniques. The details of deriving the P_k function, very different in form for the two reaction orders, are given in what follows.

4.1 First order results

For this order, the change in time t for any material property $\lambda(t)$, which in this case is the Absorbance $A(t)$ (i.e. $A(t) \equiv \lambda(t)$) is given by

$$\lambda(t) = \lambda_{\infty} - (\lambda_{\infty} - \lambda_0) \exp(-k_a t) \quad (10)$$

for a first order reaction where λ_0 refers to the measurable property value at time $t = 0$ and λ_{∞} is the value at $t = \infty$ which is usually treated as a parameter to yield the best least squares fit even if its optimized value is less for monotonically increasing functions (for positive $\frac{d\lambda}{dt}$ at all t) than an experimentally determined $\lambda(t)$ at time t . In Table 7.1 of [1] for instance, $A(t = 2160s) = 0.897 > A_{opt,\infty} = 0.882$ and this value of A_{∞} is used to derive the best estimate of the rate constant as $16.5 \pm 0.1 \times 10^{-3} \text{sec}^{-1}$.

For this reaction, the P_i of (4) refers to λ_{∞} so that $\mathbf{P} \equiv \lambda_{\infty}$ with $N_p = 1$ and $k \equiv k_a$. To determine the parameter λ_{∞} as a function of k_a according to (8) based on the *entire* experimental $\{(\lambda_{exp}, t_i)\}$ data set we invert (10) and write

$$\lambda_{\infty}(k) = \frac{1}{N'} \sum_{i=1}^{N'} \frac{(\lambda_{exp}(t_i) - \lambda_0 \exp -kt_i)}{(1 - \exp -kt_i)} \quad (11)$$

where the summation is for all the values of the experimental dataset that does not lead to singularities, such as when $t_i = 0$, so that here $N_s = 1$. We define the non-optimized, continuously deformable theoretical curve λ_{th} where $\lambda_{th} \equiv Y_{th}(t, k)$ in (5) as

$$\lambda_{th}(t, k) = \lambda_{\infty}(k) - (\lambda_{\infty}(k) - \lambda_0) \exp(-k_a t) \quad (12)$$

With such a projection of the λ_{∞} parameter P onto k , we seek the least square minimum of $Q_1(k)$, where $Q_1(k) \equiv Q$ of (8) for this first-order rate constant k in the form

$$Q_1(k) = \sum_{i=1}^N (\lambda_{exp}(t_i) - \lambda_{th}(t_i, k))^2 \quad (13)$$

where the summation is over all the experimental $(\lambda_{exp}(t_i), t_i)$ values. The resulting P_k function (9) for the first order reaction based on the published dataset is given in Fig.(1). The solution of the rate constant k corresponds to the zero value of the function, which exists for both orders. The \mathbf{P} parameters (λ_{∞} and Y_{∞}) are derived by back substitution into eqs. (11) and (15) respectively. The Newton-Raphson (NR) numerical procedure [9, p.362] was used to find the roots to P_k . For each dataset, there exists a value for λ_{∞} and so the error expressed as a standard deviation may be computed. The tolerance in accuracy for the NR procedure was $1. \times 10^{-10}$. We define the function deviation fd as the standard deviation of the experimental results with the best fit curve $fd = \sqrt{\frac{1}{N} \{\sum_{i=1}^N (\lambda_{exp}(t_i) - \lambda_{th}(t_i))^2\}}$ Our results are as follows:

$k_a = 1.62 \pm .09 \times 10^{-2} \text{s}^{-1}$; $\lambda_{\infty} = 0.88665 \pm .006$; and $fd = 3.697 \times 10^{-3}$.

The experimental estimates are :

$k_a = 1.65 \pm .01 \times 10^{-2} \text{s}^{-1}$; $\lambda_{\infty} = 0.882 \pm 0.0$; and $fd = 8.563 \times 10^{-3}$.

The experimental method involves adjusting the $A_{\infty} \equiv \lambda_{\infty}$ to minimize the fd function and hence no estimate of the error in A_{∞} could be made. It is clear that our method has a lower fd value and is thus a better fit, and the parameter values can be considered to coincide with the experimental estimates within experimental error. Fig.(2(a)) shows the close fit between the curve due to our optimization procedure and experiment. The slight variation between the two curves may well be due to experimental uncertainties.

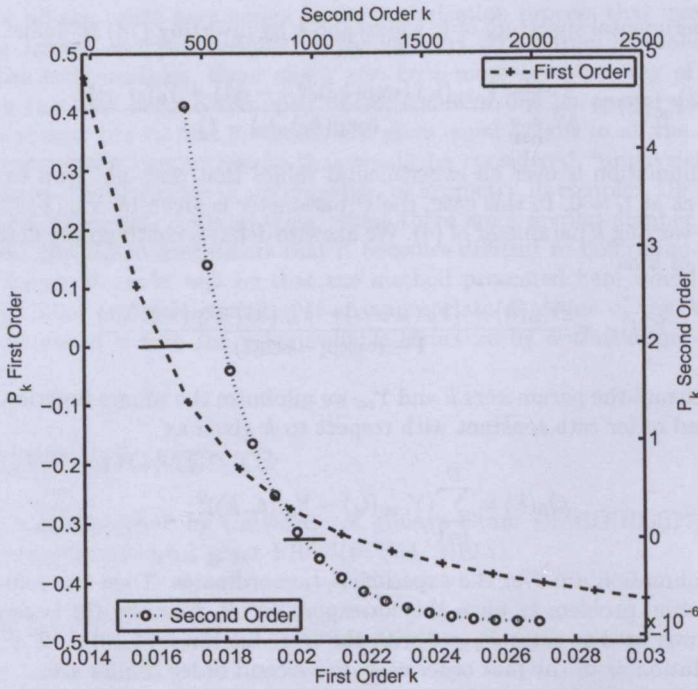
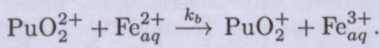


Fig. 1 P_k functions (9) for reactions (i) and (ii) of order one and two in reaction rate.

4.2 Second order results

To further test our method, we also analyze the second order reaction (2)

For Espenson, the above stoichiometry is kinetically equivalent to the reaction scheme [3, eqn. (2-36)]



which also follows from the work of Newton et al. [2, eqns. (8,9),p.1429] whose data [2, TABLE II,p.1427] we use and analyze to verify the principles presented here. The overall absorbance in this case $Y(t)$ is given by [3, eqn(2-35)]

$$Y(t) = \frac{Y_\infty + \{Y_0(1 - \alpha) - Y_\infty\} \exp(-k\Delta_0 t)}{1 - \alpha \exp(-k\Delta_0 t)} \tag{14}$$

where $\alpha = \frac{[A]_0}{[B]_0}$ is the ratio of initial concentrations where $[B]_0 > [A]_0$ and $[B] = [\text{Pu(VI)}]$, $[A] = [\text{Fe(II)}]$ and $[B]_0 = 4.47 \times 10^{-5}\text{M}$ and $[A]_0 = 3.82 \times 10^{-5}\text{M}$. A rearrangement of (14) leads to the equivalent expression [3, eqn(2-34)]

$$\ln \left\{ 1 + \frac{\Delta_0 (Y_0 - Y_\infty)}{[A]_0 (Y_t - Y_\infty)} \right\} = \ln \frac{[B]_0}{[A]_0} + k\Delta_0 t. \tag{15}$$

According to Espenson, one cannot use this equivalent form [3, p.25] "because an experimental value of Y_∞ was not reported." However, according to Espenson, if Y_∞ is determined autonomously, then k the rate constant may be determined. Thus, central to all conventional methods is the autonomous and independent status of both k and Y_∞ . We overcome this interpretation by defining Y_∞ as a function of

the total experimental spectrum of t_i values and k by inverting (14) to define $Y_\infty(k)$ where

$$Y_\infty(k) = \frac{1}{N'} \sum_{i=1}^{N'} \frac{Y_{exp}(t_i) \{ \exp(k\Delta_0 t_i) - \alpha \}}{(\exp(k\Delta_0 t_i) - 1)} + Y_0(\alpha - 1) \quad (16)$$

where the summation is over all experimental values that does not lead to singularities such as at $t_i = 0$. In this case, the \mathbf{P} parameter is given by $Y_\infty(k) = P_1(k)$, $k_b = k$ is the varying k parameter of (4). We likewise define a continuously deforming function Y_{th} of k as

$$Y(t)_{th} = \frac{Y_\infty(k) + \{Y_0(1 - \alpha) - Y_\infty(k)\} \exp(-k\Delta_0 t)}{1 - \alpha \exp(-k\Delta_0 t)} \quad (17)$$

In order to extract the parameters k and Y_∞ we minimize the square function $Q_2(k)$ for this second order rate constant with respect to k given as

$$Q_2(k) = \sum_{i=1}^N (Y_{exp}(t_i) - Y_{th}(t_i, k))^2 \quad (18)$$

where the summation are over the experiment t_i coordinates. Then the solution to the minimization problem is when the corresponding P_k function (9) is zero. The NR method was used to solve $P_k = 0$ with the error tolerance of 1.0×10^{-10} . With the same notation as in the first order case, the second order results are: $k_b = 938.0 \pm 18 \text{M s}^{-1}$; $Y_\infty = 0.0245 \pm 0.003$; and $fd = 9.606 \times 10^{-4}$.

The experimental estimates are [3, p.25]:

$$k_b = 949.0 \pm 22 \times 10^{-2} \text{s}^{-1}; Y_\infty = 0.025 \pm 0.003.$$

Again the two results are in close agreement. The graph of the experimental curve and the one that derives from our optimization method is given in Fig.(2).

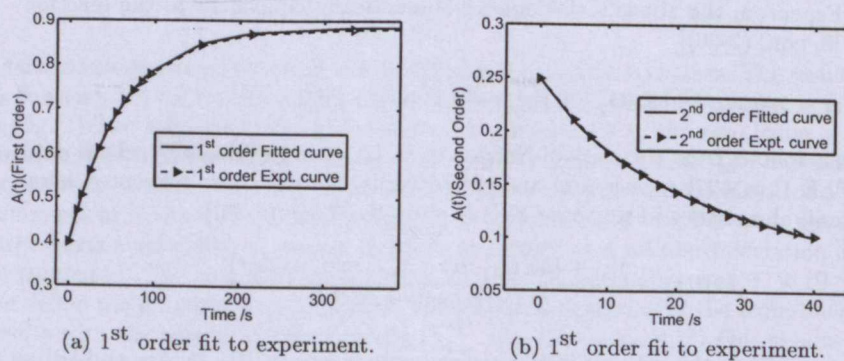


Fig. 2 Reaction (i) and (ii) results.

5 Conclusions

The results presented here show that by the method of inducing parameter dependency, it is possible to derive all the parameters associated with a theoretical curve by considering only one independent variable which serves as an independent

variable for all the other parameters in the optimization process that uses the experimental dataset as input variables in the calculus. Apart from possible reduced errors in the computations, there might also be a more accurate way of deriving parameters that are more determined by the value of one parameter (such as k here) than others; the current methods that gives equal weight to all the variables might in some cases lead to results that would be considered "unphysical". This might be so in the situations of optimization of geometry in complex DFT and ab initio quantum chemical computations, where there are a myriad number of possible mechanically stable conformers that it becomes difficult to determine the most prevalent forms. It could well be that the method presented here would indicate the average most probable structure if an appropriate analogue of the k variable is used that would induce the psot probable structure by optimization of the P_i parameters.

ACKNOWLEDGMENTS

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